Study of Small Carbon and Semiconductor Clusters Using Negative Ion Threshold Photodetachment Spectroscopy

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Abstract

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The bonding and electronics of several small carbon and semiconductor clusters containing less than ten atoms are probed using negative ion threshold photodetachment (zero electron kinetic energy, or ZEKE) spectroscopy. ZEKE spectroscopy is a particularly advantageous technique for small cluster study, as it combines mass selection with good spectroscopic resolution. The ground and low-lying electronic states of small clusters in general can be accessed by detaching an electron from the ground anion state. The clusters studied using this technique and described in this work are C_6^-/C_6 , Si_n^-/Si_n ($n = 2, 3, 4$), Ge_2^-/Ge_2 , In_2P^-/In_2P , InP_2^-/InP_2 , and Ga_2As^- . The total photodetachment cross sections of several other small carbon clusters and the ZEKE spectrum of the $I^- \cdot CH_3$ S_N2 reaction complex are also presented to illustrate the versatility of the experimental apparatus.

Clusters with so few atoms do not exhibit bulk properties. However, each specie exhibits bonding properties that relate to the type of bonding found in the bulk. C_6 , as has been predicted, exhibits a linear cumulenic structure, where double bonds connect all six carbon atoms. This double bonding reflects how important π bonding is in certain phases of pure carbon (graphite and fullerenes). The symmetric stretch frequencies observed in the C_6^- spectra, however, are in poor agreement with the calculated values. Also observed as sharp structure in total photodetachment cross section scans was an excited anion state bound by only $\sim 40 \text{ cm}^{-1}$ relative to the detachment continuum. This excited anion state appears to be a

valence bound state, possible because of the high electron affinity of C_6 , and the open shell of the anion.

The small silicon clusters differ substantially from the carbon clusters in that π bonding does not in general occur, except for in the dimer. These clusters are much more congested with close-lying electronic states. For Si_2 , transitions from two close-lying anion states to five neutral states are observed. The trimer ground state is still not known, although we observe transitions to a D_{3h} neutral from a pseudorotating anion. The Si_4^- ZEKE spectrum, in addition to showing extensive vibrational structure in the first excited neutral state, gives evidence that the close-lying excited electronic states undergo vibronic coupling. The ZEKE spectrum of Ge_2^- reveals the electronic similarity between the two Group IV dimers, although relativistic effects are more dramatic in Ge_2 .

Small group III-V mixed clusters represent a different class of small clusters; more structural isomers are available in a binary system, and the bonding between substituent atoms may have some ionicity involved. From the ZEKE spectra of In_2P^- and InP_2^- , we are able to assign the neutral ground states based on molecular orbital arguments and the atomic motion suggested by the vibrational frequencies observed in the spectra. These two open shell species exhibit interesting trends in vibrational frequencies between the anion and neutral ground states, and, in the case of InP_2 , the first excited state. The photoelectron spectra of Ga_2As^- and In_2P^- reflect remarkable electronic similarity between the two species, but the respective ZEKE spectra show that the actual bonding properties of the molecular orbitals are in fact different.

Dedicated to my parents (Mock and Jock)
and young Aurelien

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Chapter 1. Introduction

A primary objective in the field of atomic and molecular clusters is understanding the evolution of physical and chemical properties of clusters as a function of size from the atomic to bulk scales. In particular, small carbon, silicon, III-V and II-VI clusters composed of fewer than 10 atoms have been the focus of a recent upsurge in both experimental and theoretical work. While these largely uncharacterized species are intriguing by virtue of their novelty, very small clusters play important roles in several fields of study. For instance, the small carbon clusters have been found in combustion¹ and astrophysical studies.² Spectroscopic signal due to interstellar small silicon clusters has also been observed.³ The properties of small Group IV, mixed III-V and mixed II-VI clusters are also of great interest from a technological standpoint because of their potential role in chemical vapor deposition (CVD) which is a standard method for producing the high grade semiconductor wafers used in research and industry. Moreover, the dynamics and electronics of small clusters may relate to etching processes and defects in the bulk.

Experimental work on small carbon clusters has been ongoing for at least a century,⁴ but the intense interest in the other Group IV and mixed semiconductor clusters, which in part has been fueled by *ab initio* studies, has been more recent. However, spectroscopic information has proven more difficult to acquire than *ab initio* results due to the challenges of cluster study. First, most cluster sources simultaneously generate a distribution of cluster sizes, charge, and,

in some cases, oxides. Second, the electronic structure of these species are often congested with low-lying electronic states due to their dangling bonds and the potential open shells, making a complete electronic characterization a challenge. While these characteristics of small clusters may hinder more conventional optical spectroscopic techniques, negative ion photodetachment techniques are more easily applied to cluster study for the following reasons. From a practical standpoint, negative ions can be mass-selected prior to spectroscopic investigation, thereby eliminating any ambiguity regarding species identity. Moreover, by detaching an electron from various valence orbitals of the cluster anion, the low-lying neutral states, which often cannot be observed via electronic absorption from the ground neutral state, can be accessed. Vibrational frequencies in totally symmetric modes are generally observed in the ground state as accessed by the anion. The neutral ground state frequencies obtained in this method are therefore complementary to the ground state frequencies obtained in IR absorption studies, which are generally frequencies for non-totally symmetric vibrational modes.

Fixed-frequency negative ion photoelectron spectroscopy (PES) has been the most common negative ion photodetachment approach to cluster study. Smalley has applied electronically resolved negative ion ultraviolet photoelectron spectroscopy (PES) to obtain the electronic band structures of carbon,⁵ silicon,⁶ germanium,⁶ gallium arsenide,⁷ and various metal clusters.⁸ However, the 0.1 to 0.2 eV resolution of Smalley's experiment is such that detailed information about the structures or the electronic states of the clusters cannot feasibly be extracted from their spectra. Using somewhat higher resolution PES, ranging from 60 to 100 cm^{-1} , negative ion photodetachment techniques have been successfully applied to the investigation of small metal⁹ and semiconductor¹⁰ clusters. In our own group, we have obtained the PES of C_n^- ($n = 2$ through 11),¹¹ Si_n^- ($n = 2$ through 8),¹² and In_xP_y^- ($x, y = 1$ through 4)¹³ with a resolution of 80 to 100 cm^{-1} . The PES of C_n^- , Si_n^- ($n = 2$ through 4) and InP_2^- were vibrationally resolved.

However, even the higher resolution PES experiments often cannot resolve the structure due to some of the lower-frequency modes in both the anion and neutrals, which tend to congest the spectra of clusters composed of more than two atoms. On the other hand, negative ion threshold photodetachment (zero electron kinetic energy, or ZEKE) spectroscopy is a technique that offers dramatically better resolution (3 cm^{-1}) than the more conventional PES. While the combination of mass selection and good spectral resolution afforded by the ZEKE technique may appear to render PES redundant, the selection rules are more restrictive for ZEKE than for PES (see below). Because of this, ZEKE spectroscopy is most powerful when used in conjunction with PES. We have obtained ZEKE spectra of C_5^- ,¹⁴ C_6^- ,¹⁵ Si_n^- ($n = 2, 3$ and 4),^{16,17} Ge_2^- , In_2P^- and InP_2^- ,¹⁸ and Ga_2As^- . These spectra will be the subjects of the subsequent chapters in this thesis.

As mentioned above, theoretical studies on small clusters have generally preceded experimental investigations. Comparison of the ZEKE spectra with results from *ab initio* calculations is invaluable in interpreting the cluster spectra. There are several theoreticians in particular who have devoted a tremendous effort toward calculating the properties of these elusive species. Raghavachari's studies on the small silicon cluster studies were in part the motivation for our work on silicon clusters.¹⁹ His work showed that, in contrast to the better characterized linear carbon clusters, the silicon clusters tended more toward three-dimensional structures. The striking geometric differences between the calculated ground state structures of carbon and silicon clusters are illustrated in Figure (1.1). Raghavachari has also done extensive calculations on larger silicon clusters, small carbon clusters,²⁰ sulfur clusters,²¹ and several mixed semiconductor clusters.²²

Clusters containing heavier atoms present a more formidable challenge to the theoretician, since the relativistic effects in the heavy atoms can strongly influence the bonding characteristics in the cluster. Balasubramanian, however, has carried out geometry calculations, always with an extensive set of electronic states and geometric arrangements on

species such as In_3 ,²³ In_2Sb , InSb_2 , and the gallium arsenide triatomics²⁴ in addition to several silicon²⁵ and germanium clusters.²⁶

From the aforementioned experimental and *ab initio* results, it has been seen that clusters containing only several atoms generally have structural and electronic properties that do not resemble bonding in the bulk. Rather, the structures may have more contracted bonds and compact structures relative to the bulk diamond lattice (or graphite, in the case of carbon) in order to minimize the dangling bonds. This is in contrast to larger nanoparticles containing on the order of several hundred to tens of thousands of atoms, which generally exhibit crystalline structures found in the bulk, but have shifts in the phase diagrams and band structures due to high surface to volume ratios and quantum confinement effects. At which point the small clusters reach a size that the bulk crystal structure becomes energetically viable has not yet been experimentally determined, although it would appear that mobility measurements should have already determined this.²⁷ Ultimately, however, negative ion photodetachment may provide the answer.

I. Principles of negative ion photodetachment spectroscopy: anion photoelectron spectroscopy and zero electron kinetic energy, or ZEKE spectroscopy

While the focus of the subsequent chapters is on the application of ZEKE toward cluster study, in practice, these studies usually follow lower-resolution fixed-frequency negative ion photoelectron spectroscopic (PES) work. The results of the ZEKE spectra are then often presented in the context of previously obtained PES. Therefore, a brief description of negative ion PES will precede the description of the principles of ZEKE spectroscopy. Both the PES and ZEKE techniques start with the generation of an internally cold, mass-selected negative ion beam, but different photodetachment and electron detection schemes are employed.

PES: In photoelectron spectroscopy, the mass-selected negative ions are photodetached with a fixed-frequency laser yielding a neutral in some vibronic state, and electron with some excess kinetic energy per:

The kinetic energy distribution of the ejected photoelectrons is measured with an electron time-of-flight analyzer. Figure (1.2) shows a schematic of the energetics involved in this technique. The photoelectron kinetic energies (eKE) are given by

$$eKE = h\nu - EA - T_e' + T_e'' - E_{v_n'}^0 + E_{v_n''}^-, \quad \text{Eqn. (1.2)}$$

where $h\nu$ is the detachment laser photon energy, EA is the neutral electron affinity, T_e' and T_e'' are the term values of the specific neutral and anion electronic states, respectively, and $E_{v_n'}^0$ and $E_{v_n''}^-$ are the vibrational energies with respect to the zero point energies of the neutral and anion states, respectively. The electron kinetic energy distribution is therefore peaked from transitions between anion and neutral levels, as shown in Figure (1.2).

Another analytical tool in PES is the use of laser polarization to discern between overlapping electronic transitions which often occur in clusters. Photoelectrons detached from different molecular orbitals of the anion (which accesses the different neutral electronic states) will generally have different angular distributions with respect to the laser polarization. The intensity of a particular electronic band in the spectrum will therefore change relative to other electronic bands at alternative polarizations.

The intensity of transitions from a particular vibronic level of the anion to different vibrational levels within an electronic state of the neutral, v'' and v' , respectively, is assumed proportional to the Franck-Condon factors,

$$\text{Intensity} \propto |\langle v'' | v' \rangle|^2. \quad \text{Eqn. (1.3)}$$

If the anion and neutral are of the same symmetry, transitions between the ground and vibronic state of the anion to totally symmetric vibronic levels in the neutral will be the most intense in the spectrum. Moreover, geometry differences between the anion and neutral can be estimated by simulating the observed vibrational progressions. This can be achieved most simply by approximating the anion and neutral vibrational wave functions as products of harmonic oscillator wave functions. The displacement of the anion wave function along the appropriate neutral coordinate can then be varied until the simulated progression profiles match the spectrum per Eqn. (1.3). In some cases, the displacements obtained in this manner can be transformed into actual bond distance and angle differences between the anion and neutral geometries.

The energy resolution of the electron time-of-flight analyzer in the spectrometer used in the studies presented in this work is 8 meV at 0.65 eV eKE and degrades as (eKE)^{3/2} at higher electron kinetic energies. While this should be adequate to resolve most symmetric stretch progressions in the neutral carbon and silicon clusters, this is insufficient to discern rotational structure and lower frequency modes that may be active, in addition to the hot bands and sequence bands that may congest the spectra.

ZEKE: Considerably higher resolution spectra can be obtained using negative ion ZEKE spectroscopy. The energetics involved in this technique are illustrated in Figure (1.3). The method of ZEKE spectroscopy follows

$$A_x(v_n', T_e') + e^-(KE = 0) \xleftarrow{h\nu, \text{scanned}} A_x^-(v_n'', T_e''). \quad \text{Eqn. (1.4)}$$

Mass-selected negative ions are photodetached with a tunable pulsed laser rather than a fixed-frequency laser, and only those electrons with nearly zero kinetic energy are detected. This is in contrast to a total photodetachment cross section spectrum, which is obtained by collecting *all* of the photoelectrons as a function of photon energy while tuning the detachment laser through the anion detachment continuum. The total cross section would ideally resemble that shown on the upper right side of Figure (1.3): An onset of electrons occurs at detachment threshold, and at the threshold of accessing a higher-lying energy level of the neutral, more electron signal would be collected.

Because the ZEKE spectrum is obtained by discriminating against energetic electrons and collecting only those electrons detached with no excess kinetic energy (i.e., those detached at the threshold of a neutral $\leftarrow$ anion transition) the electron signal plotted against the detachment wavelength consists of peaks, as is illustrated in the lower right side of Figure (1.3). Each peak corresponds to transitions between energy levels of the anion and the neutral, since nearly zero kinetic energy electrons (ZEKE's) will be produced only when the photon energy is equal to such a transition.

Discrimination of energetic electrons is achieved by a delayed collection scheme. The negative ions are detached in a field free region, and the energetic electrons are allowed to scatter away from the neutrals and undetached anions, while the ZEKE electrons, with little to no kinetic energy relative to the neutrals and undetached ions will therefore remain close. After a certain period of time has passed (typically on the order of 200 to 600 ns), a gentle field extracts the remaining ZEKE electrons to an electron detector. In principle, the longer the ZEKE extraction is delayed, the more efficiently the energetic electrons will be discriminated against, and the better the resolution. A more detailed description the electron detection scheme can be found in Chapter 2.

This method of selectively detecting low kinetic energy electrons is similar to techniques developed by Müller-Dethlefs *et al.*²⁸ for threshold photoionization of neutrals. However, there is

a fundamental difference between ZEKE of neutral species and ZEKE of anions. Namely, in ZEKE of neutrals, neutrals are typically excited to an extremely high-lying neutral Rydberg state lying just below the detachment continuum, or a quasibound vibrationally excited Rydberg state. After allowing some time for any energetic electrons to scatter, the bound or quasi-bound neutral is field ionized by some pulsed extraction field. Because the electron is bound prior to field ionization, very long (on the order of microseconds) delay times can be employed. The quality of the neutral ZEKE spectrum is therefore sensitive to the ionizing field strength and the shape of the pulse. In contrast, ZEKE of anions involves completely free low-kinetic energy electrons which are notoriously susceptible to stray electric or magnetic fields, including the repulsive fields (space charge effects) from nearby undetached anions. The space charge effects are typically what limits the resolution of negative ion ZEKE to 2 to 3 cm^{-1} .

Because the electrons detected in an anion ZEKE are free and have very low-kinetic energy, the anion ZEKE experiment is inherently more difficult than a neutral ZEKE experiment. However, in anion ZEKE, the benefit is that one obtains information regarding neutral states, while in neutral ZEKE, the positive ions, or high-lying neutral states that resemble the positive ions, are accessed. Also, the peak intensities in anion ZEKE spectra are easier to interpret than in neutral ZEKE, as they are not confounded by Rydberg state lifetimes or coupling with other close-lying Rydberg states.

II. The Wigner threshold law, and how it applies to polyatomics

While it is desirable to obtain the higher resolution threshold photodetachment spectra for all of the carbon clusters studied using photoelectron spectroscopy, the ability to acquire threshold photodetachment spectra is contingent on the photodetachment cross section near threshold. The Wigner threshold law²⁹ gives that near threshold, the photodetachment cross section for an atomic system goes as

$$\sigma \propto \sigma_0 (E_{\text{hv}} - E_{\text{threshold}})^{\ell+1/2} \quad \text{Eqn. (1.5)}$$

where $E_{\text{hv}} - E_{\text{threshold}}$ is the difference between the detachment photon energy and the transition energy between an anion and neutral level, and ℓ is the angular momentum imparted upon the photoelectron. For $\ell = 0$ (s-wave detachment) the cross section rises sharply above threshold, but for $\ell \geq 1$ (p, d, ...-wave detachment), the cross section is very small near threshold, making the ZEKE technique insensitive to transitions other than those involving s-wave detachment.

Reed *et al.*³⁰ extended the threshold law to polyatomic anions with the end result that orbitals that transform as x, y, or z in the anion symmetry can yield s-wave photoelectrons (as well as higher wave electrons). For the linear homonuclear species we have studied, in which the π_u and σ_u orbitals transform as (x,y) and z, respectively, we have found this rule to satisfactorily predict the threshold detachment behavior. As expected, of the small carbon clusters, we were able to obtain ZEKE spectra of C_5^- and C_6^- , as the neutral $\leftarrow$ anion transition involves the removal of a π_u electron (we have not yet been successful in our attempts to obtain the ZEKE spectrum of C_9^- , which should also detach via s-wave, possibly due to strong anion $\leftarrow$ anion transitions complicating the total photodetachment cross section- see Chapter 4).

In many cases, particularly in nonlinear polyatomics, no ZEKE signal is observed. This may be due to the lack of a molecular axis upon which orbital angular momentum projection is meaningful. The ejected photoelectrons generally have contributions from many waves, and how closely the molecular orbital resembles some p- or π_u -type orbital determines the magnitude of the s-wave component in the departing photoelectron. For instance in a triatomic C_{2v} molecule, of the four characters (a_1 , a_2 , b_1 and b_2) only a_2 does not transform as x, y, or z. However, we have found empirically from our studies on Si_3^- and In_2P^- that the photodetachment cross section for an electron in an a_1 orbital may be too small to observe any

ZEKE signal. A_1 orbitals in C_{2v} molecules have no plane through which reflection results in a change in the sign of the wave function, as is the case with a p-orbital, and in the cases mentioned above, this may be the reason for the small cross section near threshold. However, consider an a_1 orbital composed of primarily the p_z orbital on the apical atom, or even composed of the two p_z -orbitals on the two side atoms. Such a_1 orbitals may yield photoelectrons with strong s-wave contribution. This may be the case for a molecule such as InP_2 , in which the bonding is reminiscent of a partially positive In atom loosely bound to a partially negative P_2 diatom, and the a_1 orbital can be described as a π_u bond between the two P atoms, but in the plane of the InP_2 molecule.

On the other hand, virtually no photodetached electrons were observed near detachment threshold for the bipyramidal Si_5^- (D_{3h}), Si_6^- (D_{4h}), and Si_7^- (D_{5h}) clusters [Si_5 and Si_6 are shown in Figure (1.1)] even though *ab initio* calculations predict the electron to be detached from a p_z -like orbital (a_2'' , a_{2u} , and a_2'' , respectively). However, calculations determining the shapes of the orbitals may show that even though reflection through the bipyramidal plane changes the sign of the orbital wave function, the distribution of "+" and "-" density on either side of the plane may cancel out any overlap with a p-orbital. In these species, there is also a substantial geometry difference between the anion and neutral, which may contribute to the problem of low ZEKE signal.

III. Application of negative ion photodetachment techniques toward the characterization of small carbon and semiconductor clusters

Some of the interesting issues in small cluster study revolve around how cluster geometries and electronics evolve as a function of the number of atoms, and how clusters composed of materials in the same periodic group compare to one another. For instance,

Figure (1.1) shows the dramatic structural differences between carbon clusters and silicon clusters.^{19,20} The linear cumulenic structures of the small carbon clusters reflect how π -bonding is favored in carbon atoms, while the tendency for silicon to form bent or three dimensional structures reflects how π -bonding is uncommon for silicon. Cyclic structures, in which cumulenic bonding dominates, are also predicted to be nearly degenerate with the linear structures for the even numbered carbon clusters with four or more atoms,²⁰ although very little experimental evidence for the existence of the cyclic structures presently exists. This may be due to the high temperature in the initial stages of cluster formation in laser vaporization sources.

The structural differences in these species can be inferred from their negative ion photodetachment spectra. Figure (1.4) shows the negative ion PES of several small carbon¹¹ and silicon clusters obtained using a 4.66 eV detachment energy. The contrasts between the C_n^- and the Si_n^- spectra are striking; the C_n^- spectra are dominated by sharp and intense origin transitions while the Si_n^- spectra, particularly for $n > 4$, are congested by broad and vibrationally unresolved electronic bands. The carbon cluster spectra show the characteristic odd-even alternation of electron affinities with the even numbered clusters having higher electron affinities than the odd numbered clusters. This is consistent with their linear, cumulenic structures, in which the odd numbered clusters closed-shell electron configurations, as opposed to the open-shell configurations of the even numbered clusters. The electron affinities also increase as a function of cluster size within the even or odd series.

With the Si_n^- PES, size trends are not as obvious, except that the spectra get more congested as a function of size. The especially broad origin transitions for the larger clusters indicate that the LUMO of the neutral species has a profound effect on the cluster geometry. *Ab initio* calculations predict the LUMO's for $n = 5, 6$, and 7 are antibonding between the apical atoms of the bipyramids. However, with so many close-lying neutral electronic states, vibronic coupling may also contribute to the congestion.

The differences between small silicon and germanium clusters are more subtle. Lower resolution UV-PES investigations on Si_n^- and Ge_n^- by Smalley et al.⁶ revealed virtually identical electronic structure for the two elements. The ZEKE spectra of Si_4^- and Ge_4^- shown in Figure (1.5) exhibit a resolved vibrational progressions in the ν_2 mode of the $^3B_{3u}$ first excited neutral state over the same wavelength range (the transition to the ground neutral state can not be observed in the ZEKE spectrum, as it involves p-wave detachment, see Sec. II). This range corresponds to the $eKE = 1.4$ to 1.7 eV range on the PES of Si_4^- shown in Figure (1.4). Aside from the difference in quality of the two spectra, the Ge_4^- progression has a 174 cm^{-1} spacing while the Si_4^- progression has a 311 cm^{-1} spacing. Considering that $\omega_e = (k/\mu)^{1/2}$, this means that $k_{2,\text{Si}_4} = 1.23k_{2,\text{Ge}_4}$. That the Ge_4 force constant is smaller is consistent with bonding trends in the periodic table.

These are just a few brief examples of how negative ion photodetachment techniques can be applied to study cluster properties. Chapter 2 describes several improvements to the ZEKE apparatus implemented to obtain the spectra. Chapters 3 through 10 give more detailed descriptions and analysis of ZEKE spectra of carbon, silicon, germanium, indium phosphide, and gallium arsenide clusters. Finally, chapter 11 presents and discusses the ZEKE spectrum of the $\text{I}^-\cdot\text{CH}_3\text{I}$ S_N2 reaction complex, showing that ZEKE spectroscopy is a powerful tool for studying dramatically different types of systems.

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Figure (1.1) Comparison of the structures of small carbon and silicon clusters (the low-lying cyclic structures predicted for C_4 and C_6 are not shown).

Figure (1.2) Energetic considerations in negative ion fixed-frequency photoelectron spectroscopy.

Figure (1.3) Energetic considerations in negative ion ZEKE spectroscopy.

Figure (1.4) PES of several small carbon and silicon clusters obtained using 4.66 eV photon energy.

Figure (1.5) ZEKE spectra of Si_4^- and Ge_4^- : ${}^3B_{3u} + e^- \leftarrow {}^2B_{2g}$ transition.

Chapter 2. Experimental modifications to the threshold photodetachment spectrometer

"If it were easy, everyone would be doing it."

— Daniel M. Neumark

The ZEKE apparatus as it was built by Kitsopoulos *et al.* has been described in detail elsewhere,¹ and aside from the several modifications described in this chapter, the basic operation is the same. A schematic of the threshold photodetachment spectrometer is shown in Figure (2.1). Briefly, cluster ions are generated in a ion source chamber, and then enter a mass-spectrometer. After mass-separation, the ion of interest is detached by a tunable light source, and only those electrons released within several cm^{-1} of a neutral $\leftarrow$ anion transition are selectively detected for the ZEKE spectrum.

The ions are generated in a cluster source based on the design developed by Smalley² (1) which will be discussed in greater detail below. The negative ions that pass through a 2 mm skimmer are collinearly accelerated to 1 keV. Mass-selection is achieved with a 1 m long beam-modulated time-of-flight mass spectrometer.³ Ion optics including an Einzel lens and a temporal compressor are situated in the ion flight tube. The mass-separated ions then pass through a 3

mm mass spectrometer defining aperture into the detection region where they are photodetached in the region labeled (2) by a (pulsed) excimer-pumped dye laser 60 cm upstream of the ion (3) and electron (4) detectors (the electron detector is located out of the plane above the 3).

The selective detection of the near-threshold electrons having nearly zero kinetic energy in the ion beam frame (ZEKE's) is achieved by photodetaching the anions when the interaction region (2) is initially field-free. A weak extraction pulse (1-4 V/cm) is then applied along the ion beam axis 200 to 300 ns after photodetachment occurs. The delay between detachment and extraction allows the higher kinetic energy electrons to spatially separate from the nearly zero kinetic energy electrons. Energetic electrons that scatter perpendicular to the ion beam axis are blocked upon extraction by the apertures (5) located between the detachment region and the electron detector, while those that scatter along the ion beam axis will emerge from the extraction region with different kinetic energies than the threshold electrons, giving them different arrival times at the detector. Discrimination against the energetic electrons is then achieved by gated integration of the threshold electron signal.

This combination of spatial and temporal filtering of energetic electrons is based on techniques developed by Müller-Dethlefs *et al.*⁴ for the photodetachment (through pulsed-field ionization) of neutrals, and gives an energy resolution of as good as 3 cm^{-1} . For several of the spectra presented in subsequent chapters, particularly the Si_2^- (Chapter 5) and Si_3^- (Chapter 6) spectra, resolution was sacrificed to increase the electron signal. The resolution of the apparatus as it was employed for these two species is estimated to be ~ 10 to 15 cm^{-1} .

I. The cluster source

As mentioned above, a cluster source similar to that developed by Smalley and coworkers² has been employed in all of the cluster studies described in the subsequent

chapters. A schematic of the cluster source is shown in Figure (2.2), and it is comprised of three major components: a molecular beam valve, a "source" piece, and a clustering channel. Briefly, the surface of a 0.25 inch OD (carbon, silicon, germanium, InP, GaAs) rod is ablated with the focused and attenuated 2nd harmonic (532 nm) output of a Nd:YAG laser operated at 20 Hz repetition rate. The rod is kept translating and rotating, so that a fresh surface is ablated with each laser shot. The resulting plasma is entrained in a pulse of a rare gas from a molecular beam valve, and then expanded through the clustering channel where clusters and cluster ions can aggregate and cool *via* collisions with other clusters or rare gas atoms. Helium is generally used as the carrier gas. It was easier to generate vibrationally cold ions using neon as the carrier gas,⁵ but neon and other heavier carrier gases also made it necessary to use greater vaporization power, which, as described below, has an undesired effect on the quality of the ions. It was also found that similarly cold ions could be generated using He by manipulating the timing between firing the molecular beam valve and the vaporization laser. The intersection of the rod, the laser beam, and the molecular beam occurs in the aluminum source piece, which attaches to both the face plate of the molecular beam valve and the clustering channel. After exiting the clustering channel, those clusters having negative charge and that pass through a 2 mm skimmer are accelerated to 1 keV into a flight tube, where the mass separation and subsequent spectroscopic investigation occurs.

The cluster source is flexible in that there are numerous parameters that can be adjusted to affect the cluster mass distribution and vibrational temperature. For instance, laser vaporization power, molecular beam valve type, carrier gas, carrier gas backing pressure, carrier gas pulse duration, timing between ablation and entrainment, length and inner diameter of the modular clustering channel, and having or not having an exit slit or cone at the end of the clustering channel are all important parameters. The Si_2^- and the C_5^- ZEKE spectra were fairly insensitive to cluster source conditions. Changing the backing pressure of the carrier gas, or grossly changing the timing of the laser beam pulse with respect to the molecular beam pulse

was found to affect the vibrational temperature of these species but as long as these two ions could be made, their spectra could be obtained. In general, however, the vibrationally coldest cluster ions were obtained using a 0.2" long, 0.15" ID clustering channel with a 0.1" ID exit slit. This is the configuration shown in Figure (2.2). The timing between the triggering of the beam valve and the ablation laser should be such that the laser hits the rod on the early part of the rising edge of the carrier gas pulse. The General Valve driver used in these studies takes slightly longer than the 250 μ s delay between the YAG trigger and actual output, so the YAG was triggered 40 to 60 μ s after the General Valve trigger.

The ability to obtain spectra of reasonable quality for the larger clusters, however, has turned out to be critically sensitive to a fairly narrow range of source conditions for each material. The C_6^- , Si_3^- and Si_4^- were much more difficult to obtain than the C_5^- and Si_2^- because of the need for much colder source conditions. No distinct threshold was observed in the total photodetachment cross section spectrum of C_6^- until the vaporization power was turned down to 4 mJ/pulse, compared to the 8 mJ/pulse vaporization power typically used for Si_2^- and C_5^- . A change in the beam valve had to be made in order to obtain Si_3^- and Si_4^- ZEKE spectra.

A. Piezoelectric molecular beam valve

When Si_4^- was generated using the same source conditions we used to obtain good C_6^- spectra, not ZEKE structure was observed. When the vaporization power was dropped to 2 mJ/pulse, some structure was observed, but it was broad and congested. However, when a piezoelectric beam valve similar to that designed by Trickl⁶ was substituted for the General Valve solenoid-type molecular beam valve that was used in the carbon cluster studies, the Si_4^- clusters were found to be dramatically cooled. The piezoelectric valve gives a sharper rise time on the pulse output, which apparently has a beneficial effect on cluster cooling- presumably because the ions have higher pressure carrier gas thrusting the plasma into the clustering

channel and throughout the subsequent expansion into the chamber. The source configuration found to generate the vibrationally coldest Si_3^- and Si_4^- spectra without further source modifications is again that shown in Figure (2.2).

Silicon clusters larger than the tetramer were found to have a nearly undetectable photodetachment cross section near threshold, precluding our obtaining ZEKE spectra for these three dimensional species.

B. Liquid nitrogen-cooled clustering channel

With the source shown in Figure (2.2) used in conjunction with the piezoelectric valve, the ZEKE spectra of the indium phosphide triatomics (Chapter 9) were also successfully obtained. The larger clusters, however, were problematic in that the detachment signal could be observed, but no structure was resolved. This was the impetus to modify the source to provide even more efficient cluster cooling by cooling the clustering channel with liquid nitrogen (although it ultimately did not result in acquiring ZEKE spectra of larger clusters).

The design of the N_2 -cooled source was made after considering sources made by Chen⁷ and Bloomfield,⁸ and is shown in Figure (2.3). It is qualitatively similar to the room-temperature source described above, but the main differences are as follows. The clustering channel is a much longer piece (1.3") made from copper, has a smaller inner bore (0.1"), and is terminated with a 0.0625" ID exit slit made from brass. The source piece is made from Vespel to thermally insulate the molecular beam valve from the cooled channel, and also has an inner bore of 0.1". Pieces of mica are placed between the contacting surfaces of the various pieces for further thermal insulation. A 1/8" copper tube carrying $\text{N}_{2(l)}$ from a chicken feeder located outside of the vacuum chamber is fastened directly to the channel. The whole chicken feeder setup is floated at -1 kV, as is the rest of the source. Thermocouples attached to the channel and the source indicate a channel temperature of approximately 100 to 115 K at equilibrium.

Even with the Vespel source piece and the mica insulating the beam valve from the cooled channel, some cooling of the beam valve still does occur. The General Valve molecular beam valve was found to be less sensitive to this cooling than was the o-ring tip of the piezoelectric valve, and is therefore used when $N_{2(l)}$ -cooling is implemented. Helium is used as the carrier gas, as it is the most thermally conductive of the rare gases.

With the $N_{2(l)}$ -cooled clustering channel, effective vibrational cooling of the clusters was only observed using certain timings between the molecular beam valve firing and the ablation laser firing. As mentioned above, in the room temperature configuration, the best cooling occurs when ablation roughly coincides with the early part of the rising edge of the molecular beam pulse. However, in the $N_{2(l)}$ -cooled configuration, the ablation laser has to be fired 100 μ s later than it is fired in the room temperature configuration. This suggests that for good thermal contact to be made between the clusters and the cooled clustering channel, the clusters must encounter high pressure of already cooled helium that has preceded the plasma into the channel. The smaller exit slit allows for the pooling of the helium in the channel. Without it, no enhanced cooling is observed.

Figure (2.4) shows a section of the Si_4^+ ZEKE spectrum obtained using the piezoelectric beam valve used in conjunction with the room temperature source (dotted line- see Chapter 7) and the liquid nitrogen-cooled source (solid line). It is clear that the sequence bands are markedly suppressed in the $N_{2(l)}$ -cooled cluster source.

II. Deflectors added to the mass spectrometer

A minor modification to the mass spectrometer that was found to enhance the cluster signal is a set of horizontal deflectors which were installed in the first differential region between the acceleration lens stack and the beam modulation plates. These deflectors compensate for any side-to-side deviation of the molecular beam off the axis of the apparatus (most likely due to

a small amount of slack in the beam valve centering piece) before the ions travel more than several centimeters at 1 keV.

III. Improvements to the detector region

The detection region of the ZEKE apparatus is fundamentally the same as that described by Kitsopoulos,¹ but a second set of laser windows has been added near the electron detector to accommodate total photodetachment cross section spectroscopy. A five-element Einzel lens for focusing the photoelectrons has replaced the previously employed three-element lens, and the magnetic shielding surrounding the flight path of the photoelectrons has been improved.

A diagram of the new detector region is shown in Figure (2.5). For this figure, in contrast to Figure (2.1), the detachment window flanges are oriented parallel to the plane and the photodetachment laser beam is thus perpendicular to the plane. The whole detector chamber was rebuilt using 8" OD, stainless steel tubing rather than the previously used 6" tube, which is accompanied by the switch from 8" to 10" conflat flanges. The same near-death Alcatel 450 Ls^{-1} turbomolecular pump (TMP) backed by a Varian 80 Ls^{-1} TMP maintains the larger chamber at a 3×10^{-9} torr operating pressure. Some of the other gross structural changes with the new detector are as follows. The electron extraction plates (1) are mounted from upstream of the ion beam axis. There are only seven molybdenum plates, the last four of which are held at ground in contrast to the 12 plates previously used. The first plate has a smaller hole: 0.5 cm compared to 0.5" previously used. This is possible because the ion beam is now defined by a 3 mm stainless steel knife-edged slit upon entering the detector region. The plate assembly is mounted onto an aluminum piece (2) that keys into the first 6-way cross. A small tube of Hypemom (a), a magnetic shielding material similar to Mu-metal, also attaches to the aluminum mounting piece. Two other layers of Hypemom (b) and the electron Einzel lens (4) are attached

to a stainless steel mounting piece that keys into the end of the second 6-way cross. The electron (5) and ion (6) detectors are roughly the same as in the previous design.

A. Total photodetachment cross section windows

The second set of detachment laser windows, mounted at Brewster's angle, allow for detachment of the negative ions immediately below the electron detector (5) in the electron and ion detection region [Figure (2.5); the Brewster's angle windows are shown from above schematically in Figure (2.1)]. This gives the apparatus the capability of collecting all of the photoelectrons as a function of photon energy when the ions are detached immediately adjacent to the electron detector. The information gained in this mode, which maps out the total photodetachment cross section of the anion, is useful for determining detachment threshold more precisely than the threshold determined from the lower-resolution photoelectron spectroscopy (PES, see Chapter 1, Sec. 1). It is also instrumental in the observation of transitions to excited anion states, if they exist, by means of two-photon detachment or autodetachment through the excited anion state. Such transitions appear as sharp features in the total photodetachment cross section, as they do in the case of C_6^- (Chapter 3).

The main difficulty with these windows was the excessive background noise resulting from stray photons impinging on the various internal surfaces of the apparatus. The worst background electron signal occurred when an extensive set of anodized aluminum skimmer light baffles having small light holes and baffled tubes protruding close to the interaction region was used. Dramatically lower background levels were attained when anodized baffles having a knife-edged, 0.5 cm ID were situated within several cm of the windows, and a larger, 1 cm ID baffle was placed flush with the window flange. No baffles protruding close to the interaction region are now used. However, background electrons are still problematic at wavelengths shorter than 270 nm.

B. Five-element Einzel lens

The five-element Einzel lens adds new flexibility to the focusing of the photoelectrons. The lens is generally run in decelerating mode, so the electrons move more slowly through the elements having some negative voltage applied. The first and last elements are always grounded, but the middle three elements can be connected in any way, as each is individually connected to separate feed-thrus. For instance, all three can be shorted together to provide the longest path of low electron kinetic energy, thereby giving a good deal of time for the energetic electrons to separate away from the threshold electrons. In such a case, a typical operating voltage is -0.6 to -0.7 V when the electrons have around 2 to 3 eV kinetic energy from the extraction. The temporal separation of the on-axis energetic electrons from the ZEKE's is dramatically improved operating in this mode: Rather than the 15 to 20 cm⁻¹ electrons arriving at the detector 50 ns prior to the ZEKE electrons as they typically did in the previous design, the separation has improved to 300 to 400 ns.

C. Improved magnetic shielding

Because the trajectories of low kinetic energy electrons are very sensitive to any stray fields (electric or magnetic) it is excruciatingly important that the inside of the detector region be made field-free. Stray electric fields from patch potentials on the surfaces of the electron optics are (usually) effectively eliminated by copious cleaning in addition to a thin layer of graphite sprayed on the surface. Stray magnetic fields can come from the earth's magnetic field, which is on the order of 0.5 Gauss (not necessarily perpendicular to the ion beam axis of the apparatus, however) and the stainless steel surfaces in the apparatus. The main objective of the modifications to the detector chamber revolve around having more effective magnetic shielding.

The previous shielding was composed of two concentric cylinders of 0.02" -thick Hyprom having 4.5" and 5.5" diameters. These cylinders were divided into two sections; an approximately 5" -long section shielding the electron extraction region, and a 17" -long section shielding the electron Einzel lens. There was, however, a 1" gap between the extraction and Einzel shields. The new design allows for continuous shielding from the detachment region to actual detection, with triple layers of Hyprom shielding the detachment region where the electrons have the least kinetic energy and are most susceptible to stray fields.

The shielding offered by a single cylinder of some high-permeable material goes as⁹

$$S_i = \frac{\mu_i t_i}{2R_i} \quad \text{Eqn. (2.1)}$$

where μ_i is the permeability, t_i is the thickness of the sheet, and R_i is the radius of the cylinder. For concentric cylinders, the shielding improves multiplicatively:

$$S = 1 + S_1 + S_2 + \dots + S_1 S_2 \left(1 - \frac{A_1}{A_2}\right) S_3 \left(1 - \frac{A_2}{A_3}\right) \dots \quad \text{Eqn. (2.2)}$$

In this equation, A_i is the surface area of the cylinders. We can compare the shielding provided by the new design and the old given an approximate permeability of 20,000 for Hyprom (this value, from the CRC Handbook, was for 20 Gauss. The actual value will be lower in a smaller magnetic field). In the old design, $t_i = 0.02"$, $R_1 = 2.25"$, and $R_2 = 2.75"$, giving $S = 1332$ in the interaction region. In the new design, $t_i = 0.02"$, $R_1 = 2.25"$, $R_2 = 2.675"$, and $R_3 = 3.25$ ($L_2 = L_3 = 4L_1$), giving $S = 54,000$. This 40-fold improvement in shielding may ultimately make the traditionally temperamental ZEKE apparatus run more reliably.

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Figure (2.1) Schematic of the threshold photodetachment (ZEKE) apparatus.

Figure (2.2) Room temperature cluster source.

Figure (2.3) Liquid nitrogen-cooled clustering channel.

Figure (2.4) Comparison of Si_4^+ ZEKE spectra obtained using the room-temperature cluster source (dotted line) and the liquid nitrogen-cooled cluster source (solid line).

Figure (2.5) Diagram of the rebuilt UHV chamber used for ZEKE detection.

Chapter 3. Study of C_5^- and C_6 with threshold photodetachment spectroscopy and autodetachment spectroscopy

Abstract

The C_6^- anion and C_6 neutral have been studied using both threshold photodetachment (ZEKE) spectroscopy and autodetachment spectroscopy of C_6^- . The threshold photodetachment spectrum yields the electron affinity of linear C_6 to high accuracy, along with the three symmetric stretch frequencies for linear C_6 and the spin-orbit splitting in the ground $^2\Pi_u$ state of the anion. Two of the symmetric stretch frequencies are significantly lower than previous *ab initio* predictions. A simple model force field is used to calculate stretching force constants and estimate bond length changes between the anion and neutral. In addition, using autodetachment spectroscopy, we have located an excited electronic state of C_6^- that lies 43 cm^{-1} below the detachment threshold. This state is very similar in geometry to neutral C_6 . Excited vibrational levels of this state autodetach with rates that depend strongly on the available autodetachment channels. The excited state is tentatively assigned to a valence state, rather than an electrostatically bound state.

I. Introduction

Elemental carbon clusters have been the subject of considerable experimental and theoretical research because of their importance in combustion¹ and astrophysics.² The state of carbon cluster research up to 1989 is described in an excellent review article by Weitrer and Van Zee.³ Prior to 1989, most of our knowledge regarding the structure and spectroscopy of small carbon clusters was from *ab initio* calculations. Experimentally, rotationally resolved spectra had only been obtained for C_2 ⁴ and C_3 .⁵ results for the larger carbon clusters (4-10 atoms) were limited to several *matrix* isolation studies^{6,7,8} and a photoelectron spectroscopy study of carbon cluster anions.⁹ However, during the last three years, new experiments have dramatically increased our understanding of the spectroscopy and structure of these species. For example, Saykally and co-workers¹⁰ have measured gas phase, rotationally resolved infrared spectra for C_3 , C_4 , C_5 , C_6 , C_7 , C_9 and C_{13} , yielding rotational constants and vibrational frequencies; Amano, Bemath, and co-workers^{11,12} have also obtained high resolution spectra for several of these species. All of the species observed in these gas phase studies appear to be linear.

Negative ion photodetachment provides another powerful experimental probe of carbon clusters. Although these experiments are typically lower resolution than infrared absorption, they offer several important advantages. One can mass select the anion prior to spectroscopic investigation, eliminating any ambiguity concerning species identification. This is important in cluster studies as most cluster sources simultaneously generate a number of different species (anions, neutrals and cations). In addition, photodetachment tends to result in excitation of totally symmetric vibrational modes of the neutral. With sufficient resolution, one can determine the frequencies of these modes. Since these are not infrared active for linear molecules, the information obtained is complementary to infrared absorption experiments.

Photoelectron spectra of the carbon cluster anions C_n^- ($n = 2$ through 29) have been obtained by Smalley and coworkers,⁹ and considerably higher resolution spectra (60-100 cm^{-1}) have been measured for C_2^- and C_3^- by Lineberger,^{13,14} and for C_2^- through C_{11}^- by our group.¹⁵ These studies show that the linear even clusters have higher electron affinities than the odd clusters, in agreement with the prediction of Pitzer and Clementi.¹⁶ The higher resolution studies also yielded numerous vibrational frequencies for the neutral clusters. Finally, we have studied C_5^- at even higher resolution using threshold photodetachment spectroscopy.¹⁷ The resolution of this technique is 3 - 8 cm^{-1} , and the resulting spectrum shows well-resolved transitions to various symmetric stretch and bending modes of C_5 , as well as fine structure due to the spin-orbit splitting in the anion.

This paper describes new experiments on the photodetachment spectroscopy of C_6^- , the goal of which is to learn about the structure and spectroscopy of C_6 and C_6^- . Several calculations have been performed on neutral C_6 predicting close-lying cyclic $^1A_1'$ (D_{3h}) and $^3\Sigma_g^-$ ($D_{\infty h}$) linear states, although the true ground state remains a point of controversy.^{18,19} Raghavachari¹⁸ and Martin²⁰ have calculated vibrational frequencies for the cyclic and linear isomers, respectively. Calculations performed on the anion have predicted a linear $^2\Pi_u$ ground state.²¹ Adamowicz²² has predicted the existence of several low-lying electronic states of linear C_6^- .

Experimentally, several infrared absorption studies have been performed on C_6 in a low temperature, rare gas matrix.^{6,23} The assignment of the observed lines to C_6 antisymmetric mode has been problematic; only recently, with extensive isotopic substitution, has a line at 1952 cm^{-1} been definitively assigned to a C_6 antisymmetric stretch. Electron spin resonance (ESR) studies²⁴ in rare gas matrices have shown that linear C_6 in a $^3\Sigma$ state exists, and that the bonding is cumulenic, in accordance with the prediction of Ref. (16). Experimental information on the anion comes from the aforementioned photoelectron spectroscopy studies.^{9,15} In addition to yielding the electron affinity of linear C_6 , 4.185 ± 0.006 eV,¹⁵ the main features in

these spectra were assigned to transitions between linear C_6^- and C_6 . However, a high energy 'tail' in our C_6^- spectrum was tentatively attributed to a high energy cyclic isomer of the anion. Coulomb explosion measurements also suggest the existence of a cyclic C_6^- isomer.²⁵

The results reported here on C_6^- are from two techniques: negative ion threshold photodetachment spectroscopy (zero electron kinetic energy, or ZEKE spectroscopy) and autodetachment spectroscopy. Figure (3.1) illustrates the energetics of both techniques. In threshold photodetachment spectroscopy, the anions are photodetached with a tunable laser, and the near-zero kinetic energy electron signal is collected as a function of laser frequency. These threshold electrons are produced only when the laser is resonant with an anion $\rightarrow$ neutral transition:

By this means, we can map out the direct photodetachment transitions between the C_6^- ground state and various vibrational (and electronic) levels of neutral C_6 with 3 cm^{-1} resolution.

In contrast, autodetachment spectroscopy²⁶ is sensitive to transitions between the ground and excited electronic states *of the anion*. The autodetachment spectrum of C_6^- is obtained by measuring the total photodetachment cross section as a function of the detachment laser frequency. In the absence of anion excited states (the usual case), the photodetachment cross section rises monotonically above the detachment threshold, although in favorable cases one can observe steps in the cross section when new anion $\rightarrow$ neutral transitions become energetically accessible.²⁷ However, if there are long-lived excited states of the anion, $(C_6^-)^*$, just above the detachment threshold, the photodetachment cross section will exhibit sharp peaks resulting from excitation to the metastable $(C_6^-)^*$ state followed by autodetachment to the neutral plus electron:

The combination of threshold photodetachment spectroscopy and autodetachment spectroscopy has been applied previously to Au_2^- and Au_6^- by Kaldor and coworkers.^{28,29}

The threshold photodetachment results presented below show well-resolved transitions between linear C_6^- and C_6 , and yield the symmetric stretch frequencies for C_6 . In addition, the photodetachment cross section results show sharp autodetachment peaks, indicating that there is an excited electronic state of C_6^- near the detachment threshold. The vibrational frequencies of this anion state are very similar to those of neutral C_6 . While C_2^- is known to undergo autodetachment,²⁶ our results are the first such observation for a polyatomic carbon cluster anion.

II. Experimental

Figure (3.2) shows a schematic top view of the apparatus employed for all of the experiments reported in this paper. The machine is described in detail elsewhere,³⁰ but the basic operation is as follows. Cold carbon clusters (anions, cations, and neutrals) are generated in a laser vaporization/pulsed molecular beam source similar to that developed by Smalley.³¹ Helium is used as the carrier gas, typically with a backing pressure of 90 psi. Laser vaporization is achieved by focussing a 4 mJ, 532 nm pulse from a frequency-doubled Nd:YAG laser (20 Hz repetition rate) onto a rotating, translating graphite rod (higher pulse energies resulted in significantly hotter ions). The negative ions that pass through a 2 mm diameter skimmer are collinearly accelerated to 1 keV. Mass selection is achieved with a 1 m long beam-modulated time-of-flight mass spectrometer.³² The mass-separated anions then enter the detection region where they are photodetached by a (pulsed) excimer-pumped dye laser in either of two locations: 60 cm upstream of the ion and electron detectors [the region labelled "A" in Figure

(3.2)] or adjacent to the ion and electron detectors in the region labelled "B" in Figure (3.2). For photodetachment of linear C_6^- , the dye laser output was doubled with a BBO crystal. The dyes used were Rhodamine 600 (300 to 310 nm), Rhodamine 590 perchlorate (287 to 300 nm) and Coumarin 540 (270 to 289 nm).

Three types of photodetachment experiments can be performed with this instrument. We can obtain threshold photodetachment spectra and "partially discriminated" photodetachment cross sections by photodetaching the anions at "A". Total photodetachment cross sections are obtained by photodetachment at "B", directly below the electron detector [marked with the $\otimes$ in Figure (3.2)]. In all three experiments, the electron signal is normalized with respect to the ion current and laser power. Each mode of operation will now be described in more detail.

Threshold photodetachment spectra are obtained by adapting the zero electron kinetic energy (ZEKE) spectroscopy method developed by Müller-Dethlefs et al.³³ to negative ion photodetachment. In these experiments, C_6^- clusters are photodetached in region A. The ejected photoelectrons are extracted with a pulsed field of about 2 V/cm, which is applied 200 ns after the photodetachment laser pulse. This delay allows the higher energy electrons to separate spatially from the threshold electrons that have nearly zero kinetic energy. Once the field is applied, the energetic electrons with significant velocity perpendicular to the ion beam direction are prevented from reaching the detector by a series of apertures between the extraction region and electron detector. Threshold electrons and higher energy electrons scattered along the ion beam axis pass through a 60 cm long Einzel lens and are then deflected into the electron detector with a weak field. While these higher energy electrons cannot be discriminated against by the apertures, they emerge from the extraction region with different kinetic energies than the threshold electrons, due to the spatial separation along the beam axis that occurs prior to applying the extraction pulse. The higher energy electrons can then be discriminated against with a gated detection scheme, in which only those electrons arriving at

the detector within a 35 ns window are counted. This combination of spatial and temporal discrimination yields an electron kinetic energy resolution of 3 cm^{-1} . The resulting peak for an ideal atomic system (one which undergoes s-wave detachment near threshold^{30,34}) is shown in Figure (3.3a).

If the C_6^- clusters are photodetached at A and the extraction pulse is applied with no delay, one obtains a "partially discriminated" photodetachment cross section scan. The electron extraction field immediately accelerates all of the photoelectrons toward the electron detector. However, those photoelectrons produced with a significant perpendicular velocity component are still spatially discriminated against by the apertures *en route* to the electron detector. This is therefore a variation on the "steradiancy detector" described many years ago by Spohr *et al.*³⁵ and Baer *et al.*³⁶ The result is an asymmetric peak which is about 150 cm^{-1} wide [Figure (3.3b)]; the collection efficiency drops off dramatically for electrons produced with more than 150 cm^{-1} kinetic energy. Hence, scans performed in this mode of operation are referred to as "partially discriminated" photodetachment cross section scans.

Finally, to measure the total photodetachment cross section, the clusters are photodetached via the second set of laser windows at region B, which lies just below the electron detector. All of the photoelectrons are collected with a 10 V/cm extraction field. The resulting cross section for an ideal atomic system (s-wave photodetachment) will resemble the spectrum in Figure (3.3c).

If direct photodetachment is all that is occurring, there is little reason to perform anything other than threshold photodetachment spectroscopy with this instrument. However, electrons resulting from autodetachment processes will often have considerably more than 3 cm^{-1} kinetic energy and will therefore not be observed in a threshold photodetachment spectrum, so the instrument must be operated in one of the other two modes to study autodetachment. In the "partially discriminated" mode of operation, only relatively low energy electrons from autodetachment will be collected efficiently, while virtually all the photoelectrons produced by

autodetachment will be collected in the total cross section mode. Differences in the intensity of autodetachment peaks obtained in these two modes can serve as a qualitative measure of the electron kinetic energy resulting from autodetachment.

In addition to the above experiments, photodetachment power studies and two-color, two-photon photodetachment scans are reported in this paper. These are done in order to ascertain the importance of single photon vs. multiphoton detachment for the various peaks observed in the total photodetachment cross section. The photodetachment power studies entail counting electrons produced in region B as a function of laser pulse energy for a particular detachment wavelength. The electrons are counted for 5000 to 6000 laser shots at a given laser power and normalized to the collected ion current. In the two-color, two photon scans, C_6^- is photodetached at "B" by copropagating, simultaneous laser pulses from the doubled dye laser and the second harmonic of a Nd:YAG laser (532 nm). The two laser pulses are made simultaneous with the aid of a photodiode. For these experiments, the dye laser fluence was 25 mJ/cm² (0.5 mJ/pulse) and the 532 nm fluence was 100 mJ/cm² (2 mJ/pulse). Any enhancement of the photodetachment signal by the YAG laser provides strong evidence for two photon processes (see below).

III. Results

Figures (3.4a, b, and c) show the results of the three types of scans discussed in the experimental section for C_6^- . Figure (3.4a) shows the threshold photodetachment spectrum, Figure (3.4b) shows the partially discriminated cross section, and Figure (3.4c) shows the total photodetachment cross section.

The threshold photodetachment spectrum is dominated by peak A located at 296.65 nm. There are also three irregularly spaced peaks with approximately one third the intensity of peak A at higher energies. The positions and relative energies of these peaks, labelled D, G and I,

are listed in Table (3.1). A less intense peak is observed 29 cm^{-1} to the red of each of these peaks; these smaller peaks are labelled a, d, g and i. All of the peaks in Figure (3.4a) are approximately 17 cm^{-1} wide (FWHM). The rising baseline toward higher photon energies is due to background photoelectrons generated by stray photons impinging on various metal surfaces in the extraction region.

In the partially discriminated cross section scan [Figure (3.4b)], the direct photodetachment transitions [Eqn. (3.1)] are evident as distinct thresholds, which are at the same wavelengths as the peaks seen in the threshold photodetachment spectrum. These thresholds are also labelled A, D, G and I. The electron signal near each threshold has the general appearance of the model spectrum in Figure (3.3b), rising sharply then decreasing gradually in intensity as the photon energy increases. In addition, a series of sharp peaks are observed which do not appear in Figure (3.4a). These are due to transitions to excited states of the anion followed, in most cases, by autodetachment [Eqn. (3.2)]. Four manifolds of these peaks lie just to the red of the four direct detachment thresholds and are labelled SA, SD, SG and SI in reference to the thresholds to which they correspond. There are also two fairly intense individual peaks (b_0 and e_0) that do not appear to correspond to direct photodetachment thresholds.

In the total photodetachment cross section scan [Figure (3.4c)] the direct detachment thresholds, again labelled A, D, G and I, are considerably less distinct than in Figure (3.4b). On the other hand, the autodetachment peaks are more intense relative to the direct detachment thresholds. The most intense peaks in each of the four manifolds SA, SD, SG, and SI, are labelled a_0 , d_0 , g_0 , and i_0 . In addition, several sharp but less intense autodetachment peaks not observed in the partially discriminated scan appear in the total cross section scan; these are labelled b_0 , c_0 , etc. In both Figures (3.4b) and (3.4c), the SA manifold does not dominate over the other sharp peak manifolds as peak A in Figure (3.4a) dominates over the rest of the peaks. However, the SD, SG and SI manifolds in the total cross section scan have comparable

intensities, while in the partially discriminated scan, they decrease in intensity toward the higher photon energies. The positions and relative energies of the labelled peaks are listed in the first three columns of Table (3.2). Note that peak m_0 is not shown in Figure (3.4c), but it has approximately the same intensity as peak k_0 . Also, there are several broad peaks in Figure (3.4c) which have not been assigned.

Figures (3.5a, b) and (3.6a, b) show expanded scale, finer step scans of the SA and SB manifolds, respectively. Figures (3.5a) and (3.6a) show the partially discriminated cross section, while Figures (3.5b) and (3.6b) show the total cross section. These figures reveal that these manifolds consist of several peaks of 5 to 7 cm^{-1} FWHM, many of which are actually partially resolved doublets with a characteristic splitting of $\sim 1.7 \text{ cm}^{-1}$. This splitting is most likely due to the contours of unresolved rotational transitions. The rotational constant for C_6^- is expected to be around 0.04 cm^{-1} , so individual rotational transitions cannot be observed at our current resolution (0.4 cm^{-1}). This splitting does not appear in peaks belonging to the higher energy SG and SI manifolds. Table (3.3) lists the peak positions and relative energies for Figure (3.5b). For those peaks which appear as doublets, the peak positions and relative energies refer to the center of the doublet.

The total cross section and partially discriminated scans of the the SA manifold at 297 nm are very different. The most intense feature in Figure (3.5b) is the a_0 doublet at 297.019 nm. This is almost completely missing in the partially discriminated scan, and implies that the corresponding electrons are highly energetic. Note that the largest peak in the SA manifold in Figure (3.4b) is a_1 , not a_0 . The a_2 peak and the a_3 doublet in Figure (3.5b) are also virtually absent in Figure (3.5a). The differences between Figures (3.6a) and (3.6b) are not quite as dramatic. The most intense feature in the total cross section scan, the d_0 doublet at 292.84 nm, is much smaller relative to the other features in the partially discriminated scan.

Figures (3.7a) and (3.7b) show total cross section scans from 292 to 298 nm under two different ion source conditions. The He backing pressure in Figure (3.7a) is considerably higher,

so the vibrational temperature in Figure (3.7a) should be lower than in Figure (3.7b). The data show that the intensities of peaks a_0 and d_0 are largely unaffected by source conditions, but the features just to the red of each of these peaks are more intense in Figure (3.7b). These features are attributed to sequence bands from vibrationally excited C_6^- and are discussed in more detail below.

Figure (3.8) shows a log-log plot of the electron signal (in the total cross section mode) vs. photodetachment laser pulse energy at 297.026 nm and 297.186 nm. These wavelengths correspond to the more intense peaks of the a_0 and a_1 doublets, respectively. The slope of the a_0 curve is approximately 1 while that of the a_1 curve is 0.5, indicating that the a_0 peak intensity depends linearly on laser pulse energy, while the a_1 intensity varies as the square root of the pulse energy. Hence, the a_1 transition appears more strongly saturated than the a_0 transition.

Figures (3.9a) and (3.9b) show the results of the two-color, two-photon scans performed on C_6^- for the SA manifold and part of the SD manifold, respectively. These scans are taken in the total photodetachment cross section mode and show the effect of an additional, simultaneous 532 nm pulse on the electron signal. The results are superimposed on scans obtained under the same anion conditions and tunable dye laser power, but with no 532 nm pulse. Many of the peaks in these two regions exhibit a change in intensity with the addition of the 532 nm, but the most dramatic effect occurs for the 297.019 nm doublet (a_0); its intensity increases by a factor of three in the presence of both laser pulses. Almost no change in intensity was observed for the 297.179 nm doublet (a_1). The changes are less dramatic in Figure (3.9b); the intensity of the largest feature, the d_0 doublet, increases by a factor of 1.6 in the two-color scan. The relative intensities of the peaks in the one-color and two-color scans are given in Table (3.4).

IV. Analysis and Discussion

A. Threshold photodetachment spectrum

1) Peak assignments

The C_6^- threshold photodetachment spectrum is dominated by peak A; peaks D, G, and I are about a factor of three smaller. We assign peak A to the origin of the $C_6 \leftarrow C_6^-$ direct photodetachment transition, while the higher energy peaks are assigned to transitions to vibrationally excited C_6 levels. The dominance of the origin transition indicates a small geometry change between the anion and neutral.

The doublet structure of the peaks of the threshold photodetachment spectrum strongly supports previous assignments of the C_6^- photoelectron spectrum in this energy range to a transition between linear C_6^- and linear C_6 , as opposed to a transition between cyclic structures. The linear anion and neutral ground state term symbols are $^2\Pi_u$ ^{21,22} and $^3\Sigma_g^-$ ^{16,19} respectively. The $^2\Pi_u$ state is split into two spin-orbit components with $\Omega = 3/2$ (the lower of the two) and $\Omega = 1/2$; if the splitting is small enough, both states will be significantly populated in the ion beam. Since the neutral $^3\Sigma_g^-$ state has no corresponding fine structure, each vibrational transition in the photodetachment spectrum should be a doublet, as we observe. The splitting in each doublet of 29 cm^{-1} is therefore the spin-orbit splitting C_6^- . For each doublet, the larger peak is from the $\Omega = 3/2$ level, and the smaller from the spin-orbit excited $\Omega = 1/2$ level. The intensity ratio gives an electronic temperature of approximately 40 K. For comparison, the spin-orbit splitting in the $^2\Pi_u$ state of C_5^- is 26 cm^{-1} .¹⁷

The electron affinity of linear C_6 is given by the energy at which peak A occurs, $4.180 \pm 0.001\text{ eV}$. For comparison, the best previous experimental value, from our C_6^- photoelectron spectrum, was $4.185 \pm 0.006\text{ eV}$.¹⁵ *Ab initio* studies have also predicted electron affinities for linear C_6 in this range.^{22,37}

We next consider the vibrational structure in our spectrum. In a photodetachment spectrum where the anion and neutral have different equilibrium geometries but the same overall symmetry, one expects progressions in totally symmetric vibrational modes of the neutral to dominate.³⁸ Linear C_6 has three totally symmetric modes (all symmetric stretches), and peaks D, G, and I are assigned to transitions to the fundamentals of the three modes. The resulting vibrational frequencies are $\nu_3 = 489 \pm 10 \text{ cm}^{-1}$ (from peak D), $\nu_2 = 1322 \pm 10 \text{ cm}^{-1}$ (peak G), and $\nu_1 = 2061 \pm 10 \text{ cm}^{-1}$ (peak I). Our ν_1 value is close to Martin's *ab initio* value of 2167 cm^{-1} .²⁰ However, our ν_2 and ν_3 frequencies are about 400 and 200 cm^{-1} lower, respectively, than the *ab initio* values. The experimental and calculated frequencies are summarized in Table (3.1).

Note that cyclic C_6 in D_{3h} symmetry has only two totally symmetric modes; the *ab initio* study by Raghavachari and Binkley³⁹ predicts (scaled) frequencies of 1142 cm^{-1} and 800 cm^{-1} for these modes. Thus, the number of transitions to vibrationally excited states in our spectrum is consistent with a linear $\leftarrow$ linear transition.

2) C_6 force constants

Since *ab initio* calculations overestimate the ν_2 and ν_3 frequencies, we have performed a simple, one-dimensional vibrational analysis on C_6 in order to determine the force constants that would reproduce our observed frequencies. The most general one-dimensional harmonic potential in symmetrized internal coordinates is

$$V = \frac{1}{2} (k_1 s_1^2 + k_2 s_2^2 + k_3 s_3^2 + k_4 s_4^2 + k_5 s_5^2) + k^{\text{antisym}} s_4 s_5 + k^{\text{sym},1} s_2 s_3, \quad \text{Eqn. (3.3)}$$

$$+ k^{\text{sym},2} s_1 s_3 + k^{\text{sym},3} s_1 s_2$$

where s_1 , s_2 , and s_3 are symmetric combinations of the internal coordinates [$s_1 = 2^{-1/2}(\Delta r_a + \Delta r_e)$, $s_2 = 2^{-1/2}(\Delta r_b + \Delta r_d)$, and $s_3 = \Delta r_c$] and s_4 and s_5 are antisymmetric combinations [$s_4 = 2^{-1/2}(\Delta r_a -$

Δr_e) and $s_5 = 2^{-1/2}(\Delta r_b - \Delta r_d)$]. The internal coordinates and all of the couplings between them as given by Eqn. (3.3) are illustrated in Figure (3.10). Because this is a six-body problem confined to one-dimension, there is one translational degree of freedom and five vibrational degrees of freedom, corresponding to three symmetric stretches and two antisymmetric stretches. Therefore, in our attempts to reproduce our symmetric stretch frequencies, we will also generate two antisymmetric stretch frequencies.

As mentioned in the introduction, Vala and coworkers confirmed that a 1952 cm^{-1} IR line absorbed by carbon clusters trapped in rare-gas matrices is due to a C_6 antisymmetric stretch (v_4).²³ A frequency close to this has also been assigned to the v_4 mode of C_6 in the *gas phase* in work done by Saykally and coworkers.⁴⁰ Years before, Thompson and coworkers attributed a 1197 cm^{-1} line to the lower frequency antisymmetric stretch (v_5).⁷ Most of the assignments made in that work have since been reassigned, but this particular line has neither been disputed nor confirmed as of yet. Both of these frequencies are in reasonable agreement with calculations; Martin predicts the two antisymmetric stretches to be 1244 cm^{-1} and 2009 cm^{-1} for the v_5 and v_4 modes, respectively.²⁰

There are more force constants in Eqn. (3.3) than there are frequencies to fit, and it is desirable to use the smallest possible number of parameters to fit the vibrational frequencies. First, we assume no coupling between the bonds ($k^{\text{antisym}}, k^{\text{sym}, 1-3} = 0$) and $k_1 = k_4$, $k_2 = k_5$ giving the potential

$$2V = k_1(\Delta r_a^2 + \Delta r_e^2) + k_2(\Delta r_b^2 + \Delta r_d^2) + k_3\Delta r_c^2. \quad \text{Eqn. (3.4)}$$

The symmetric stretch frequencies can be fit using Eqn. (3.4), and the antisymmetric stretches obtained, 1112 cm^{-1} and 1971 cm^{-1} , are close to the matrix values, but the resulting three force constants ($k_1 = 7.67\text{ mdyne/\AA}$; $k_2 = 10.44\text{ mdyne/\AA}$; $k_3 = 3.93\text{ mdyne/\AA}$) are so different as to be

unrealistic. For example, *ab initio* calculations on C_6 predict the central C-C bond to be slightly shorter than the others,²⁰ which is inconsistent with k_3 being the smallest force constant.

Alternatively, we can set all k_i 's equal and assume coupling only between adjacent bonds ($k^{\text{sym},2} = 0$, $k^{\text{sym},3} = k^{\text{antisym}}$) which gives the potential

$$V = \frac{1}{2}(\Delta r_a^2 + \dots + \Delta r_e^2) + k^{\text{sym},3}(\Delta r_a \Delta r_b + \Delta r_d \Delta r_e) + k^{\text{sym},1}(\Delta r_b \Delta r_c + \Delta r_c \Delta r_d) \quad \text{Eqn. (3.5)}$$

Setting $k_1 = 7.28$ mdyne/Å, $k^{\text{sym},3} = -2.65$ mdyne/Å and $k^{\text{sym},1} = 1.23$ mdyne/Å reproduces the observed symmetric stretches, but also gives $\nu_4 \approx 2052$ cm^{-1} , which is slightly high, and $\nu_5 = 809$ cm^{-1} . While this model appears to be more realistic than the previous model, it produces an anomalously low ν_5 frequency. It is interesting to note that when typical carbon-carbon double bond force constants (~ 9.6 md/Å) are used in Eqs. (3.4) or (3.5), symmetric stretch frequencies very similar to the *ab initio* results are obtained.^{18,20,41} As these are significantly higher than the experimental frequencies, the average bond order in C_6 appears to be somewhat less than two.

Further calculations including more coupling constants were performed to reproduce the 1197 cm^{-1} antisymmetric stretch frequency along with our observed symmetric stretch frequencies. However, even with a great deal of coupling, a very small center bond force constant was always required. Calculations performed with the restriction that the center bond remain comparable to the other bonds consistently produced a ν_5 frequency around 800 cm^{-1} . This raises the possibility that the ν_5 frequency, like the observed ν_2 and ν_3 frequencies, is much lower than predicted, and that the matrix assignment of the 1197 cm^{-1} line to the ν_5 mode in C_6 is incorrect. We note that a weak, unassigned line at 814 cm^{-1} was seen by Weltner and McLeod in one of the first matrix isolation studies of carbon clusters, and that the ν_5 absorption is predicted to be considerably less intense than the ν_4 absorption. While our force constant analysis cannot be regarded as definitive, it suggests that it would be worthwhile to perform the

same isotopic substitution studies on the 1197 cm⁻¹ and 814 cm⁻¹ lines as were used to confirm the assignment of the 1957 cm⁻¹ line to C₆, or to study these transitions in a rotationally-resolved gas phase experiment.

3) C₆⁻/C₆ geometry change

The intensities of the peaks in the threshold spectrum are sensitive to the geometry change between the anion and neutral, and this change can be determined (approximately) by simulating the spectrum within the Franck-Condon approximation. The intensity of a transition between vibrational levels v'' and v' of the anion and neutral, respectively, is assumed proportional to the Franck-Condon factors (FCF):

$$I(v' \leftarrow v'') \propto \left| \langle \chi'_{\text{vib}} | \chi''_{\text{vib}} \rangle \right|^2. \quad \text{Eqn. (3.6)}$$

The vibrational wave functions, χ_{vib} , are taken to be a product of three harmonic oscillator wave functions corresponding to the three symmetric stretches. Since the anion symmetric stretch frequencies are unknown, the anion potentials are taken to be identical to the neutral potentials (hence with the same frequencies), only displaced along the normal coordinate. This displacement is adjusted until the relative intensities in the simulation match those in the spectrum. Figure (3.11) shows the Franck-Condon simulation of the threshold photodetachment spectrum along with the actual spectrum. The three normal mode displacements in the simulation are $\Delta Q_1 = 0.033 \text{ (amu)}^{1/2}\text{\AA}$, $\Delta Q_2 = 0.034 \text{ (amu)}^{1/2}\text{\AA}$, and $\Delta Q_3 = 0.058 \text{ (amu)}^{1/2}\text{\AA}$. These displacements reproduce the four peak intensities and do not result in appreciable transitions to overtone or combination levels of C₆.

In order to convert the normal mode displacement quantities to bond length changes, we first require a potential energy function in terms of bond length displacements and force constants which reproduces the experimental frequencies. We use the potential of Eqn. (3.5)

with the three force constants that gave the best fit to the symmetric stretch frequencies (listed previously).

To proceed further, we also require the sign of each normal mode displacement upon photodetachment. Unfortunately, the Franck-Condon factors depend only on the magnitudes of the displacements. There are eight possible combinations of signs in the three normal mode displacements, each yielding a different set of bond length changes. We can choose the most reasonable combination by comparing *ab initio* calculations of the anion^{22,37} and neutral^{18,20,41} geometries with the bond length changes from each combination. Calculations on C_6 predict the C-C bond lengths in the range of 1.29 Å which decrease slightly (by 0.02 Å) from the outermost to the central bond. In contrast, larger bond length variations are predicted in C_6^- ; Adamowicz²² finds $r_a = 1.292$ Å ([outermost bond- see Figure (3.10)], $r_b = 1.341$ Å, and $r_c = 1.290$ Å, while Watts and Bartlett³⁷ find $r_a = 1.258$ Å, $r_b = 1.340$ Å, and 1.237 Å. The most consistent result is that r_b in the anion is significantly greater, about 0.050 Å, than in the neutral, a physically reasonable result since the $2\pi_u$ orbital from which photodetachment occurs is antibonding between the two carbon atoms.¹⁹

With our force constants, this result is reproduced only when all three normal coordinate displacements of the anion relative to the neutral to be positive. [Figure (3.10) shows what is meant by positive for each normal mode.] This yields $\Delta r_a = 0.005$ Å (anion-neutral), $\Delta r_b = 0.057$ Å, and $\Delta r_c = -0.057$ Å. Varying the ΔQ_n in the Franck-Condon simulation so that the simulated peak intensities have uncertainty falling within the experimental signal-to-noise changes the resultant bond length differences by about ± 0.005 Å. Although geometry changes are in better overall agreement with Bartlett's calculations than those of Adamowicz, they do result from several significant approximations and should be treated with appropriate caution. It should also be noted that the calculated geometries on which we base the sign of our normal coordinate displacement were determined in the same calculations that overestimated the ν_2 and ν_3 (and

possibly ν_3) frequencies. However, geometries obtained in *ab initio* calculations are generally more reliable than frequencies.

4) Comparison to the C_5^- threshold photodetachment spectrum

The overall appearance of the C_5^- and C_6^- spectra is qualitatively different. In the C_6^- spectrum, only transitions to excited symmetric stretch levels of C_6 are seen. These are all about one third the intensity of the origin transition. In contrast, in the C_5^- spectrum, transitions to several bend levels in the neutral are evident and are nearly as intense as the transition to the C_5 ($\nu_2 = 1$) symmetric stretch level. However, the transitions to excited vibrational states of C_5 are at least a factor of ten less intense than the origin. Transitions of this intensity would not be observable in the C_6^- spectrum because the signal-to-noise is such that the transitions would be obscured.

The higher intensity symmetric stretch transitions in the C_6^- spectrum imply larger bond length changes upon photodetachment. This is consistent with *ab initio* calculations of the C_5 and C_5^- geometries. It therefore appears that the addition of an electron to the LUMO of C_5 , the $2\pi_u$ orbital has less effect on the bond lengths than the addition of an electron to the (half-filled) $2\pi_u$ LUMO in C_6 .

B. Partially discriminated and total photodetachment cross section spectra

1) Peak assignments

Both the partially discriminated and total photodetachment cross section scans [Figures (3.4b) and (3.4c)] feature fairly intense manifolds of sharp peaks $\sim 43\text{ cm}^{-1}$ to the red of the direct detachment thresholds, which correspond to the ZEKE peaks seen in Figure (3.4a). These peaks are presumably due to transitions to a $(C_6^-)^*$ excited electronic state of the anion. Since these peaks so closely follow the direct detachment thresholds, they are assigned to the same vibrational transitions as the corresponding peaks in the threshold photodetachment spectrum.

That is, the SA manifold marks the origin of the $(C_6^-)^* \leftarrow C_6^-$ transition, and the SD, SG, and SI manifolds are assigned to the 3_0^1 , 2_0^1 , and 1_0^1 transitions, respectively.

This assignment explains the observation of the 3_0^1 , 2_0^1 , and 1_0^1 transitions. The upper states in these transitions, namely the $v_1 = 1$, $v_2 = 1$, and $v_3 = 1$ levels of the excited $(C_6^-)^*$ state, can all decay to the $v = 0$ level of neutral C_6 by vibrational autodetachment. However, the SA manifold lies to the red of the detachment continuum. If this manifold includes the band origin, then the $v = 0$ level of the $(C_6^-)^*$ excited state lies below the $v = 0$ level of linear C_6 . Thus, autodetachment from the $(C_6^-)^* v = 0$ level should not be energetically possible. The SA manifold therefore requires further discussion. We also need to explain the sharp peaks (b_0 , e_0 , etc.) that do not obviously correspond to peaks in the threshold photodetachment scan. In addition, there are congested clumps of peaks to the red of several of the strong transitions a_0 , d_0 , g_0 , and i_0 in Figures (3.4b) and (3.4c) which need to be explained.

SA manifold. All of the peaks in the SA manifold appear at a lower photon energy than the minimum needed to remove an electron from ground state C_6^- to form linear C_6 . Two possible explanations for the appearance of this manifold in our photodetachment spectra are illustrated in Figure (3.12).

Figure (3.12a) shows that autodetachment can occur if peaks in the SA manifold are 'hot band' transitions originating from vibrationally excited anion states, thereby requiring less energy to excite the C_6^- to a state lying above the detachment continuum. This hypothesis can be tested by varying the cluster source conditions to produce hotter ions, and observing how the intensities of the SA peaks vary relative to each other and to peaks in the higher-lying manifolds. The results [Figures (3.7a) and (3.7b)] show that the intensities of peaks a_0 and d_0 are insensitive to source conditions, but the peaks just to the red of a_0 and d_0 are noticeably larger in the 'hotter' scan [Figure (3.7b)]. Thus, the peaks to the red of peak a_0 in the photodetachment cross section arise from the situation in Figure (3.12a); they are sequence band transitions from vibrationally excited C_6^- to vibrationally excited levels of $(C_6^-)^*$ with sufficient energy to

autodetach. However, the temperature studies suggest that peak a_0 at 297.019 nm is indeed the origin of the $(C_6^-)^* \leftarrow C_6^-$ transition, and its presence still requires explanation.

The most likely explanation for peak a_0 is that it results from a resonant two-photon transition where the first photon excites the ground anion electronic state to a bound excited anion state, and the second photon detaches the excited anion [Figure (3.12b)]. Resonant two photon detachment through an intermediate state was first observed by Lineberger for C_2^- in 1972.⁴² This explanation is consistent with several observations. In the first place, Figures (3.5a) and (3.5b) show that peak a_0 is virtually absent in the partially discriminated scan, indicating that the electron kinetic energy associated with this peak is considerably higher than for the peaks to the red. This is just what would occur if peak a_0 results from two-photon absorption, whereas the other peaks are from one-photon absorption just above the detachment threshold followed by autodetachment.

Furthermore, the results in Figure (3.8) indicate that the power dependence of peak a_0 differs from the other peaks in the SA manifold. The dependence of the intensity of peak a_0 on laser pulse energy is approximately linear, which at first glance suggests an unsaturated, one-photon process. However, the intensity of the adjacent peak, a_1 , is proportional to the (pulse energy)^{1/2}, which suggests a *saturated* one-photon transition. Although not conclusive, the a_0 power dependence is consistent with a two-photon process in which the first step (between the two bound anion levels in our hypothesis) is strongly saturated.

Finally, we consider the two-color studies shown in Figure (3.9). These were inspired by related work of Brauman and co-workers⁴³ on organic anions. Figure (3.9) shows a low power (0.5 mJ/pulse) total cross section scan with and without a simultaneous, more intense pulse (2 mJ/pulse) at 532 nm. The intensity of peak a_0 in the two-color scan is substantially increased, while that of peak a_1 is essentially unchanged. The 532 nm photon cannot detach ground state C_6^- , but can detach electronically excited $(C_6^-)^*$. Our results indicate that the $(C_6^-)^*$ state for peak a_0 is sufficiently long-lived so that it can be photodetached by a second photon,

whereas the upper state for peak a_1 autodetaches too rapidly for the second photon to make any difference. This further supports the idea that peak a_0 is a transition to a level of $(C_6^-)^*$ which is bound with respect to autodetachment, while peak a_1 is a transition to a level above the detachment threshold.

All of this evidence shows that peak a_0 indeed is the vibrational origin of the $(C_6^-)^* \leftarrow C_6^-$ transition. Based on a comparison with the threshold photodetachment scan, the $v = 0$ level of the excited anion state lies 43 cm^{-1} below the $v = 0$ level of neutral C_6 . This explains why the intensity of peak a_0 in the total cross section scan [Figure (3.4c)] is lower relative to the 1_0^1 , 2_0^1 , and 3_0^1 transitions than in the threshold photodetachment spectrum [Figure (3.4a)], where the origin transition is dominant. If, in the total cross section scan, peak a_0 is the only major peak that results from two-photon absorption, it is not surprising that its intensity is anomalously low.

Other manifolds. The assignment of the less intense but sharp features in the total cross section scan is not so obvious since there are no corresponding peaks in the neutral spectrum. While peak f_0 appears to be the 3_0^2 transition, the remaining peaks are most likely due to transitions to bend and antisymmetric stretch levels in the upper anion state; such transitions are allowed so long as the vibrational quantum number of the active mode changes by an even number.

Although no calculations for vibrational frequencies have been performed for the $(C_6^-)^*$ state, its symmetric stretch frequencies are essentially identical to those of neutral C_6 . Assuming this holds for the non-totally symmetric vibrations as well, the less intense autodetachment peaks can be tentatively assigned by comparison with the corresponding frequencies from *ab initio* calculations performed on linear neutral C_6 .²⁰ The assignments and comparison with *ab initio* values are shown in Table (3.2). For example, peak b_0 , 186 cm^{-1} to the blue of the origin, is assigned to the 9_0^2 transition; the ν_9 (π_u) mode is predicted to be the lowest frequency bend mode (216 cm^{-1} for two quanta).²⁰ Peak c_0 , 390 cm^{-1} to the blue of the origin, is assigned to the 7_0^2 transition, in accordance with the calculated energy of 446 cm^{-1} for

the $\nu_7 = 2$ level; the ν_7 mode, a π_g bend, is predicted to be the next-lowest frequency bending mode. Similarly, peak e_0 at 626 cm^{-1} to the blue of the origin is assigned to the 8_0^2 transition and peak h_0 found at 1674 cm^{-1} to the blue of the origin is assigned to the 5_0^2 transition. These latter two assignments are very tentative, since the deviation from the *ab initio* frequencies is significant, although the assigned ν_5 frequency is close to the ν_5 frequency determined in the one-dimensional calculation on C_6 using Eqn. (3.5). The remaining sharp autodetachment peaks all appear at energies which are sums of the preceding bend and stretch frequencies, so they are assigned to combination transitions.

Sequence Bands. Finally, we consider the sequence bands which are most evident to the red of peaks a_0 and d_0 ; see Figures (3.5) and (3.6). The temperature studies [Figure (3.7)] show that most of these are transitions from vibrationally excited C_6^- in its $^2\Pi_u$ state to excited vibrational levels of the $(C_6^-)^*$ state. The assignment of these features is not straightforward; several of the peaks are only partially resolved, particularly in Figure (3.5b). However, there is a pattern to the peak spacings, with intervals of 18 cm^{-1} , 23 cm^{-1} , and 29 cm^{-1} appearing several times. In addition, the assignment is aided by comparing differences in peak intensities in the partially discriminated and total cross section scans, which are sensitive to the energy of the ejected electron, and the enhancement of peak intensities in the two-photon, two-color scan [Figure (3.9)], which is sensitive to the lifetime of the upper state with respect to autodetachment. Sets of peaks for which the intensities vary in the same way are most likely due to a common (or similar) upper state. Also, any two peaks split by 1.7 cm^{-1} are assigned to the same vibronic transition; as discussed above, this splitting is probably due to rotational contours in which individual rotational transitions are not resolved.

Peaks a_0 , a_2 , and a_3 appear in the total cross section scan but are missing in the partially discriminated scan. Peaks a_0 and a_3 are both doublets split by 1.7 cm^{-1} . They are separated by 29 cm^{-1} , which is the previously determined spin-orbit interval in the $^2\Pi_u$ ground state of C_6^- , and are both significantly enhanced in the two-color, two-photon experiment. Thus,

we assign a_0 to the 0_0^0 transition originating from the $2\Pi_{3/2}$ level of C_6^- , and peak a_3 to the same transition originating from the spin-orbit excited $2\Pi_{1/2}$ level. This assignment implies that the spin-orbit splitting in the $(C_6^-)^*$ is negligible, a point which will be addressed later, and that the upper state of peak a_3 , like that of peak a_0 , is bound with respect to autodetachment. Peak a_2 is discussed below.

Peak a_1 , 18 cm^{-1} to the red of peak a_0 , is the second most intense feature in Figure (3.5b) and the most intense feature in Figure (3.5a). The significant intensity of this peak and its strong temperature dependence suggest it originates from the lowest excited vibrational level of C_6^- , which, based on *ab initio* calculations on neutral C_6 , should be the $\nu_9 = 1$ bending level. We therefore assign peak a_1 to the 9_1^1 sequence band. Our previous assignment of peak b_0 to the 9_0^2 transition, yields 93 cm^{-1} for the ν_9 frequency in the $(C_6^-)^*$ state, so the assignment of peak a_1 yields a ν_9 frequency of 111 cm^{-1} for the C_6^- ground state. With this assignment, the broad a_4 peak in Figure (3.5a), which is approximately 16 cm^{-1} to the red of the a_1 doublet, is assigned to the 9_2^2 transition. The assignment of these peaks to transitions involving the ν_9 mode is consistent with the observation of peak a_1 with high intensity in the partially discriminated scans [Figures (3.4b), (3.5a)]. The decay of the $\nu_9 = 1$ level of $(C_6^-)^*$ by vibrational autodetachment will result in a photoelectron with only 50 cm^{-1} of kinetic energy [obtained by subtracting 43 cm^{-1} , the amount by which the vibrationless $(C_6^-)^*$ state is bound, from 93 cm^{-1} , the $\nu_9 = 1$ vibrational energy in the $(C_6^-)^*$ state], and this will be collected efficiently in the partially discriminated mode of operation.

Peak a_6 is 29 cm^{-1} to the red of peak a_1 , the same interval between peaks a_3 and a_0 , so we assign it to the 9_1^1 transition from the spin-orbit excited $2\Pi_{1/2}$ level of C_6^- . The small peak a_8 , 16 cm^{-1} to the red of peak a_6 , is then assigned to the 9_2^2 transition from the same spin-orbit level. The relative intensities of peak a_6 and a_1 are similar in Figures (3.5a) and (3.5b), lending further support to our assignment.

Peak a_2 is 25 cm^{-1} to the red of peak a_0 , and peak a_5 is 23 cm^{-1} to the red of peak a_1 . It is reasonable to assign peak a_2 to the 7_1^1 sequence band transition, since the ν_7 bending mode should be the second lowest frequency vibration in C_6^- . Our previous assignment of peak c_0 to the 7_0^2 transition gives $\nu_7 = 195\text{ cm}^{-1}$ in the $(C_6^-)^*$ state, so assigning peak a_2 to the 7_1^1 transition yields $\nu_7 = 220\text{ cm}^{-1}$ in the anion ground state. Peak a_5 is then the $7_1^1 9_1^1$ combination transition. We assign peak a_7 , 15 cm^{-1} to the red of peak a_5 , to the $7_1^1 9_2^2$ transition.

Note that peak a_2 is prominent in the total cross section scan but not in the partially discriminated scan, while peaks a_5 and a_7 are clearly visible in the partially discriminated scan. This indicates that the ejected photoelectrons are less energetic for peaks a_5 and a_7 . Vibrational autodetachment from the $\nu_7 = 1$ level of $(C_6^-)^*$ (the presumed upper level for peak a_2) to the C_6 ground state results in a photoelectron with 152 cm^{-1} of kinetic energy. On the other hand, both the $(\nu_7 = 1, \nu_9 = 1)$ and $(\nu_7 = 1, \nu_9 = 2)$ levels of the $(C_6^-)^*$ can autodetach via a $\Delta\nu_9 = -1$ transition, yielding 50 cm^{-1} electrons in both cases. Hence, the observed intensities of the three peaks in Figures (3.5a) and (3.5b) is qualitatively consistent with our assignment.

Table (3.3) gives a summary of all of the sequence band assignments. Several of these assignments, particularly those involving the ν_7 mode, must be regarded as somewhat tentative. Also, we have not considered complications from Renner-Teller activity in the excited bending modes for the anion $^2\Pi_u$ ground state. A possible contribution from this effect is the additional feature a_1' in Figure (3.5b). The $a_1'-a_1$ feature is noticeably broader than the a_0 doublet and in fact appears to be two superimposed doublets separated by 2 cm^{-1} . This could directly reflect the Renner-Teller splitting in the ν_9 mode of the anion.

2) Autodetachment mechanism and autodetaching state lifetimes.

The mechanisms for autodetachment of negative ions and the analogous process, autoionization of neutrals, have been extensively discussed in the literature.^{44,45,46,47} For our $(C_6^-)^*$ state, where the $\nu = 0$ level is bound but all vibrationally excited levels lie above the

detachment threshold, vibrational autodetachment is the most likely mechanism. In this case, autodetachment occurs by a breakdown of the Born-Oppenheimer approximation. The electronic wave functions for the excited anion state and neutral are coupled via the nuclear vibrational kinetic energy operator T_{vib} , and autodetachment occurs when one (or more) quanta of vibrational energy in the anion is converted to electronic energy, resulting in the ejection of an electron.

More specifically, the vibrational autodetachment rate from the initial state with $v_k = n$ is given by⁴⁵

$$\text{rate} \propto \frac{2\pi}{\hbar} \left| \langle \Psi_f | \hat{T}_{vib} | \Psi_i \rangle \right|^2 \rho, \quad \text{Eqn. (3.7)}$$

where $\Psi_i = \psi_{el,i} \chi_{vib,i}$ and $\Psi_f = \psi_{el,f} \chi_{vib,f}$ are the vibronic wave functions for the excited anion and (neutral + electron), respectively, and ρ is the density of states for the (neutral + electron) continuum. The matrix element in Eqn. (3.7) is given by

$$\langle \Psi_f | \hat{T}_{vib} | \Psi_i \rangle = \frac{-\hbar}{\mu} \left\langle \chi_{vib,f} \left\langle \psi_{el,f} \left| \frac{d}{dQ_k} \psi_{el,i} \right| \frac{d}{dQ_k} \chi_{vib,i} \right\rangle \right\rangle. \quad \text{Eqn. (3.8)}$$

If the inner integral over electronic coordinates is assumed constant, and $\chi_{vib,i}$ and $\chi_{vib,f}$ are taken to be harmonic oscillator wave functions, then only $\Delta v_k = -1$ transitions are allowed. This propensity rule was used in the previous section in determining the electron kinetic energies from autodetachment out of excited vibrational levels of the $(C_6^-)^*$ state, although for several of these states, $\Delta v_k = -1$ transitions are the only possible transitions.

The lifetimes of autodetaching states are best determined by measuring spectral linewidths. Unfortunately, we cannot resolve individual rovibronic transitions in these spectra. We can estimate limits on the lifetimes, however, based on a few observations.

We first consider the transitions to excited symmetric stretch levels of the $(C_6^-)^+$ state. Peak d_0 , the 3_0^1 transition, shows the characteristic 1.7 cm^{-1} splitting attributed to rotational contours. This splitting is not resolved for peaks g_0 (2_0^1) and i_0 (1_0^1). If this lack of structure is due to lifetime broadening, then the autodetachment lifetimes of the $v_1 = 1$ and $v_2 = 1$ levels are less than 1 ps, while that of the $v_3 = 1$ level is longer (actually much longer, as shown below). However, in the absence of full rotational resolution, we cannot rule out spectral congestion as the source of the broadening of the 2_0^1 and 1_0^1 transitions.

We obtain another, more interesting measure of autodetachment lifetimes from the two-photon, two-color scans [see Figure (3.9) and Table (3.4)]. If the intensity of a peak is enhanced in those scans, then the state accessed by the ultraviolet photon is either bound and has a fluorescence lifetime comparable to or greater than the laser pulse width (peaks a_0 , a_3), or it is quasibound with its autodetachment lifetime comparable to or greater than its fluorescence lifetime as well as the laser pulse width (predissociation should not be energetically allowed). In the latter case, the autodetachment lifetime must be in the nanosecond range. We find that peaks d_0 , d_2 , a_2 , and a_7 are noticeably enhanced; the first two are the two spin-orbit components of the 3_0^1 transition, and the second two are sequence band transitions in which the upper state can autodetach only by a $\Delta v_7 = -1$ transition. Hence, the lifetimes for autodetachment through the v_7 and v_3 modes are at least several nanoseconds. On the other hand, the peaks in which the upper state can autodetach via a $\Delta v_9 = -1$ transition (a_1 , a_6) show no enhancement, but the 1.7 cm^{-1} splitting is still resolvable. So long as the fluorescence lifetime is similar for the $v_3 = 1$, $v_7 = 1$, and $v_9 = 1$ levels of the $(C_6^-)^+$ state, this result means that the autodetachment lifetime of a state which can autodetach by a $\Delta v_9 = -1$ transition is greater than 2 ps, but is significantly shorter than the autodetachment lifetime of a state that must autodetach by a $\Delta v_7 = -1$ or $\Delta v_3 = -1$ transition.

This mode-specific effect is striking and deserves further discussion. The density of states factor ρ in Eqn. (3.7), which is proportional to the (electron kinetic energy) $^{1/2}$, is smaller

for a $\Delta v_9 = -1$ transition than for a $\Delta v_7 = -1$ or $\Delta v_3 = -1$ transition. Thus, $\langle \Psi_f | T_{vib} | \Psi_i \rangle$ must be substantially larger for a $\Delta v_9 = -1$ transition. This will be the case if the inner integral in Eqn. (3.8) over the electron coordinates, $\langle \psi_{el,f} | d / \psi_{el,i} \rangle / dQ_k$, is larger for the v_9 mode than for the other two modes, which, in turn, requires that the derivative of the $(C_6^-)^*$ electronic wave function with respect to Q_9 is large. While the nature of $\psi_{el,i}$ is uncertain (see next section), the v_9 mode is a low-frequency, large amplitude bending mode. One might therefore expect the electronic wave function to be quite different at the classical turning points for the $v_9 = 1$ level than at the equilibrium geometry, while for a higher frequency, lower amplitude mode, this effect would not be so pronounced. A more quantitative treatment along the lines developed by Simons⁴⁸ would be extremely useful in understanding the autodetachment phenomena observed here.

3) Nature of the excited anion state.

The molecular orbital configurations of the C_6^- and C_6 ground states are

The $(C_6^-)^*$ excited electronic state can result from excitation from one of the lower-lying orbitals to the partially-filled $2\pi_u$ orbital, or by promotion of a $2\pi_u$ electron to a higher-lying, empty orbital. The correspondence between vibrational features in the C_6^- threshold photodetachment and autodetachment spectra indicates that $(C_6^-)^*$ and neutral C_6 have similar nuclear geometries. This is consistent with the second type of excited state, with the added proviso that the $2\pi_u$ electron is promoted to a non-bonding orbital.

The nature of this orbital is of considerable interest. Autodetachment has previously been observed from two types of excited electronic states in molecular negative ions: valence states, in which the highest occupied molecular orbital is a 'conventional' molecular orbital, and

electrostatically bound states, in which the outermost electron is in a very diffuse orbital and is bound to the neutral core via long-range electrostatic attraction. An example of the former is C_2^- ,²⁶ while examples of the latter include dipole-bound states, such as in CH_2CHO^- ⁴⁹ and CH_2CN^- ,⁵⁰ and the 'image charge-bound' states proposed to explain autodetachment in Au_6^- .⁵¹

The $(C_6^-)^*$ state does not appear to be a clear-cut example of either type of excited state. The similarity between the $(C_6^-)^*$ and C_6 nuclear geometries is what would be expected if $(C_6^-)^*$ were electrostatically bound, consisting of an electron weakly interacting with the neutral C_6 core. The apparent absence of spin-orbit splitting in the $(C_6^-)^*$ state is consistent with such a picture. In addition, the small binding energy (43 cm^{-1}) is characteristic of such a state. While $(C_6^-)^*$ obviously cannot be a dipole-bound state, an 'image charge-bound' state (or, perhaps more accurately, a 'polarization-bound' state) cannot be ruled out. These states have not been nearly as thoroughly investigated as dipole-bound states,⁵² but such a state might result if the polarizability of the π -electron network in the C_6 core were sufficiently high. However, we do not observe autodetachment near the detachment threshold for C_4^- or C_8^- . If $(C_6^-)^*$ is an electrostatically bound state, it appears to be a special case among carbon cluster anions.

The $(C_6^-)^*$ state could also result from excitation to an excited valence orbital. While bound valence-excited states for anions are rare, C_6^- is an open-shelled molecule with a high electron binding energy and has several low-lying, unfilled π orbitals, so the existence of such a state would not be surprising. This is supported in the work by Adamowicz,²² who calculated vertical excitation energies to eight bound excited anion states of C_6^- which involve only valence orbitals. In particular, an optically accessible $2\Pi_g$ state is predicted to lie just below the detachment threshold; this state results from excitation of a $2\pi_u$ electron to a low-lying π_g^* orbital.

If this state is actually the observed $(C_6^-)^*$ state, then the π_g^* orbital must be completely non-bonding, so that the excited anion state geometry is similar to that of the neutral. In addition, we observe the same spin-orbit splitting (29 cm^{-1}) in the autodetachment spectrum as

in the threshold photodetachment spectrum, indicating negligible spin-orbit interaction in the $(C_6^-)^*$ state (there is none in the $C_6\ ^3\Sigma_g^-$ state). Thus, if the $(C_6^-)^*$ state is indeed a $^2\Pi_g$ state, it must be very good example of Hund's case (b) coupling. Whether these constraints on the π_g^* orbital eliminate it from consideration remain to be seen. Of course, the upper state could also be a Σ_g state resulting from excitation of a $2\pi_u$ electron to a σ_g orbital; this would be consistent with the observed spin-orbit structure. No such states have been predicted near the detachment threshold, however.

The above discussion shows that the classification of the $(C_6^-)^*$ state as an electrostatically bound or valence state is difficult. Both labels have their attractions and their pitfalls. In our view, the evidence points more towards a valence state at this point. More insight should result from rotationally-resolved resonant two-photon detachment experiment^r via the bound $(C_6^-)^*$ levels. In addition, *ab initio* studies of the geometries, and not just the vertical excitation energies, of the C_6^- excited states would be extremely useful.

V. Conclusion

We have performed two types of photodetachment spectroscopy on C_6^- : threshold photodetachment (ZEKE) spectroscopy, which maps out transitions between C_6^- and C_6 , and autoderachment spectroscopy, which reveals an excited state of C_6^- 43 cm^{-1} below the detachment threshold.

The vibrational and spin-orbit structure in the threshold photodetachment spectrum is consistent with a transition between linear C_6^- and C_6 . The spectrum yields the three symmetric stretch frequencies of C_6 , as well as the spin-orbit splitting in the C_6^- ground $^2\Pi_u$ state. Two of our three frequencies are noticeably lower than previous *ab initio* harmonic results. From these frequencies and the peak intensities, we have used a simple force field model to derive force constants and bond displacements between the anion and neutral. In order to match the

experimental frequencies, the force constants between adjacent carbon atoms had to be dropped significantly from typical carbon-carbon double bond force constants.

The autodetachment results show that the $(C_6^-)^*$ state is very similar to the neutral linear C_6 state. We observe transitions to the origin and excited symmetric stretch levels of the $(C_6^-)^*$ state which are all shifted 43 cm^{-1} to the red of corresponding features of the threshold photodetachment spectrum. Since the $v = 0$ level of the $(C_6^-)^*$ state is bound with respect to the linear neutral, the electron signal we observe from this state results from a two-photon process. We also observe weaker transitions to excited bending and antisymmetric stretch levels of the $(C_6^-)^*$ state, as well as sequence bands originating from vibrationally excited levels of the C_6^- ground state. Two-color, two-photon studies indicate differing autodetachment lifetimes for the various vibrational levels of the $(C_6^-)^*$ state; autodetachment by a $\Delta v_3 = -1$ transition (π_u bend) is noticeably faster than $\Delta v_3 = -1$ (symmetric stretch) or $\Delta v_7 = -1$ (π_g bend) transitions. We lean towards assigning the $(C_6^-)^*$ state as a valence-excited state rather than an electrostatically bound state. *Ab initio* calculations predict a valence-excited $^2\Pi_g$ state near the detachment threshold, but the $(C_6^-)^*$ state does exhibit several properties one would expect in an electrostatically bound state.

Finally, we point out that while this experiment shows no evidence for a cyclic C_6 state close in energy to the linear C_6 state, the existence of such a state cannot be ruled out. Any transitions from a linear anion to cyclic neutral will be spread out over a large energy range due to the substantial geometry change and therefore would be difficult to observe in this experiment. Although our earlier C_6^- photoelectron spectrum showed a low energy 'tail' which may have come from cyclic C_6^- , which is predicted to lie about 1 eV above the linear anion geometry, no such tail was seen in the threshold photodetachment spectrum. This may indicate less cyclic C_6^- under the beam source operating conditions used here. In any case, if there is a cyclic C_6 state lower in energy than linear C_6 , then the levels of the excited $(C_6^-)^*$ state which are bound with respect to linear C_6 should be able to autodetach to cyclic C_6 . It may be possible

to determine if this occurring by measuring the C_6^- photoelectron spectrum at the photon energy corresponding to peak a_0 . *This experiment will be carried out shortly in our laboratory.*

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Table (3.1) Peak positions, relative energies, and assignments for the threshold photodetachment spectrum of C_6^- .

Peak	Position (nm)	Rel. Energy (cm^{-1})	Assignment	Calculation (Martin) ²⁰
A	296.65	0	Origin ^a	-
D	292.41	489(10)	3_0^1	673
G	285.45	1322(10)	2_0^1	1759
I	279.56	2061(10)	1_0^1	2167

^aThis corresponds to an Electron Affinity of 4.180(0.001) eV

Table (3.2) Peak positions, relative energies, and assignments for the total cross section spectrum of C_6^- . The calculated energies are based on an MP2/6-31G* calculation [Ref. (20)] predicting the harmonic frequencies: $\nu_1 = 2167$, $\nu_2 = 1759$, $\nu_3 = 673$, $\nu_4 = 2009$, $\nu_5 = 1244$, $\nu_6 = 551$, $\nu_7 = 223$, $\nu_8 = 432$, and $\nu_9 = 108$.

Peak	Position (nm)	Rel. Energy (cm ⁻¹)	Assignment	Calculation ²⁰ (cm ⁻¹)
a _n	297.019	0	Origin	-
b _n	295.386	186(2)	9 ₀ ²	216
c _n	293.622	390(2)	7 ₀ ²	446
d _n	292.84	480(2)	3 ₀ ¹	673
e _n	291.60	626(2)	8 ₀ ²	862
f _n	288.77	962(3)	3 ₀ ²	1346
g _n	285.92	1307(5)	2 ₀ ¹	1759
h _n	282.95	1674(5)	5 ₀ ²	2488
i _n	279.91	2058(5)	1 ₀ ¹	2167
j _n	279.87	2063(5)	5 ₀ ² 7 ₀ ²	2934
k _n	279.17	2153(5)	5 ₀ ² 3 ₀ ¹	3161
l _n	276.28	2527(5)	1 ₀ ¹ 3 ₀ ¹	2840
m _n	270.31	3327(5)	1 ₀ ¹ 2 ₀ ¹	3926

Table (3.3) Positions, relative energies and proposed assignments for the peaks found within the SA manifold.

Peak	Position (nm)	Rel. Energy (cm ⁻¹)	Assignment
a ₀	297.019	0	Origin
a ₁	297.179	-18.1(1)	9 ₁ ¹
a ₂	297.241	-25.1(2)	7 ₁ ¹
a ₃	297.277	-29.2(2)	S-O
a ₄	297.317	-33.7(3)	9 ₂ ²
a ₅	297.380	-40.9(3)	7 ₁ ¹ 9 ₁ ¹
a ₆	297.439	-47.5(3)	9 ₁ ¹ plus S-O
a ₇	297.509	-55.5(3)	7 ₁ ¹ 9 ₂ ²
a ₈	297.582	-63.7(3)	9 ₂ ² plus S-O

Table (3.4) Peak intensity changes between the one-photon and two-color, two-photon scans in the SA and SD manifolds.

Peak	Wavelength (nm)	<u>Intensity (blue+green)</u> Intensity (blue only)
a₀	297.019	3.0
a ₁	297.179	1.1
a ₂	297.254	1.5
a ₃	297.277	1.8
a ₅	297.439	1
a ₇	297.509	1.9
d₀	292.84	1.6
d ₁	292.99	1
d ₂	293.09	1.9

Figure (3.1) Energy level diagram illustrating autodetachment and threshold photodetachment transitions. The transitions to the neutral levels yield the zero-kinetic-energy electrons [Eqn. (3.1)] and the transitions to the excited anion levels are followed by autodetachment [Eqn. (3.2)].

Figure (3.2) Diagram of the tunable photodetachment instrument: (A) interaction region for threshold photodetachment; (B) interaction region for the total cross section experiment; (1) detachment windows; (2) electron extraction plates; (3) magnetic shielding; (4) electron Einzel lens; (5) ion detector. Electron detector is located directly above the $\otimes$.

Figure (3.3) Idealized appearance of photodetachment signal in the absence of autodetachment for the three modes of operation of the instrument: (a) threshold photodetachment spectrum, (b) "partially discriminated" spectrum, and (c) total photodetachment cross section.

Figure (3.4) (a) Threshold photodetachment spectrum of C_6^- . (b) Partially discriminated photodetachment cross section spectrum of C_6^- . (c) Total photodetachment cross section of C_6^-

Figure (3.5) (a) Expanded-scale, finer-step scan of the SA manifold obtained in partial discrimination mode. (b) Expanded-scale, finer-step scan of the SA manifold obtained in total cross section mode.

Figure (3.6) (a) Expanded-scale, finer-step scan of the SD manifold obtained in partial discrimination mode. (b) Expanded-scale, finer-step scan of the SD manifold obtained in total cross section mode.

Figure (3.7) (a) Total photodetachment cross section spectrum of C_6^- obtained under normal ion source conditions. (b) Total photodetachment cross section spectrum of C_6^- obtained from ions generated with low carrier gas pressure.

Figure (3.8) Anion photodetachment as a function of detachment pulse energy for peaks a_0 and a_2 in the SA manifold.

Figure (3.9) (a) Two-photon, two-color scan (solid line) of SA manifold using 0.5 mJ/pulse of tunable UV light and 2 mJ/pulse of 532 nm light. The superimposed spectrum (circles) show same spectrum in the absence of the 532 nm light. (b) Same for SD manifold.

Figure (3.10) Parameters for the one-dimensional vibrational calculation for C_6 with the three symmetric and two antisymmetric stretch normal coordinates.

Figure (3.11) Franck-Condon simulation of the threshold photodetachment spectrum of C_6^- using symmetric stretch normal coordinate displacements described in text.

Figure (3.12) Possible explanations for peaks in the C_6^- photodetachment cross section at photon energies below the detachment threshold [SA manifold, Figure (3.4c)]. (a) Peaks are hot bands from vibrationally excited C_6^- . (b) Peaks are from transitions to bound states which are subsequently photodetached by absorption of a second photon.

Chapter 4. Structure in the total photodetachment cross sections of C_n^- ($n = 4, 6 - 9$)

I. Introduction

In the previous chapter, sharp structure in the total photodetachment cross section of C_6^- due to autodetachment or two-photon detachment of an excited C_6^- state was presented.¹ Similar sharp structure in the cross section of C_2^- has been previously observed by Lineberger.² In the case of C_2^- , an excited valence state of the anion is bound with respect to the detachment continuum, but autodetachment becomes energetically possible in the vibrationally excited levels of the excited anion state. This is the same scenario that has been proposed for C_6^- , but the excited anion state is much closer to the detachment continuum in C_6^- than in C_2^- . While no sharp structure has been observed in the total photodetachment cross sections for any small carbon cluster anions other than C_2^- and C_6^- , *broad* features observed in the C_4^- , C_6^- , C_7^- , C_8^- and C_9^- cross section spectra will be the focus of this chapter.

Bound or quasibound anion states have been observed for a number of molecules, and the nature of these excited anion states can take one of several different forms. They can be valence-bound excited states, such as with C_2^- . Large organic molecules such as TCNQ³ can also have bound excited anion states because of large unfilled orbitals. The general criteria for

bound valence states are that the anion is open-shell, which allows for close-lying electronic states, and higher electron affinities, which allows low-lying states to be bound with respect to the detachment continuum. There are also electrostatically bound states (EBS). For instance, excited but bound anion states can exist in situations where the corresponding neutral has a large enough dipole to weakly bind an electron in a diffuse dipolar orbital. These dipole bound anion states have been observed in species such as NH^- ,⁴ $\text{C}_2\text{H}_3\text{O}^-$,⁵ FeO^- ,⁶ CH_2CN^- and PtN^- .⁷ If the neutral core lacks a dipole but is especially polarizable, an image charge bound (ICB) anion state can exist, as is the case with the Au_6^- ring.⁸ These electrostatically bound states are usually bound by around 100 cm^{-1} with respect to the detachment continuum, and have vibrational frequencies very similar to the neutral core.

Bound excited valence states of anions in general are not common. They are, however, feasible in these linear carbon clusters, particularly the even-numbered species, because of their high electron affinity and unfilled π orbitals. It may therefore seem surprising that no sharp autodetachment features have been observed for C_4^- and C_8^- , which are also open-shelled and have high electron affinities. However, the extra electron in the ground electronic states of C_4^- and C_8^- is in an antibonding π_g orbital, while for C_2^- and C_6^- , the electron is in bonding orbitals (σ_g for C_2^- and π_u for C_6^-), making the excitation energetics different for these various species. For comparison, Table (4.1) summarizes the neutral and anion electronic orbital occupancies for the small carbon cluster chains⁹ along with the neutral electron affinities. The electron affinities for C_5 and C_6 are from the previously obtained ZEKE spectra of C_5^- and C_6^- ,^{1,10} the remaining electron affinities are from the fixed-frequency photoelectron spectra of the carbon cluster anions.¹¹

The principle purpose of this chapter is to present the structure observed in the total photodetachment cross sections of C_n^- ($n = 4, 6 - 9$). The spectra themselves and the qualitative discussions on the spectral structure that follow can serve as a starting point for future studies on the electronic properties of small carbon cluster anions. Most of the structure

presented below is very broad, and seems to be more indicative of anion states lying above the detachment continuum. However, for C_6^- , C_7^- and C_9^- , spectral features coincide with detachment thresholds, which suggests some interesting interaction between the electron and the neutral core near the continuum.

II. Experimental

The apparatus used to obtain the total photodetachment cross section scans has been described in detail previously (Chapter 3, Sec. II), but the basic operation is as follows. The carbon cluster anions, neutrals, and cations are generated using a laser-vaporization/pulsed molecular beam source based on a design developed by Smalley.¹² The second harmonic output of a Nd:YAG laser (2 to 6 mJ/pulse) operated at a 20 Hz repetition rate is focused onto the surface of a rotating, translating carbon rod. The resulting plasma is entrained in a pulse of helium carrier gas from a General Valve solenoid-type molecular beam valve, and is expanded through a 0.25" long channel where clustering and cooling occurs. Upon expanding from the channel, the negative clusters that pass through a 2 mm skimmer are colinearly accelerated to 1 keV, and separated out by mass in a 1 m beam-modulated TOF mass spectrometer. The mass-separated clusters then pass through a 5 mm defining slit into a detector region, where the negative ion of interest can be selectively photodetached using a XeCl excimer-pumped tunable dye laser. The ions are detached in a constant field of approximately 2 V/cm, which immediately extracts the detached electrons to a dual microchannel plate detector. The electron signal is collected as a function of laser wavelength, and is normalized to the laser power and ion signal.

For detachment of C_4^- , Rhodamine 610, Rhodamine 590, and Coumarin 540 laser dyes were used. For C_6^- , Rhodamine 590 and Coumarin 540 laser dyes were used for the above-threshold spectra, and QUI was used for the below-threshold spectra. QUI was also used in

obtaining the C_7^- spectrum, and QUI and DMQ were used to obtain the C_8^- spectrum. The QUI and pTP dyes were used for the C_9^- spectrum.

III. Results

The total photodetachment cross section spectra of C_4^- and C_6^- - C_9^- are presented as the solid lines in Figures (4.1) - (4.3). The spectra are grouped according to their common features. In the C_7^- and C_9^- spectra, shown in Figure (4.1), the structure appears very near the detachment continuum. There is also structure found 2700 cm^{-1} to lower photon energy in the C_9^- spectrum. In the C_4^- and C_6^- spectra, shown in Figure (4.2), there is broad structure above the detachment continuum (along with the sharp structure in the case of C_6^- , as was discussed in Chapter 3). The C_8^- and also C_6^- spectra in Figure (4.3) show broad structure around 1 eV below the detachment continuum. On all of the spectra, the 4.65 eV PES have been superimposed as a dashed line onto the detachment wavelength (nm) scale of the total photodetachment cross section spectra (solid lines).¹¹ The most intense peak in the PES is the origin transition, and thus serves as a guide to where the detachment continuum is located.

Some of the structure in the cross section spectrum of C_7^- [Figure (4.1), upper panel] is fairly sharp, and peak A_1 appears to be right at the detachment continuum. Peaks A_1 and A_2 , spaced by 244 cm^{-1} , are actually partially resolved doublets with a characteristic spacing of approximately 25 cm^{-1} . The A_1 doublet is 30 cm^{-1} wide full width at half maximum (FWHM), and A_2 is 40 cm^{-1} wide FWHM. Peak B is approximately 150 cm^{-1} wide and is approximately 200 cm^{-1} to the red of peak A_1 . The peak positions and relative energies are listed in Table (4.2).

The total cross section of C_9^- [Figure (4.1), bottom panel] in the region of the detachment continuum overlaps with, and is startlingly similar to the PES. Peaks A_1 and A_3 exhibit the 496 cm^{-1} vibrational spacing observed in the PES. There is also a shoulder, A_2 , found 200 cm^{-1} to the blue of A_1 . The 350 cm^{-1} wide (FWHM) peaks in the total cross section

are slightly broader than those in the PES. Additional structure is found below the detachment continuum; peaks B_1 , B_2 and B_3 form a 420 cm^{-1} progression, and the energy spacing between B_1 and A_1 is 0.34 eV (2720 cm^{-1}). Peaks B_n are 250 cm^{-1} wide and appear to have some additional, only partially resolved fine structure spaced by 90 cm^{-1} . Although the peaks are very broad, it does appear that the 420 cm^{-1} B_n spacing corresponds to a different (anion) state than does the 496 cm^{-1} progression. Peak positions and relative energies for the total cross section of C_9^- are listed in Table (4.3).

The structure observed in the total cross section of C_4^- [Figure (4.2), top panel] starts approximately 1700 cm^{-1} (0.21 eV) above the detachment continuum. The structure is broad and irregular, and is on the rising slope of the background signal of the apparatus. The positions and relative energies of the structure are listed in Table (4.4). While there is no obvious pattern to the structure, peaks A_2 , A_3 and A_4 may form a progression with a spacing on the order of 700 to 800 cm^{-1} . Peak A_3 is 90 cm^{-1} wide, FWHM.

The sharp structure in the C_6^- total photodetachment cross section [shown in the lower panel of Figure (4.2)], as mentioned before, has been elaborated upon in Chapter 3. However, there are several broad features that were not discussed. For instance, just above the origin threshold and the threshold for a vibrational level are approximately 200 cm^{-1} wide bumps, labeled A_1 and A_2 . These are obviously correlated with the detachment thresholds. There is also a distinct triplet, labeled T, found approximately 1800 cm^{-1} above the detachment continuum. The spacing between the peaks in the triplet T is approximately 70 cm^{-1} . The positions and relative energies of this structure are listed in Table (4.5).

Table (4.5) also lists the broad structure observed in the total cross section of C_6^- found almost 1 eV below the detachment continuum, which is shown in the top panel of Figure (4.3). Peak A_1 is at a 3.22 eV detachment energy and the electron affinity of C_6 is 4.180 eV . The structure is roughly in three clumps spaced by approximately 1000 cm^{-1} .

Similar structure was observed 1 eV below the detachment continuum for C_8^- , as is shown in the lower panel of Figure (4.3). Peak A_1 is at 3.33 eV detachment energy, and the electron affinity of C_8 is 4.35 eV. As with several other clusters, peak A_1 is a partially resolved doublet with a splitting of 44 cm^{-1} . Peak A_2 has partially resolved structure as well, and A_1 , A_2 and A_3 appear to form an approximately 590 cm^{-1} progression. The remaining broad structure is listed in Table (4.6). It is worth noting that the lower-intensity A_7 feature is an entirely reproducible group of 18 cm^{-1} -wide peaks in a configuration reminiscent of the triplet (T) found in the total cross section spectrum of C_6^- [Figure (4.2), bottom panel] except that the energy spacing of the C_8^- peaks are approximately half that of the C_6^- triplet.

IV. Analysis

Schematics of the several processes that could result in broad structure in the total photodetachment cross section scans are shown in Figure (4.4). Cases (a) and (b) show one-photon transitions that could result in broad structure above and below the detachment continuum, respectively. The first (a) shows transitions from the ground anion state to a quasi-bound excited anion state that lies above the detachment continuum, and autodetaches quickly, which would result in broad (depending on the lifetime of the autodetaching state) structure that lies just above the detachment continuum. The second scenario (b) shows transitions from a low-lying excited anion state to a quasi-bound anion state which quickly autodetaches. This model could explain broad structure slightly below the detachment continuum and possibly above the threshold as well.

Cases (c) and (d) in Figure (4.4) are two-photon processes, which are possible given adequate laser power. Case (c) is a scenario in which the ground anion state absorbs one photon in a transition to a bound excited anion state, which is followed by detachment by a second photon to the detachment continuum. This is the type of process responsible for some

of the *sharp* structure observed below the detachment continuum in the C_6^- and C_2^- total photodetachment cross sections, but also for the broader structure below threshold for larger organic molecules.³ However, given the simplicity and high symmetry in the small carbon clusters, it doesn't seem likely that this process could generate broad structure well below detachment threshold. In case (d), the anion absorbs two photons, the *sum* of the two photons being resonant with a very high-lying quasi-bound anion state which very quickly autodetaches. This process, though it should be much weaker than the other three described above, would definitely yield broad structure found well below the detachment continuum.

There may be other, more complicated processes occurring as well, such as photofragmentation followed by detachment. These possibilities will not be addressed in this chapter. Again, the total cross section spectra presented here are to be taken as starting points for future work, but several observations regarding each spectrum will be made here.

C_7^- cross section: The relatively sharp structure observed in this spectrum is reminiscent of the sharp two-photon and autodetachment features observed in the C_6^- total cross section spectrum [lower panel of Figure (4.2) and Chapter 3], although it is a factor of four broader. It is difficult to determine from the superimposed PES whether the anion state lies above or below the detachment continuum, but the observation that peak A_1 is less intense than A_2 suggests that A_1 may be from a two-photon detachment process [case (c) in Figure (4.4)] whereas peak A_2 is from a one-photon process [case (a) in Figure (4.4)]. The doublet profile of peak A_1 likely reflects the spin-orbit splitting in the anion; it is similar to the spin-orbit splitting in C_5^- and C_6^- . The spacing between peaks A_1 and A_2 , 218 cm^{-1} , could be two quanta in a low-frequency bend mode. The broad feature labeled B_1 does not appear to have any connection to A_1 and A_2 , and it may possibly be an electronic hot band as depicted in case (b), a two-photon process depicted in case (d) of Figure (4.4), or another more complicated process.

C₉⁻ cross section: The peaks near the detachment continuum in the C₉⁻ total cross section scan are much more broad than those in the C₇⁻ spectrum, and therefore most likely to be transitions of type (a) in Figure (4.4). The lifetimes of the excited anion states are obviously short. While peaks A₁, A₂, and A₃ are nearly equally spaced, the profile of these three peaks does not suggest a vibrational progression. Rather, A₃ appears to correlate with the lowest frequency symmetric stretch of the neutral, and A₂ is likely a transition to two quanta in a low-frequency bend mode. It is remarkable that the cross sections of both C₉⁻ and C₇⁻ have features that line up so closely with the neutral ← anion origin in the PES. The width of the features in the cross section argue against an electrostatically bound state, which is necessarily bound with respect to the detachment continuum and would yield 5 - 6 cm⁻¹ wide structure (convoluting the resolution of the laser with the expected rotational manifold). However, for two (three, including C₆⁻, see below) carbon cluster anions to have quasibound excited states nearly coinciding with the respective detachment continua must be more than a coincidence.

One possibility stems from the effective potential between the electron with the neutral,

$$V_{\text{eff}} = \frac{-\alpha}{r^4} + \frac{\ell(\ell+1)}{r^2}, \quad \text{Eqn. (4.1)}$$

where the first term is the electrostatic attraction between the electron and the carbon cluster having polarizability α , and the second term is the centrifugal contribution to the effective potential from the angular momentum of the photoelectron, ℓ . For $\ell > 0$ (p, d, ...-wave electrons), there is some barrier in the potential, which, depending on α and ℓ (for larger α , the barrier is lower and at greater r , and for smaller α , the barrier can be higher and closer to the neutral core), might support a quasibound resonance. Such resonances have been observed in atomic ionization cross sections, and while the atomic quasibound neutral resonances are on the order of eV wide (versus the 0.01 eV wide features in the C₉⁻ cross section), in the situation described here, the quasibound level would be very near threshold, so the electron wouldn't be

extraordinarily energetic, and the barrier might be broad. This explanation is wildly speculative, and should be treated with appropriate caution.

The band at lower detachment energy may be an electronic hot band, with transitions of type (b) in Figure (4.4), or a two-photon process such as case (d). If case (b), the 420 cm^{-1} spacing between B_1 , B_2 and B_3 may again be activation in the lowest-frequency symmetric stretch of the upper state, or, if either the lower or upper excited anion states are Renner-Teller distorted, it could be a relatively extended progression in a band mode.

C_4^- cross section: Not much can be said regarding the broad and irregular structure above the detachment continuum observed in the C_4^- cross section spectrum. This structure must be due to transitions of type (a) depicted in Figure (4.4). Peaks A_2 , A_3 and A_4 appear to have some similar combination structure tailing to higher detachment energy. Otherwise, no other patterns are obvious.

C_6^- cross section: The broad bumps found above the detachment continuum of C_6^- labeled A_1 and A_2 in the C_6^- total cross section spectrum [bottom panel, Figure (4.2)]. Their close correlation with detachment thresholds is similar in nature to the structure in the C_9^- spectrum. The total cross section of C_5^- (not shown), while much simpler than the cross sections of C_4^- and C_6^- through g^- , also exhibited a broad but distinct bump just to the blue of the sharp detachment threshold. Clearly, some electrostatic effects are affecting the cross section.

The structure observed well below the detachment continuum of C_6^- [upper panel, Figure (4.3)] is particularly broad and noisy, and are most likely due to transitions of type (d) in Figure (4.4). Energetically, it is possible that a resonant process [case (b)] is occurring, but the broadness of the features argue against this. Moreover, two-color scans in which the second photon (532 nm, 2nd harmonic output of a YAG) plus the blue photon was sufficient to detach C_6^- were performed, and no enhancement of the structure was observed. If the process were of type (c), the color of the second photon would be irrelevant, so long as it was adequate for

detachment, in which case the addition of the second photon should result in signal enhancement (see Chapter 3, Sec. III and Sec. IV.B.2).

Based on this, the upper state must lie 2.28 eV above the detachment continuum. Several additional points are worth noting. Peaks A_1 , A_3/A_4 , and A_6/A_7 form a 900 cm^{-1} progression, but because of the nature of the transition, it reflects an 1800 cm^{-1} progression in the upper state. This is a reasonable value for the highest frequency symmetric stretch. Peaks A_2 and A_5 appear to form 300 cm^{-1} progressions off of Peaks A_1 and A_3/A_4 , respectively, which gives a 600 cm^{-1} frequency for the upper state. This is close to the predicted lowest-frequency symmetric stretch of neutral C_6 , although the ZEKE spectrum yielded 480 cm^{-1} for this mode in the ground neutral state.

C_6^- cross section: The structure observed well below the detachment continuum of C_8^- [bottom panel, Figure (4.3)], as with C_6^- , appears to be transitions of type (d) depicted in Figure (4.4). Two-color experiments were also performed for C_8^- as they were for C_6^- , which further support this characterization. Based on this, the upper state lies 2.28 eV above the detachment continuum. This, coincidentally, is identical to the energy of the C_6^- upper state above the C_6^- detachment continuum. Peaks A_1 , A_2 and A_3 form a 500 cm^{-1} progression, which gives a 1000 cm^{-1} frequency for the upper state. Peaks A_5 , A_6 and A_7 form another 500 cm^{-1} progression with a different profile, and the two progressions may correspond to different electronic transitions.

V. Conclusions

The work presented here, if nothing else, illustrates how interesting the electronic properties of small carbon cluster anions are. The narrow and broad features observed in the total photodetachment cross sections of C_4^- , C_6^- , C_7^- , C_8^- and C_9^- presented here will hopefully inspire future investigations into these elusive species.

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Table (4.1) Electronic configurations and electron affinities of the linear carbon clusters and configurations of the corresponding anions.

	Neutral State	Electronic configuration	Electron Affinity (eV)	Anion ground state	Anion configuration
C ₂	$1\Sigma_g^+$	$\dots(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$	3.273	$2\Sigma_g^+$	$\dots(3\sigma_g)^1$
C ₃	$1\Sigma_g^+$	$\dots(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4$	1.995	$2\Pi_g$	$\dots(1\pi_g)^1$
C ₄	$3\Sigma_g^-$	$\dots(1\pi_u)^4(4\sigma_u)^2(5\sigma_g)^2(1\pi_g)^2$	3.882	$2\Pi_g$	$\dots(1\pi_g)^3$
C ₅	$1\Sigma_g^+$	$\dots(1\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2(1\pi_g)^4$	2.855	$2\Pi_u$	$\dots(2\pi_u)^1$
C ₆	$3\Sigma_g^-$	$\dots(1\pi_u)^4(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2$	4.180	$2\Pi_u$	$\dots(2\pi_u)^3$
C ₇	$1\Sigma_g^+$	$\dots(1\pi_u)^4(1\pi_g)^4(8\sigma_g)^2(7\sigma_u)^2(2\pi_u)^4$	3.358	$2\Pi_g$	$\dots(2\pi_g)^1$
C ₈	$3\Sigma_g^-$	$\dots(1\pi_u)^4(1\pi_g)^4(8\sigma_u)^2(9\sigma_g)^2(2\pi_u)^4(2\pi_g)^2$	4.373	$2\Pi_g$	$\dots(2\pi_g)^3$
C ₉	$1\Sigma_g^+$	$\dots(1\pi_u)^4(1\pi_g)^4(2\pi_u)^4(10\sigma_u)^2(11\sigma_g)^2(2\pi_g)^4(3\pi_u)^2$	3.684	$2\Pi_u$	$\dots(3\pi_u)^3$

Table (4.2) Peak positions and relative energies for the C_7^- total photodetachment cross section spectrum [Figure (4.1), top panel].

Peak	Position (nm)	Relative energy (cm^{-1})
B	372.8	-180
A_1	370.70	-25
	370.35	0
A_2	367.38	218
	367.04	244

Table (4.3) Peak positions and relative energies in the C_9^- total photodetachment cross section spectrum [Figure (4.1), bottom panel].

Peak	Position (nm)	Relative energy (cm^{-1})
B_1	375.2	0
	374.0	86
B_2	369.35	422
	368.30	499
B_3	363.6	850
A_1	340.45	0
A_2	337.55	252
A_3	334.8	496

Table (4.4) Peak positions and relative energies for the C_4^- total photodetachment cross section spectrum [Figure (4.2), upper panel].

Peak	Position (nm)	Relative energy (cm^{-1})
A_1	302.8	0
A_2	291.55	1274
	290.0	1458
	289.5	1517
A_3	284.9	2075
	283.96	2191
	282.68	2351
	280.7	2600
	279.8	2715
A_4	279.3	2779
	278.0	2946
	276.95	3082
A_5	275.4	3286
A_6	271.2	3848
	270.2	3985
	269.4	4094

Table (4.5) Positions and relative energies of *broad* structure observed in the total photodetachment cross section spectrum of C_6^- [Figure (4.2), lower panel and Figure (4.3) upper panel].

Peak	Position (nm)	Relative Energy (cm^{-1})
Above detachment continuum		
A ₁	296	0
A ₂	292	462
T	289.1	0
	288.5	72
	287.95	138
Below detachment continuum		
a ₂	392.4	-497
a ₁	389.0	-274
A ₁	384.9	0
	383.7	81
A ₂	379.8	349
A ₃	371.55	934
A ₄	369.5	1083
A ₅	366.1	1334
A ₆	360.5	1759
A ₇	358.0	1952

Table (4.6) Peak positions and relative energies for the C_8^- total photodetachment cross section spectrum [Figure (4.3), lower panel].

Peak	Position (nm)	Relative Energy (cm^{-1})
a_2	378.0	-370
a_1	376.2 375.6	-243 -201
A_1	373.4 372.79	-44 0
A_2	366.6 366.01 365.0 364.2	453 497 573 633
A_3	358.5	1069
A_4	355.2	1485
A_5	352.88 352.24 351.6	1514 1565 1617
A_6	347.2 346.7 345.9	1977 2019 2085
A_7	342.45 341.45 340.6 340.2 339.67	2377 2462 2535 2570 2616

Figure (4.1) Total photodetachment cross section spectra of C_7^- and C_9^- (solid lines) and the corresponding anion PES (dashed line).

Figure (4.2) Total photodetachment cross section spectra of C_4^- and C_6^- above the respective detachment continua (solid lines) and the corresponding PES (dashed line).

Figure (4.3) Total photodetachment cross section spectra of C_6^- and C_8^- below the respective detachment continua (solid lines) and the corresponding PES (dashed line).

Figure (4.4) Possible transitions for the structure observed in the total photodetachment cross sections of small carbon clusters.

Chapter 5. Reassignment of the Si_2^- photodetachment spectra

Upon reanalysis of our silicon cluster data, we have discovered that our analysis of our Si_2^- photoelectron and threshold photodetachment spectra reported previously¹ is incorrect. The mistake lies in improperly correlating peaks seen in the photoelectron spectrum (PES) with those found in the threshold photodetachment (or zero electron kinetic energy - ZEKE) spectrum. Figure (5.1) shows the PES of Si_2^- with the detachment laser wavelength of 355 nm (3.493 eV) and polarization 90° with respect to the electron detection. Figure (5.2) shows the ZEKE spectrum of Si_2^- corresponding to the 1.1 - 1.4 eV region in the 3.49 eV PES. A more recently obtained, higher resolution PES (dotted line) taken using 2.98 eV photon energy has been superimposed onto the ZEKE spectrum (solid line) in Figure (5.2). Originally, we believed that peaks "d" and "C" in the PES corresponded, respectively, to the triplet feature at 555 nm and the doublet feature found at 570 nm in the ZEKE spectrum. However, a more careful calibration indicates that the triplet corresponds to peak D in PES, and that peak d is absent in the ZEKE spectrum. The energy interval between 570 nm and 555 nm is 532 cm^{-1} . Peaks "d" and "C" on the PES are separated by only 350 cm^{-1} , while "D" and "C" are separated by 550 cm^{-1} . The ZEKE spectrum shown in Figure (5.2) has been relabelled to correctly reflect the correspondence with the PES peaks.

This change affects the relative energies of the low-lying states of Si_2 and Si_2^- , which are displayed in Figure (5.3). Peaks A through F are assigned to transitions between two nearly degenerate doublet states of the anion and the two nearby triplet states of the neutral. The assignment of the ZEKE spectrum is the same as before: the triplets (peaks D,E) are due to $^3\Pi_u \leftarrow ^2\Sigma_g^+$ transitions, and the doublets (peaks B,C) are from $^3\Sigma_g^- \leftarrow ^2\Pi_u$ transitions. (The triplet and doublet structure is from the spin-orbit fine structure in the $^3\Pi_u$ and $^2\Pi_u$ states, respectively). However, the PES assignment is now altered: peak D is the $^3\Pi_u \leftarrow ^2\Sigma_g^+$ transition, while peak d is the $^3\Pi_u \leftarrow ^2\Pi_u$ transition; this assignment was reversed in our previous paper. Peak d is observed in the PES but not the ZEKE spectrum because it is a p-wave transition involving ejection of a photoelectron with orbital angular momentum $\ell = 1$; the threshold photodetachment spectrometer is sensitive only to s-wave ($\ell = 0$) photodetachment transitions, since, according to the Wigner threshold law,² these are the only transitions with substantial cross sections near the detachment threshold.

The implications of this reassignment are as follows. Since peak D corresponds to a higher energy transition than peak d, the $^2\Sigma_g^+$ state of the anion must lie below, rather than above, the $^2\Pi_u$ state. This means that the energy of peak C no longer corresponds to the electron affinity of Si_2 because it is not the transition between the lowest electronic states of the anion and neutral. The "electron affinity" transition, from the anion $^2\Sigma_g^+$ state to the neutral $^3\Sigma_g^-$ state, is a two-electron transition, involving both photodetachment and rearrangement of the remaining electrons. Such a transition is, in general, too weak to be observed in either the PES or ZEKE spectrum. We therefore do not see the electron affinity transition here, although the electron affinity can be extracted from the observed transitions.

A similar error was made in the singlet manifold, peaks G-L. The transitions are shown in Figure (5.3). Figure (5.4) shows the threshold photodetachment spectrum in the 0.6 to 0.95 eV energy region in the PES. The peak found at 451 nm was originally believed to correspond to peak I in the PES. However, with our improved PES data calibration, we now know that it

corresponds to peak J in the PES. The 451 nm peak was correctly assigned to the $b^1\Pi_u \leftarrow ^2\Sigma_g^+$ transition. Peak I in the PES is then assigned to the $b^1\Pi_u \leftarrow ^2\Pi_u$ transition, a p-wave transition that will not be observed in the ZEKE spectrum. The relative position of these two peaks is consistent with the $^2\Sigma_g^+$ state being the ground state of the anion.

Several of the peak labels on Figs. 5 and 6, and Table 1 in Ref. [1] should be changed in order to properly reflect the relationship between the PES and the threshold photodetachment spectrum. As mentioned before, "d_{1,2,3}" and "e_{1,2,3}" in Figure 5, Ref. [1] should be changed to "D_{1,2,3}" and "E_{1,2,3}." Likewise, peaks "i" and "j" in Figure 6, Ref. [1] should be changed to "J" and "j." Figures (5.2) and (5.4) presented here have these new labels. Also indicated by vertical lines in Figures (5.2) and (5.4) are the positions of peaks d and l taken from the newly calibrated PES data.

Table (5.1) lists these threshold spectral peaks by the new label along with the position and assignment. Additionally, the p-wave transitions observed only in the PES are included in Table (5.1) with the improved energy position. These are marked by an asterisk (*). Several of these peaks have different assignments than they were given in Ref. [1] as a result of the above discussion.

Table (5.2) summarizes the excitation energies of the anion and neutral states based on the the correct ordering of the anion states.³ The correct electron affinity of Si₂, 2.201 ± 0.01 eV, is also given. Vibrational frequencies and spin-orbit splittings remain unchanged for all of the states. Note that r_e for the $^3\Pi_u$ state is $2.155 \text{ \AA}$;⁴ a typographical error was made in Ref.[1].

Interestingly, calculations performed on the anion by Bruna et al.,⁵ Nimlos et. al.⁶ and Raghavachari et. al.⁷ predict the $^2\Sigma_g^+$ state to be the ground state. In fact, the highest level calculation performed by Raghavachari predicted the Π state to lie 22 meV above the Σ state, which is remarkably close to our experimental value of 25 meV. It should also be noted that Weltner has recently corroborated this reassignment with IR spectra of neutral Si₂ in rare gas

matrices.⁸ From his spectra, he found the $^3\Pi_u - ^3\Sigma_g^-$ splitting to be 313 cm^{-1} , which is well within the error bars of our value, $331 \pm 80\text{ cm}^{-1}$.

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Table (5.1) Peak positions and assignments for the ZEKE spectrum of Si₂⁺. Peaks marked with an asterisk were not seen on the ZEKE spectrum, and are taken from the PES spectrum.

Peak	Position (eV)	Assignment
B ₂	2.095	$X^3\Sigma_a^-(v'=0) \leftarrow {}^2\Pi_{1/2}(v''=1)$
B ₁	2.109	$X^3\Sigma_a^-(v'=0) \leftarrow {}^2\Pi_{3/2}(v''=1)$
C ₂	2.150	$X^3\Sigma_a^-(v'=0) \leftarrow {}^2\Pi_{1/2}(v''=0)$
c	2.165	$D^3\Pi_2(v'=0) \leftarrow {}^2\Sigma_a^+(v''=1)$
C ₁	2.176	$X^3\Sigma_a^-(v'=0) \leftarrow {}^2\Pi_{3/2}(v''=0)$
c	2.183	$D^3\Pi_0(v'=0) \leftarrow {}^2\Sigma_a^+(v''=1)$
d*	2.222	$D^3\Pi_u(v'=0) \leftarrow {}^2\Pi_u(v''=0)$
c ₂	2.225	$X^3\Sigma_a^-(v'=1) \leftarrow {}^2\Pi_{1/2}(v''=0)$
D ₁	2.235	$D^3\Pi_2(v'=0) \leftarrow {}^2\Sigma_a^+(v''=0)$
D ₂	2.242	$D^3\Pi_1(v'=0) \leftarrow {}^2\Sigma_a^+(v''=0)$
D ₃	2.250	$D^3\Pi_0(v'=0) \leftarrow {}^2\Sigma_a^+(v''=0)$
e*	2.287	$D^3\Pi_u(v'=1) \leftarrow {}^2\Pi_u(v''=0)$
E ₁	2.301	$D^3\Pi_2(v'=1) \leftarrow {}^2\Sigma_a^+(v''=0)$
E ₂	2.309	$D^3\Pi_1(v'=1) \leftarrow {}^2\Sigma_a^+(v''=0)$
E ₃	2.316	$D^3\Pi_0(v'=1) \leftarrow {}^2\Sigma_a^+(v''=0)$
F*	2.326	?
G ₁	2.597	$a^1\Delta_g(v'=0) \leftarrow {}^2\Pi_{1/2}(v''=0)$
G ₂	2.611	$a^1\Delta_g(v'=0) \leftarrow {}^2\Pi_{3/2}(v''=0)$
H ₁	2.657	$a^1\Delta_g(v'=1) \leftarrow {}^2\Pi_{1/2}(v''=0)$
H ₂	2.672	$a^1\Delta_g(v'=1) \leftarrow {}^2\Pi_{3/2}(v''=0)$
M ₁	2.715	$a^1\Delta_g(v'=2) \leftarrow {}^2\Pi_{1/2}(v''=0)$
M ₂	2.729	$a^1\Delta_g(v'=2) \leftarrow {}^2\Pi_{3/2}(v''=0)$
I*	2.722	$b^1\Pi_u(v'=0) \leftarrow {}^2\Pi_u(v''=0)$
J	2.745	$b^1\Pi_u(v'=0) \leftarrow {}^2\Sigma_a^+(v''=0)$
K*	2.787	$c^1\Sigma_a^+(v=0) \leftarrow {}^2\Sigma_a^+(v''=0)$
j	2.812	$b^1\Pi_u(v'=1) \leftarrow {}^2\Sigma_a^+(v''=0)$
L*	2.826	?

Table (5.2) Excitation energies for the low-lying states of Si_2 and Si_2^- .

	State	T_e (eV)
Si_2 E.A. = 2.201 ± 0.010 eV	$d^1\Sigma_g^+$	1.152 ± 0.010
	$c^1\Sigma_g^+$	0.586 ± 0.010
	$b^1\Pi_u$	0.544 ± 0.010
	$a^1\Delta_g$	0.435 ± 0.002
	$D^3\Pi_u$	0.041 ± 0.010
	$X^2\Sigma_g^-$	0
Si_2^-	$2^1\Pi_u$	0.025 ± 0.010
	$2^1\Sigma_g^+$	0

Figure (5.1) Photoelectron spectrum of Si_2 . The detachment wavelength is 355 nm.

Figure (5.2) ZEKE spectrum of Si_2^- showing transitions to the triplet states of Si_2 .

Figure (5.3) One-electron transitions between the low-lying states of Si_2^- and Si_2 . Those marked with an asterisk are p-wave transitions. Multiple letters correspond to different vibrational transitions [see Table (5.1)].

Figure (5.4) ZEKE spectrum of Si_2^- showing transitions to the singlet states of Si_2 .

Chapter 6. Threshold Photodetachment (ZEKE) Spectroscopy of Si_3^-

Abstract

The threshold photodetachment (ZEKE) spectrum of Si_3^- is presented and discussed. The spectrum shows well-resolved vibrational structure. A comparison with several *ab initio* calculations shows that the spectrum is due to transitions to the $^3\text{A}_2'$ (D_{3h}) state of Si_3 . The symmetric stretch and degenerate e' frequencies for the Si_3 $^3\text{A}_2'$ state are determined to be $501 \pm 10 \text{ cm}^{-1}$ and $337 \pm 10 \text{ cm}^{-1}$, respectively. Additional structure observed in the spectrum suggests that the negative ion is a fluxional, Jahn-Teller distorted species. The ZEKE spectrum shows no evidence for transitions to the $^1\text{A}_1$ state of the neutral, which is predicted to lie very close to the $^3\text{A}_2'$ state. A comparison of the ZEKE and previously obtained photoelectron spectrum of Si_3^- suggests that these two states are close in energy, but that transitions to the singlet state are very weak in the ZEKE spectrum.

I. Introduction

The study of small silicon clusters has been motivated by their importance in astrophysics¹ and chemical vapor deposition processes.² The desire to characterize these species experimentally has been further fueled by a series of *ab initio* studies that have predicted interesting electronic properties and structural trends as a function of cluster size.³ However, other than for the dimer,^{4,5} experimental work on these elusive species is sparse; thus far, for example, vibrationally resolved spectra have been obtained only for Si₃ and Si₄,^{6,7,8} and no rotationally resolved spectra have been observed for any species larger than the dimer. In our laboratory, we are focussing on probing the electronic and vibrational structure of these clusters by performing high resolution photodetachment spectroscopy experiments. This paper discusses the results of such a study performed on Si₃.

Silicon trimer has been the object of considerable theoretical efforts, starting with the work by Grev and Schaefer⁹ and by Raghavachan¹⁰ in 1985. The results of their calculations for an extensive set of molecular structures indicated that, in contrast with the well-known linear structure of C₃,¹¹ Si₃ is strongly bent, with two close lying electronic states: the ¹A₁ (C_{2v}) and ³A₂' (D_{3h}) states. Both calculations predict the singlet C_{2v} structure to be the ground state, but the calculated spacing between the two states is less than 1 kcal/mol. More recent calculations have yielded similar results.^{12,13,14,15} The negative ion of Si₃, while less studied, is also interesting from a theoretical standpoint. Röhlfing and Raghavachan^{16,17} reported a ²A₁ (C_{2v} geometry) ground state which results from Jahn-Teller distortion of a ²E' configuration, with the corresponding ²B₂ saddle point lying only 160 cm⁻¹ higher in energy. Raghavachan^{10,16,17} has calculated vibrational frequencies for the anion as well as the low-lying neutral states, and frequencies for the neutral states have also been calculated by Dixon¹² and Depristo.¹⁴

The experimental work to date on $\text{Si}_3/\text{Si}_3^-$ has not been of sufficient quality to test the *ab initio* predictions concerning electronic and vibrational structure. The negative ion photoelectron spectrum (PES) of Si_3^- obtained by Smalley and coworkers¹⁸ revealed several electronic bands, but the resolution was insufficient to make any assignments. In the vibrationally resolved PES of Si_3^- obtained by our group,⁶ we observed that the band associated with the lowest Si_3 electronic state exhibited an extended vibrational progression with a characteristic frequency of $360 \pm 40 \text{ cm}^{-1}$, in poor agreement with the calculated frequencies of the purported ground $^1\text{A}_1$ state. However, this progression was congested and poorly resolved, and a better quality spectrum was clearly needed for comparison with the *ab initio* work. A similar frequency was observed in emission spectra obtained by Gole and coworkers⁷ and attributed to Si_3 .

In this paper, the substantially higher resolution threshold photodetachment (zero kinetic energy electron, or ZEKE) spectrum of Si_3^- is presented. As with the ZEKE spectra we obtained for Si_2^- and Si_4^- ,^{5,8} more detailed information regarding both the Si_3 anion and neutral electronic states is extracted from the spectrum presented below than could be determined from the PES. The spectrum, which could be obtained over only a small part of the energy range probed by the PES, shows well-resolved transitions between what appear to be the ground electronic states of the anion and neutral trimer. This spectral structure, however, is still not reconcilable with the predicted $^2\text{A}_1$ anion and $^1\text{A}_1$ neutral ground state frequencies.^{10,12,14,17} Instead, it appears that the band is due to transitions to the neutral $^3\text{A}_2^- (\text{D}_{3h})$ state which, as mentioned above, is predicted to be nearly degenerate with, but slightly higher in energy than the calculated neutral ground $^1\text{A}_1$ state. The ZEKE spectrum also exhibits additional structure not resolved in the PES. In order to satisfactorily assign this structure, it is necessary to treat the anion as a fluxional, Jahn-Teller distorted species rather than as a rigid molecule.

II. Experimental

The threshold photodetachment spectrometer used in this study is described in detail elsewhere,¹⁹ but the basic operation is as follows. A beam of cold silicon cluster anions is generated in a laser vaporization/pulsed molecular beam source and is mass-selected using time-of-flight. The cluster of interest is then photodetached using an excimer-pumped dye laser operated at 20 Hz. The electrons detached with nearly zero kinetic energy (ZEKE) are collected as a function of photon wavelength. The selective detection of ZEKE electrons, based on the method developed by Müller-Dethlefs *et al.*,²⁰ gives an energy resolution of as good as 3 cm^{-1} . However, because of the small photodetachment cross section of Si_3^- , some resolution was sacrificed for increased signal; the resolution for the spectrum presented below is estimated to be 10 to 15 cm^{-1} . The signal was averaged for 1500 shots at each wavelength and normalized to both laser power and ion current. The two dyes used to obtain the spectrum were Coumarin 540 and Coumarin 503.

III. Results

Figure (6.1) shows the PES of Si_3^- previously obtained with a detachment wavelength of 355 nm (3.493 eV).⁶ Band X represents transitions to the lowest electronic state(s) of Si_3 , while band B is a transition to a more highly excited state. The inset shows band X on an expanded y-axis (dotted line) with the newly obtained ZEKE spectrum superimposed onto the PES energy scale. We observed a ZEKE spectrum for this band only. The data collection was considerably more time consuming than in our recent study of Si_4^- ;⁸ the photodetachment cross section near threshold was much smaller for Si_3^- than for Si_4^- , and the trimer ions were more difficult to produce. Figure (6.2) shows the ZEKE spectrum of band X on an expanded scale showing the detachment wavelength. The spectrum is dominated by a 337 cm^{-1} progression formed by the

18-20 cm⁻¹ wide (FWHM) peaks labeled 0, 1, 2, 3, and 4. Peak 0' is not a member of this progression; it lies 385 cm⁻¹ to lower photon energy of peak 0, which appears to be the origin of the main progression. This 337 cm⁻¹ progression is congested with lower intensity peaks, sometimes hardly discernible from the noise, spaced fairly regularly about the progression members. For example, peaks 1', 2', ..., 5' are found ~80 cm⁻¹ to the red of peaks 0, ... 4, respectively. Peaks a₁, a₂ and a₃ are found ~80 cm⁻¹ to the blue and peaks b₁, b₂, and b₃ are found roughly 160 cm⁻¹ to the blue of peaks 1, 2, and 3, respectively. There are no corresponding peaks a₀ or b₀ to the blue of peak 0. Additional structure occurs to the red of the origin. The fairly intense peak 1'' is found 128 cm⁻¹ to the red of peak 0, and two very low intensity peaks, labelled a and b, occur at ~280 and 565 cm⁻¹ to the red of peak 0, respectively. The peak labels, positions and relative energies are summarized in Table (6.1).

IV. Analysis and Discussion

A. Assignment of electronic and vibrational structure

The highest level calculations (QCISD(T)/6-31G*) performed by Rohlfing and Raghavachari¹⁷ have predicted both the anion and neutral ground states to be isosceles (C_{2v}) triangles where the Si-Si-Si bond angle (θ) is 65.2° for the ²A₁ anion ground state and 79.6° for the ¹A₁ neutral ground state. The neutral structure is the result of Jahn-Teller distortion of the ¹E' (D_{3h}) state, which is formed by the

$$(1a_1')^2(1e')^4(2a_1')^2(1a_2'')^2(2e'')^2 \quad \text{config. (6.1)}$$

configuration. This distortion to C_{2v} geometry, which causes the degenerate e' orbitals to split into a₁ and b₂ orbitals, results in the ¹A₁ state with the

$$(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_1)^2(b_2)^2 \quad \text{config. (6.2)}$$

configuration and a more acute 1B_2 state. The 1A_1 state is calculated to be much lower in energy than the 1B_2 state due to second order Jahn-Teller stabilization effects. The undistorted (D_{3h}) ${}^3A_2'$ state, which has been calculated to be nearly degenerate with the 1A_1 state,^{9,10,17} has the orbital occupancy of config. (6.1) with parallel spins in the $2e'$ orbitals.

The anion ground state is obtained by adding an electron to the $2e'$ orbital of config. (6.1), resulting in a ${}^2E'$ state. This state is also subject to Jahn-Teller distortion to the previously mentioned 2A_1 state with the orbital occupation

$$\dots(a_1)^2(b_1)^2(b_2)^2(a_1)^1 \quad \text{config. (6.3)}$$

and a 2B_2 state with $\theta \approx 57^\circ$. At the Hartree-Fock level, the 2B_2 is the ground state and the 2A_1 is the saddle point on the typical J-T distorted potential, but upon including electron correlation effects, these are reversed and the 2A_1 becomes more stable at the QCISD(T) level by $\sim 160 \text{ cm}^{-1}$.^{16,17} This energy difference corresponds to the pseudorotation barrier.

The 337 cm^{-1} progression seen both in the PES [Figure (6.1)] and, more definitively, in the ZEKE spectrum appears to be due to transitions between the ground anion state and vibrational levels in the ground neutral state. Because of the large bond angle difference between the 2A_1 anion and the 1A_1 neutral, the symmetric bend mode (ν_2) should be the most active in the spectrum. However, this mode is consistently calculated to be approximately 150 to 170 cm^{-1} ,^{9,10,14,17} which is approximately half the observed frequency. The symmetric stretch mode (ν_1), which could also be active in the spectrum, has a calculated frequency of 551 cm^{-1} , much higher than the observed frequency. This suggests that the band in our spectrum does not represent transitions to the 1A_1 neutral state.

Alternatively, the calculated e' frequency of the ${}^3A_2'$ (D_{3h}) state is in better agreement with the spacing in the observed progression. Raghavachari¹⁷ and Schaefer⁹ calculated a frequency of approximately 285 cm^{-1} for the e' mode using the QCISD(T) and SCF methods, respectively. Density functional studies on the D_{3h} structure performed by Dixon,¹² Dupuis,¹³ and DePristo¹⁴ yielded values around 340 cm^{-1} for the e' frequency. Because the calculated e' frequency is in better agreement than either of the 1A_1 frequencies with the observed 337 cm^{-1} progression, we believe that the band in the ZEKE spectrum is due to the ${}^3A_2' + e' \leftarrow {}^2A_1$ transition and that the 337 cm^{-1} progression can be assigned to transitions to levels in the ν_2 (e') mode of the neutral; this was first suggested in Dixon's comparison of *ab initio* frequencies with the experimental photoelectron and emission spectra.¹² Although long progressions seen in photodetachment spectra are generally only in totally symmetric modes of the neutral, one component of the e' vibration transforms as the symmetric ν_2 (a_1) bend mode of the C_{2v} anion. Therefore, in the rigid molecule limit (the first situation that we will treat), transitions from the totally symmetric ground state of the anion to any quanta in the neutral mode are allowed. Hence we assign each peak n to a 2_0^n transition.

Based on further comparison of the ZEKE spectrum with *ab initio* frequency calculations, we can assign peak b_1 to the 1_0^1 transition, yielding $501 \pm 10\text{ cm}^{-1}$ for the neutral ν_1 frequency. This is in good agreement with all of the calculations for the symmetric stretch (ν_1) frequency of the ${}^3A_2'$ state, but the density functional studies again give the closest value, approximately 500 cm^{-1} . Peaks $b_2, \dots, b_4$ can then be assigned to $\nu_1 + n\nu_2$ ($1_0^1 2_0^n$) combination bands.

The structure found at lower photon energy from the origin was found to depend on ion source conditions, suggesting that they are transitions from vibrationally excited levels of the anion (hot band transitions). The most intense hot bands are those labeled $0'$ and $1''$, with peaks b and a being less intense. Because the ν_2 mode is the most active in the spectrum, we can tentatively assign $0'$ to the 2_1^0 transition. The position of peak $0'$ with respect to the origin

would give an anion frequency of 385 cm^{-1} , which is in poor agreement with the calculated value, 297 cm^{-1} .¹⁷ Peak b, found 565 cm^{-1} from the origin, can be tentatively assigned to the 1_1^0 transition, giving the anion ν_1 frequency in fairly good agreement with the 533 cm^{-1} calculated frequency.¹⁷

The remaining structure found to higher photon energy from the origin, such as peaks n' and a_n , also appears to be due to transitions from excited vibrational levels in the anion. Based on the ν_1 and ν_2 anion and neutral frequencies determined above, sequence bands originating from either the $\nu_2 = 1$ or $\nu_3 = 1$ anion levels should fall to the red of the corresponding 2_0^0 transition, in the energetic vicinity of peaks n' . Peaks a_n , slightly to the blue of each 2_0^0 transition, could then be sequence bands in the ν_3 mode, giving an anion frequency of less than 337 cm^{-1} for this mode.

Since we have determined that neutral Si_3 state in the ZEKE spectrum has D_{3h} symmetry, we can attempt to extract information regarding the anion geometry most simply by assuming that the anion has a rigid, C_{2v} structure. With this assumption, we can treat the profile of the progression by performing spectral simulations within the Franck-Condon approximation, where we assume the vibrational wave functions of the anion and neutral are the products of three harmonic oscillators representing the three normal modes. The intensity of a transition between vibrational levels in the anion and neutral is therefore proportional to the Franck-Condon factors of the two levels. The neutral and anion frequencies are fixed by the above assignments; note that the neutral is treated as a C_{2v} species with $\nu_2 = \nu_3 = 337\text{ cm}^{-1}$ (where ν_3 in this instance corresponds to the component of the neutral degenerate mode that transforms as b_2 in C_{2v} geometry).

This "rigid anion" simulation is shown in the second panel of Figure (6.3). The profile of the 337 cm^{-1} progression was well matched by assuming a normal mode displacement (from anion to neutral) of $\Delta Q_2 = 0.095\text{ \AA}\cdot\text{amu}^{1/2}$, given that the anion frequency for this mode is 385 cm^{-1} . The lower intensity b_n peaks (the $1_1^0 2_0^0$ transitions) were accounted for by assuming $\Delta Q_1 =$

0.03 Å·amu^{1/2}. These two displacements compare well to the predicted displacements between the anion and neutral based on Raghavachari's geometry calculations and our own determination of the normal mode coordinates: $\Delta Q_2 = 0.117 \text{ Å} \cdot \text{amu}^{1/2}$ and $\Delta Q_1 = 0.03 \text{ Å} \cdot \text{amu}^{1/2}$.

The intensities of all transitions originating from vibrationally excited levels in the anion are dependent on vibrational temperature. In general, the lower frequency modes tend to have lower temperatures than the higher frequency modes. This is not unusual since different modes are expected to cool with different efficiencies in a molecular beam. Temperatures for the various levels are included in the figure caption.

While the geometry changes between the anion and neutral determined from this simple treatment are in good agreement with the calculated geometries, the rigid anion simulation exhibits several inadequacies in reproducing the positions and intensities of the sequence bands, namely, the a_n and n' peaks. First, the difference in frequencies between the anion and neutral symmetric bend produces sequence bands of the type 2_1^{n+1} , marked with circles on the simulation shown in Figure (6.3). These occur approximately 50 cm⁻¹ to the red of the main 2_0^n peaks. Also contributing to the intensity of these simulated peaks are $1_1^1 2_0^n$ sequence bands, which occur 65 cm⁻¹ to the red of the 2_0^n peaks. This is in contrast with the actual position of peaks n' , which are found 80 cm⁻¹ to the red of the main peaks. This discrepancy is small but significant. Additionally, as mentioned above, peaks a_1 , a_2 , and a_3 can be proposed as $2_0^n 3_1^1$ transitions, which would yield an anion ν_3 frequency of approximately 270 cm⁻¹ (the frequency used in the rigid anion simulation shown). However, this also produces a fairly intense sequence band to the blue of the origin, marked with a star, which is hardly present in the actual spectrum. There is also no structure in the experimental spectrum where the 3_2^2 sequence bands are predicted to lie (these are marked with an "x" on the Franck-Condon simulation). Finally, this analysis implies anion ν_2 and ν_3 frequencies of 385 and 270 cm⁻¹, respectively. This frequency ordering is unusual for a C_{2v} molecule with a bond angle greater than 60°, and is the reverse of the calculated ordering ($\nu_2 = 297 \text{ cm}^{-1}$, $\nu_3 = 370 \text{ cm}^{-1}$).¹⁷ Taken together, all of

these problems suggest that the analysis is partially flawed, and that it is naive to treat the anion as a simple, rigid C_{2v} molecule with uncoupled modes.

B. Inclusion of Jahn-Teller distortion in Si_3^-

Since the barrier to pseudorotation in Si_3^- is calculated to be only 160 cm^{-1} , an alternative approach to that outlined above is to analyze the ZEKE spectrum by treating the anion as fluxional, rather than as a rigid molecule. This situation arises in symmetric molecules having a set of spatially degenerate electronic states which are vibronically coupled by a degenerate vibration. The end result is a Jahn-Teller distortion of the molecule along the corresponding normal coordinate, removing the electronic degeneracy with the lowering of symmetry. In the case of Si_3^- , we have a species distorted from a symmetric D_{3h} equilibrium geometry because the e' degenerate vibration couples the two components of the $^2E'$ electronic state (see section A).

The $E \times e$ coupling problem can be approached most simply by assuming that the vibronic coupling term is linear with respect to the e' normal coordinate, i.e., no barrier to pseudorotation. In the basis of the two electronic states, and with the degenerate two-dimensional harmonic oscillator expressed in polar coordinates (ρ, ϕ) , the vibrational energies and wave functions are determined from,

$$\begin{bmatrix} H_0 - E & k\rho e^{-i\phi} \\ k\rho e^{i\phi} & H_0 - E \end{bmatrix} \begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix} = 0, \quad \text{Eqn. (6.1)}$$

where H_0 is the unperturbed Hamiltonian, k is a unitless parameter such that $\omega_2 k^2/2$ is the stabilization energy from the distortion, ω_2 , in this instance, is the harmonic frequency of the e' mode in the undistorted molecule (often referred to as ω_0), and $\chi_{\pm}$ are the undistorted

vibrational wave functions associated with the two electronic states. The implications of this have been studied extensively by Longuet-Higgins,²¹ and Whetten,²² for example, and this treatment has been applied to, among other molecules, the analysis of Cu₃,²³ Na₃,²⁴ Ag₃,²⁵ and Li₃²⁶ spectra. These studies demonstrate that even for moderate values of the distortion parameter k , one expects an extended progression in the e' mode for a transition between a Jahn-Teller distorted state and an undistorted D_{3h} state. This is exactly the situation for the Si₃ (³A₂') ← Si₃⁺ transition in our ZEKE spectrum. The key question, then, is whether the smaller peak energies and intensities can be better explained assuming a Jahn-Teller distorted anion rather than a rigid, C_{2v} anion.

We first consider the anion energy levels. For k sufficiently large, the vibrational energy level patterns should approximately follow the familiar formula for a freely pseudorotating species,²¹

$$E = \hbar\omega_1\left(\nu_1 + \frac{1}{2}\right) + \hbar\omega_2\left(\nu_2 + \frac{1}{2}\right) + Aj^2, \quad \text{Eqn. (6.2)}$$

where ω_1 is the symmetric stretch frequency, ω_2 is as defined above, ν_1 and ν_2 are the quantum numbers associated with ω_1 and ω_2 , and j is the half-integer pseudorotation quantum number. The pseudorotation constant A is inversely proportional to the reduced mass and the square of the equilibrium distortion along the e' coordinate ($\hbar^2/2\mu\rho_o^2$). This produces an energy level pattern similar to that shown in Figure (6.4), where the anion levels are labelled (ν_1, ν_2, j). Deviations from the energy level pattern of Eq. (6.2) occur when k^2 is small (very small distortion), or when there is any barrier to pseudorotation.

In the limit of linear vibronic coupling [Eq. (6.1)], transitions from a particular j level of the anion are allowed to $l = j \pm 1/2$ levels in the neutral, where l is the vibrational angular momentum for the (D_{3h}) neutral species. The allowed neutral ← anion transitions (and the forbidden transition, peak a, which is discussed below) are indicated by arrows in Figure (6.4). This figure

suggests an alternate explanation for several of the lower intensity peaks in the ZEKE spectrum, namely, that they are "hot bands" originating from excited pseudo-rotational states of the anion, rather than from excited vibrational levels as assumed in the "rigid anion" Franck-Condon analysis. Thus, the sequence transitions between the $0,0,3/2$ level and the neutral $v_2 \geq 1$ levels would account for peaks $2' - 4'$, etc., while the transitions from the $0,0,5/2$ level to the neutral $v_2 \geq 2$ levels account for peaks $a_1 - a_3$.

We can determine if this assignment is reasonable by computing the pseudorotation constant A in Eqn. (6.2) from the energy difference between peaks 1 and $2'$ in the experimental spectrum, assuming that these are the $0,1,1 \leftarrow 0,0,1/2$ and the $0,1,1 \leftarrow 0,0,3/2$ transitions, respectively. This difference is 80 cm^{-1} , yielding $A = 40 \text{ cm}^{-1}$ and $\sqrt{\mu}\rho_0 = 0.11 \text{ Å-amu}^{1/2}$. The latter value is very similar to the $0.095 \text{ Å-amu}^{1/2}$ normal coordinate displacement determined from the Franck-Condon simulation as well as the *ab initio* displacement, indicating that our value for A is certainly acceptable. However, with such a small distortion, Eqn. (6.2) may not give a good approximation of the actual energy levels.

To proceed further, we need to simulate the ZEKE spectrum including the effects of Jahn-Teller coupling in the anion. This requires that we solve Eqn. (6.1) for the anion wave functions and energy levels, varying k to best match the intensity pattern of the main bending progression. The energy levels are obtained in terms of ω_2 , the (undistorted) harmonic e' frequency, which can then be extracted by scaling the simulated spectrum to match the spacing between peaks 0 and $0'$. Intensities are determined by calculating the overlap between the anion and neutral nuclear wave functions; as before, the symmetric stretch mode is assumed to be uncoupled to the e' mode. The anion bend eigenfunctions of Eqn. (6.1) are linear combinations of harmonic oscillator wave functions with frequency ω_2 , and, for the purpose of intensity calculations only, the neutral e' wave functions are taken to be harmonic with frequency ω_2 . As long as the neutral e' frequency of 337 cm^{-1} differs only slightly from ω_2 (which it does; see below), this approximation will have a negligible effect on the calculated intensities.

Transitions from levels as high as the (1,0,3/2) level ($\sim 650\text{ cm}^{-1}$) were considered in these simulations.

The best simulation, shown in the third panel of Figure (6.3), was obtained with $k = 1.9$. As expected, such a small k gives vibrational and pseudorotational energy levels deviating slightly from Eqn. (6.2). For instance, the separation of the first two $j = 1/2$ levels is $\sim 1.1\omega_2$ [as opposed to ω_2 , per Eqn. (6.2)] which should equal the 385 cm^{-1} frequency determined from hot band 0'. From this we find $\omega_2 = 350\text{ cm}^{-1}$, which, as would be expected, falls between the calculated a_1 (297 cm^{-1}) and b_2 (370 cm^{-1}) frequencies for the distorted 2A_1 state.¹⁷ Moreover, the energies of the $j = 5/2$ and $j = 3/2$ levels with respect to the ground $j = 1/2$ level are not at a ratio of 3:1, as given by Eqn. (6.2).

The overall agreement with the experimental spectrum is reasonable, supporting the assignments discussed above. One nice feature is that the peak marked with the $\star$ in the rigid anion simulation is absent, in better agreement with the experiment; this peak would correspond to the $(0,1,1) \leftarrow (0,0,5/2)$ transition, which is forbidden by the $l = j \pm 1/2$ selection rule. However, the linear Jahn-Teller simulation still has some shortcomings. The energy separation between the two lowest levels of the anion, the $(0,0,1/2)$ and $(0,0,3/2)$ levels, is $0.311\omega_2$ (110 cm^{-1}). Consequently, transitions originating from the $(0,0,3/2)$ level, marked with circles in the simulation, are slightly to the red of the experimental sequence bands, peaks 2' - 4'. This small overestimation of the $j = 3/2$ level has also been seen in other calculations for several of the excited states of Na_3 .²⁷ As with the "rigid anion" simulation, $\Delta v_1 = 0$ sequence bands from the $1,0,1/2$ anion level fall approximately 50 to 60 cm^{-1} to the red of the main progression members, so there are two peaks to the red of each of the main peaks 1 - 3, as opposed to one in the experimental spectrum. Finally, the small peak a, found $\sim 90\text{ cm}^{-1}$ to the red of the origin, energetically appears to be the transition from the $(0,0,5/2)$ level to the ground vibrational level of the neutral, but this transition is not allowed because of the (l,j) selection rule.

We can, however, attempt to better align the n' sequence bands both by increasing k slightly, which lowers the energy of the (0,0,3/2) level, and by including the quadratic coupling term $\frac{1}{2}g\rho^2e^{\pm 2i\phi}$ in Eqn. (6.1). This results in a barrier to pseudorotation given by $E_{\text{loc}} = gk^2\omega_a/(1-g^2)$,²¹ which splits the degenerate $j = 3/2$ levels substantially.²² Additionally, this quadratic term couples the $j = 1/2$ level with the $j = 5/2$ level (through the p^2 term), resulting in nonzero intensity for the (0,0,0) $\leftarrow$ (0,0,5/2) transition believed responsible for peak a. The effects of these two modifications are shown in the bottom panel of Figure (6.3). For this simulation, $k = 2.0$, and $g = 0.005$ in the quadratic coupling term. With these parameters, $E_{\text{loc}} = 7 \text{ cm}^{-1}$, the (0,0,3/2) level is split by 20 cm^{-1} [the resulting levels are labelled (0,0,3/2 $\pm$) in Table (6.1)], and the stabilization energy is 725 cm^{-1} . We now observe only one resolved peak to the red of each of the peaks 1 - 3, and the placement agrees with the experimental peaks 2' - 4'. The simulation shows several weak features which appear to correspond to peak a as well as some of the other peaks to the red of the origin.

We also attempted to adjust the linear and quadratic parameters to give a greater barrier to pseudorotation, as it has been calculated to be 160 cm^{-1} . However, the spectrum could not be simulated assuming such a high barrier. For instance, with $k = 1.8$ and g determined using $E_{\text{loc}} = 160 \text{ cm}^{-1}$, the simulated bend progression was far too extended. We also varied k and g to give a larger barrier and a shorter progression, but the sequence band structure obtained from these variations was in much worse agreement with the experimental sequence band structure.

While none of the three simulations shown in Figure (6.3) exactly match the experimental spectrum (most notably, peak 1" is still unassigned), the quadratic Jahn-Teller treatment is superior to the other two. The "rigid anion" treatment did not correctly match the experimental sequence band transitions, and the anion ν_2 and ν_3 frequencies determined from this analysis were the reverse of the calculated values. In the linear Jahn-Teller limit, several of the simulated sequence peaks were again mispositioned, but the overall profile of the spectrum

was better matched. The quadratic Jahn-Teller coupling treatment yields a closer overall match of the simulated and experimental peaks. Moreover, the quadratic model is consistent with the *ab initio* prediction of a small barrier to pseudorotation, although we find the barrier to be even lower than calculated. The peak assignments based on the quadratic Jahn-Teller simulations are given in Table (6.1). Several of the peaks consist of overlapping transitions, and in these cases, the transitions are listed in order of descending contribution. Note that the composition of peaks 2' - 4' is quite different from peaks 0' and 1', even though they appear to be part of a single progression. Also note that there are no changes in the assignments of peaks n, b_n, and 0' from the rigid anion analysis of section A, although the notation is somewhat different.

C. Role of the 1A_1 state

Figure (6.1) shows that the extent of the ZEKE spectrum is considerably less than that of band X in the PES. Moreover, the ZEKE intensity falls off dramatically just where band X degenerates into a mass of unresolved signal at lower electron kinetic energies. This congested signal in the PES is most likely due to transitions to the 1A_1 state of the neutral. From the calculated anion and neutral geometries and the form of the normal coordinates, we determine the normal mode displacement to be $0.043 \text{ \AA}\cdot\text{amu}^{1/2}$ and $0.314 \text{ \AA}\cdot\text{amu}^{1/2}$ for the ν_1 and ν_2 modes, respectively. Displacement of this magnitude would produce a much longer progression in the ν_2 mode (in addition to significant activation in the ν_1 mode) than what is observed in the ZEKE spectrum of the X band.

As a first order approach to determine the extent to which the ${}^1A_1 \leftarrow e^- \leftarrow {}^2A_1$ transition contributes to the PES X band, we can simulate this transition at an arbitrary origin and then convolute it with the PES experimental resolution. We can then add it to the simulation of the $\nu_{1,2} + e^- \leftarrow {}^2A_1$ transition, also convoluted with the PES resolution, adjusting the origin and the

electronic transition moment of the 1A_1 simulation until the profile of the PES X band is matched. Figure (6.5) shows the result of the added simulations with the origin of the $^1A_1 + e^- \leftarrow ^2A_1$ transition placed 10 meV below the origin of the $^3A_2' + e^- \leftarrow ^2A_1$ transition. However, we hesitate to make any final comment as to the actual ground state based on this somewhat crude analysis.

It still remains that this transition to the 1A_1 state is not apparent in the ZEKE spectrum. This state is formed by removing the lone a_1 electron from the ion [refer to config. (6.3)], while the $^3A_2'$ state is formed by removing a b_2 electron. Following the Wigner threshold law,²⁸ and the selection rules developed by Reed *et al.*,²⁹ the total photodetachment cross sections near threshold for both of these states should be proportional to $\sigma_e(E_{\text{AV}} - E_{\text{threshold}})^{1/2}$, which rises sharply just above photodetachment threshold (s-wave detachment). However, it appears to be the case that σ_0 near threshold for the former transition is considerably smaller than for the latter. Interestingly, band B in the Si_3^- photoelectron spectrum, which was assigned to the $^3A_1 + e^- \leftarrow ^2A_1$ transition,¹⁷ also involves the removal of a lower-lying a_1 electron. While band B is the most prominent feature in the PES, the cross section near threshold for this band was too small to obtain higher resolution ZEKE spectra.

V. Conclusions

The analysis of the extensive vibrational structure in the ZEKE spectrum of Si_3^- shows that the spectrum is due to the $^3A_2' + e^- \leftarrow ^2A_1$ transition. Progressions in the bending and symmetric stretch modes of the neutral are observed, yielding frequencies of 337 cm^{-1} and 530 cm^{-1} , respectively. A comparison of these frequencies with *ab initio* values shows that agreement is best with several of the density functional calculations. The ZEKE spectrum shows several smaller features in addition to the main progressions. These are best explained

by treating the anion as a fluxional species with some pseudorotational excitation; the smaller peaks are then assigned to sequence bands originating from these excited levels of the anion.

A comparison of the Si_3^- PES and ZEKE spectrum suggests that Band X in the PES consists of overlapping transitions to the neutral $^1\text{A}_1$ and $^3\text{A}_2'$ states, but the transitions to the $^1\text{A}_1$ state do not appear in the ZEKE spectrum. This is presumably due to a small photodetachment cross section for the transition to the singlet state near the detachment threshold. Unfortunately, this means we cannot determine which state of Si_3 is the true ground state, although simulations of band X using *ab initio* geometries suggest that it is the singlet state.

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Table (6.1) Peak positions, relative energies, and proposed assignments for Si_3^- ZEKE spectrum. The assignments, shown as $^3A_2' (v_1, v_2, m) \leftarrow ^2A_1 (v_1, v_2, j)$, are based on quadratic Jahn-Teller spectral simulation (see text). Uncertainties in peak positions are given in parentheses. When more than one transition contributes to a peak, the transitions are listed in order of decreasing contribution.

Peak	Position (nm)	Relative Energy (cm^{-1})	Possible transition in order of descending intensity
b	555.55	-565(15)	$(0,0,0) \leftarrow (1,0,1/2)$
0'	550.05	-385(12)	$(0,0,0) \leftarrow (0,1,1/2)$
a	546.95	-282(10)	$(0,0,0) \leftarrow (0,0,5/2)$
1''	542.40	-128(10)	?
1'	540.55	-65(20)	$(1,0,0) \leftarrow (1,0,1/2)$
0	538.65	0(7)	origin
2'	531.20	260(10)	$(0,1,1) \leftarrow (0,0,3/2^\pm), (1,1,1) \leftarrow (1,0,1/2)$ $(0,2,0) \leftarrow (0,1,1/2)$
1	529.05	337(10)	$(0,1,0) \leftarrow (0,0,1/2)$
a ₁	526.85	416(15)	$(0,2,2) \leftarrow (0,0,5/2)$
b ₁	524.40	504(15)	$(1,0,0) \leftarrow (0,0,1/2), (0,3,1) \leftarrow (0,1,3/2)$
3'	521.95	594(15)	$(0,2,2) \leftarrow (0,0,3/2^\pm), (0,3,3) \leftarrow (0,0,7/2)$ $(0,3,1) \leftarrow (0,1,1/2), (0,2,0) \leftarrow (1,0,1/2)$
2	519.74	675(10)	$(0,2,0) \leftarrow (0,0,1/2)$
a ₂	517.79	748(15)	$(0,3,2) \leftarrow (0,0,5/2)$
b ₂	515.34	840(15)	$(1,1,1) \leftarrow (0,0,1/2), (0,4,2) \leftarrow (0,1,3/2)$
4'	513.0	928(20)	$(0,3,1) \leftarrow (0,0,3/2), (0,4,4) \leftarrow (0,0,7/2)$ $(0,4,0) \leftarrow (0,1,1/2), (1,3,1) \leftarrow (1,0,1/2)$
3	510.94	1007(10)	$(0,3,0) \leftarrow (0,0,1/2)$
a ₃	508.39	1106(20)	$(0,4,2) \leftarrow (0,0,5/2)$
b ₃	506.64	1173(15)	$(1,2,0) \leftarrow (0,0,1/2), (0,5,1) \leftarrow (0,1,3/2)$
5'	504.30	1264(30)	$(0,4,1) \leftarrow (0,0,3/2), (0,5,3) \leftarrow (0,0,7/2)$ $(0,5,1) \leftarrow (0,1,1/2), (1,4,0) \leftarrow (1,0,1/2)$
4	502.39	1340(10)	$(0,4,0) \leftarrow (0,0,1/2)$

Figure (6.1) Photoelectron spectrum of Si_3^- obtained using 3.493 eV photon energy with the threshold photodetachment (ZEKE) spectrum superimposed on the inset.

Figure (6.2) Threshold photodetachment spectrum of Si_3^- .

Figure (6.3) Experimental spectrum and three simulations (see text): Rigid anion, linear Jahn-Teller (LJT), and quadratic Jahn-Teller (QJT). All three simulations assume 337 cm^{-1} (e') and 500 cm^{-1} (a_1) neutral frequencies. The rigid anion simulation assumes the following anion frequencies (and temperatures): $\nu_1 = 560\text{ cm}^{-1}$ (500K), $\nu_2 = 385\text{ cm}^{-1}$ (450K), $\nu_3 = 270\text{ cm}^{-1}$ (350K). LJT assumes 120K for 0,0,3/2 level, 250K for 0,0,5/2 level, 350K for 0,1,1/2 level (385 cm^{-1} above ground), 350K for 0,0,7/2 level, and 400K for the (0,1,3/2), (1,0,1/2), and (1,0,3/2) levels. QJT assumes 150K for the 0,0,3/2 levels (degeneracy broken), otherwise, temperatures are the same as LJT simulation.

Figure (6.4) Schematic of Si_3 and Si_3^- energy levels and some of the transitions proposed in the spectral assignment. See Table (6.1) for complete assignment.

Figure (6.5) Simulation of band X in the Si_3^- photoelectron spectrum including contributions from (a) the $^3A_2' + e^- \leftarrow ^2A_1$ transition, in which the experimental ZEKE spectrum is convoluted with the lower resolution of the photoelectron spectrometer, and (b) the $^1A_1 + e^- \leftarrow ^2A_1$ transition, which was simulated using *ab initio* frequencies and geometries for the anion and neutral. Origins for the two bands are indicated with arrows; the origin for the singlet band is adjusted to best match the experiment.

Chapter 7. Study of Si_4 and Si_4^- using Threshold Photodetachment (ZEKE) Spectroscopy

Abstract

The threshold photodetachment (ZEKE) spectrum of Si_4^- is presented. Although no transitions to the ground state of Si_4 are observed, we obtain detailed information on the anion and several of the low-lying excited states of neutral Si_4 . The spectrum shows a long progression of well-resolved transitions between the D_{2h} $^2B_{2g}$ rhombus anion and v_2 vibrational levels of the first excited D_{2h} $^3B_{3u}$ neutral. The length and spacing of the progression is consistent with *ab initio* calculations performed by Rohlfing and Raghavachari, [J. Chem. Phys. **96**, 2114 (1992)] but some of the sequence bands observed within the progression are not. We also observe transitions to the Si_4 $^1B_{3u}$ state which is found at a lower excitation energy than predicted. The perturbed vibrational structure in this band is attributed to vibronic coupling to a nearby electronic state which is "dark" with respect to ZEKE spectroscopy. The ZEKE spectra are compared to the previously obtained photoelectron spectra of Si_4^- as well as *ab initio* calculations on Si_4^- and Si_4 .

I. Introduction

The study of small silicon clusters has been an area of interest because of their importance in astrophysics¹ and CVD processes.² These species are of considerable interest from a purely spectroscopic perspective as well, since *ab initio* calculations^{3,4,5} predict dramatic changes in the geometry and bonding in silicon clusters as the number of atoms is varied. However, from an experimental viewpoint, the spectroscopy of silicon clusters is quite poorly characterized with the exception of the dimer,⁶ for which several rotationally-resolved electronic transitions have been observed. The development of laser vaporization cluster sources has facilitated photofragmentation,⁷ photoionization,⁸ and "reactive etching" studies,⁹ of the larger clusters, but these experiments have revealed little regarding specific cluster structures and bonding. Several absorption lines seen in silicon vapors trapped in rare gas matrices were tentatively attributed to Si_3 and Si_4 , but no analysis of these lines was pursued.^{10,11}

There have been several gas phase spectroscopic studies of silicon clusters with three or more atoms. With the exception of the emission spectroscopy study of Gole and co-workers,¹² in which several transitions from two excited electronic states attributed to Si_3 were observed, this work has involved negative ion photodetachment experiments on silicon cluster anions.^{13,14,15,16,17} While the resolution obtained in photodetachment experiments is typically lower than IR absorption techniques, they offer the advantage of mass-selection prior to spectroscopic investigation, thereby eliminating any ambiguity concerning species identification. Such experiments have also revealed a great deal about the electronic structure of metal clusters¹⁸ and carbon clusters.¹⁹

Electronically resolved negative ion photoelectron spectra (PES) of Si_n^- ($n = 3$ through 12) have been obtained by Smalley and coworkers.¹⁴ Higher resolution PES have been

measured by Ellison for Si_2^- ,¹⁵ and by our group for Si_2^- - Si_4^- .^{16,17} These studies have shown that silicon clusters are rich with low-lying electronic states, and the higher resolution studies revealed vibrational structure associated with several of the neutral $\leftarrow$ anion electronic transitions. We have also studied Si_2^- at even higher resolution using threshold photodetachment (Zero electron kinetic energy, or ZEKE²⁰) spectroscopy.¹⁶ The ZEKE spectrum exhibited fine structure due to spin-orbit splitting both in the anion and neutral dimer, and this proved invaluable in sorting the low-lying electronic states in Si_2^- and Si_2 .

In the case of our Si_3^- and Si_4^- photoelectron spectra, even though vibrational structure is resolved in several of the bands, the assignment of the vibrational and electronic features is greatly facilitated by comparing the experimental spectra to the *ab initio* work of Raghavachari, Rohlfing, and co-workers.^{3,4} For example, their calculations on Si_4 and Si_4^- predicted the ground states to be the $^1\text{A}_g$ and the $^2\text{B}_{2g}$ states, respectively, both of which have planar rhombus (D_{2h}) structures. Based on the calculated geometries, which are quite similar, one would expect to see a short progression in the ν_2 mode of Si_4 with a frequency of 357 cm^{-1} . This is consistent with the experimental spectra,¹⁷ shown in Figure (7.1), thereby supporting the *ab initio* geometries.

Rohlfing and Raghavachari⁴ have also investigated the excited states of Si_4 with a rhombus (or near rhombus) equilibrium geometry. They determined that at least six electronic states accessible by detachment of the anion ground state ($^2\text{B}_{2g}$) lie within 2 eV of the neutral ground state, and assigned the three excited state bands in our spectrum (bands A, B, and C¹⁷) to transitions to the $^3\text{B}_{3u}$, $^3\text{B}_g$, and $^3\text{B}_{1u}$ states of Si_4 . They also raised the possibility that one of the bands (band B) consisted of overlapping transitions other low lying excited states of Si_4 . The band assignments according to Ref. 4 are indicated in Figure (7.1).

The partially resolved vibrational features in Figure (7.1) suggest that a higher resolution photodetachment spectrum will reveal considerably more structure. This is the motivation for

the work presented here, in which we report the results of threshold photodetachment (ZEKE) spectroscopy on Si_4^- . In these experiments, mass-selected anions are photodetached with a tunable laser, and only those electrons with nearly zero kinetic energy are detected. The resolution of our ZEKE spectrometer is around 3 cm^{-1} , considerably better than the photoelectron spectrometer used for Figure (7.1) ($80\text{-}100 \text{ cm}^{-1}$).

Threshold photodetachment spectroscopy is most powerful when used in tandem with photoelectron spectroscopy. While all neutral $\leftarrow$ anion electronic transitions involving removal of a single electron can be seen in the photoelectron spectrum of an anion, this is not so for the ZEKE spectrum. According to the Wigner²¹ threshold law, the photodetachment cross section near the threshold for a neutral $\leftarrow$ anion transition goes as

$$\sigma \propto (E_{\text{photon}} - E_{\text{threshold}})^{\ell+1/2}, \quad \text{Eqn. (7.1)}$$

where ℓ is the photoelectron angular momentum. For: $\ell = 0$ (s-wave) detachment, the cross section rises sharply above threshold, but for $\ell \geq 1$ (p-wave, etc.) the cross section is very small near threshold. Hence, ZEKE spectroscopy of anions is sensitive only to s-wave detachment. While sometimes inconvenient, this feature is often useful in assigning neutral $\leftarrow$ anion electronic transitions, since s-wave detachment can only result from removal of an electron from particular orbitals.²² This type of analysis was used in our study of Si_2^{-16} as well as in the work presented here.

The Si_4^- threshold photodetachment spectrum shows well resolved bands involving transitions between the $\text{Si}_4^- \text{ } ^2\text{B}_{2g}$ state and two excited electronic states of neutral Si_4 . The lower energy band, assigned to the transition to the $\text{Si}_4 \text{ } ^3\text{B}_{3u}$ state, is particularly clean, and from it we obtain several vibrational frequencies for the anion and neutral which are in partial agreement with the *ab initio* results of Rohlfing and Raghavachari.⁴ The higher energy band

appears to be strongly perturbed, most likely because of vibronic coupling to an overlapping Si_4 excited state which is "dark" with respect to ZEKE spectroscopy. The nature of the electronic states that are involved in this band is discussed in light of the *ab initio* calculations.

II. Experimental

Figure (7.2) shows a schematic top view of the threshold photodetachment apparatus. It is described in detail elsewhere,²³ but the basic operation is as follows. Cold silicon clusters (anions, cations, and neutrals) are generated in a laser vaporization/pulsed molecular beam source similar to that developed by Smalley.²⁴ Helium is used as the carrier gas, typically with a backing pressure between 50 and 80 psi. Use of a piezoelectric valve²⁵ rather than the solenoid-type molecular beam valve (General Valve) used in previous cluster studies was found to greatly enhance cluster cooling. Laser vaporization is achieved by focussing a 2 mJ, 532 nm pulse from a frequency-doubled Nd:YAG laser (20 Hz repetition rate) onto a rotating, translating silicon rod. The negative ions that pass through a 2 mm diameter skimmer are collinearly accelerated to 1 keV. Mass selection is achieved by a 1 m long beam-modulated time-of-flight mass spectrometer. The mass separated ions then enter the detector region where they are photodetached by a (pulsed) excimer-pumped dye laser. The dyes used for photodetachment of Si_4^- were Coumarin 503 (479-553 nm), Exalite 416 (402-427 nm), DPS (399-415 nm), BBQ (367-405 nm), QUI (368-402 nm), DMQ (346-377 nm), pTp (332-350), and, doubled with a β -barium borate (BBO) crystal, Rhodamine 640 (310-332 nm) and Rhodamine 590 (287-300 nm).

Threshold photodetachment spectra are obtained by adapting the ZEKE spectroscopy method developed by Müller-Dethlefs *et al.*²⁰ to negative ion photodetachment. In this experiment, the Si_4^- is photodetached in the region marked by the x on Figure (7.2). The photoelectrons are extracted with a delayed, pulsed field. This allows the higher energy

photoelectrons to spatially separate from the threshold electrons, which have nearly zero kinetic energy. The energetic electrons that scatter away from the ion beam axis are discriminated against by apertures located in the detector region. Those that scatter along the ion beam arrive at the detector at different times from the threshold electrons and are discriminated against by gated integration of the threshold electrons. This combination of spatial and temporal discrimination yields an electron energy resolution of 3 cm^{-1} .

As an alternative mode of operation, the photoelectrons can be extracted immediately upon photodetachment. This results in spectral features that are 150 cm^{-1} wide but have considerably higher intensity. While no high resolution information can be obtained in this mode of operation, it is useful as a first order method of locating the s-wave photodetachment thresholds, especially when the photodetachment signal is too small to obtain ZEKE spectra.

Total photodetachment cross section scans were also performed for Si_4^- to determine whether any high-lying (autodetaching or bound) excited anion states existed for Si_4^- as they did for C_6^- .²⁶ No such states were found, and this experiment will not be discussed further.

III. Results

The spectrum of Si_4^- obtained on the threshold photodetachment apparatus is shown superimposed on the photoelectron spectrum of Si_4^{-17} in Figure (7.3). In the ZEKE mode of operation, we saw the two bands labelled A' and B'. Band A' corresponds well with band A seen in the PES, but band B' falls primarily on the rising edge of band B in the PES. No structure is seen in the ZEKE spectrum for the remainder of the energy range spanned by the PES band B. Band C', which corresponds to band C in the PES, could only be observed in the partially discriminated mode of operation due to its low signal intensity; this is why the features in this band are broader. No signal corresponding to band X (the transition to the Si_4 ground state) in

the PES could be observed in either the ZEKE or partially discriminated mode. Hence, the three observed bands all involve transitions to excited states of Si_4^- . The bands will now be examined in greater detail.

A. Band A'

Band A' in the threshold photodetachment spectrum shows a progression of up to 14 peaks which corresponds to the partially resolved vibrational structure seen previously in the Si_4^- PES.¹⁷ The PES had to be shifted along the abscissa by -0.03 eV in order to fully align the PES and ZEKE progressions. Assuming this shift applies to the entire photoelectron spectrum, the electron affinity of Si_4 previously obtained from the PES should be changed slightly to 2.17 ± 0.01 eV. Figure (7.4) shows a finer-step, signal averaged scan of this band. Clearly, each member of this progression consists of groups of smaller peaks found to either side of a single, more intense peak. The intense peak in each group is labelled by number and the positions and spacings of these peaks are listed in Table (7.1). The average peak spacing is 312 cm^{-1} .

Figure (7.5) shows a more expanded scale scan of the two groups of peaks around peaks 3 and 4. The more intense side peaks, labelled a_n through e_n , shade to higher photon energy relative to the most intense peak (peak n) in each group, while the less intense side peaks, labelled f_n and g_n , shade to lower photon energy. The positions and energies of these side progressions are listed in Table (7.2) for the two groups shown in Figure (7.4). All of the main and side peaks are between 16 and 20 cm^{-1} wide (FWHM). We note that this pattern of peaks occurs, with some intensity variation, for every group of peaks in band A'.

The intensities of peaks a_n through g_n are dependent on source conditions. When we produced ions using a solenoid-type pulsed molecular beam valve (i.e., higher temperature) instead of the piezoelectric valve, a_n and b_n were as intense as the main peak n while c_n through

e_n remained unresolved in a broad signal with half the intensity of the n - a_n - b_n triplet. The intensities of peaks g_n and f_n are also dependent on source conditions, although they never exceeded one half the n peak intensity. This source condition dependence indicates that these peaks are due to transitions from vibrationally excited levels of the anion, or, "hot-band" transitions. The assignments of these peaks are addressed in the following section.

At first glance, peaks a_n through e_n appear to belong to one progression with a spacing of $\sim 25 \text{ cm}^{-1}$. However, the intensity distribution of these peaks indicate otherwise. Peak b_n is typically of comparable intensity to a_n , whereas peak c_n is quite small compared to b_n , if it can be resolved at all. Therefore, peaks a_n through e_n appear to involve two vibrational modes. For instance, b_n has an average spacing from n of 53 cm^{-1} , and d_n is 51 cm^{-1} from b_n on average, and for several of the main spectral features, an e_n peak can also be seen approximately 50 cm^{-1} to the blue of peak d_n . The a_n peaks are spaced approximately 30 cm^{-1} from peak n for low n , but this spacing decreases down to 26 cm^{-1} to higher values of n . The same effect is seen for the energy difference between c_n and b_n in those cases where c_n is well enough resolved. Therefore, we believe that n , b_n , d_n and e_n belong to a 50 cm^{-1} progression in one mode, and that n , a_n , and c_n represent shorter 30 cm^{-1} progressions in a second mode.

The side peaks found to the red of the main peak are fewer and less intense. The f_n peaks are found approximately $25 \pm 5 \text{ cm}^{-1}$ to the red of peak n . In some cases, such as for $n = 5$, f_n appears to be hardly resolved from the main peak. The g_n peaks are found approximately $53 \pm 5 \text{ cm}^{-1}$ to the red of the main peaks n . Figure (7.4) shows that the intensities of the g_n peaks relative to the main peaks is not constant throughout the progression; for $n = 0 - 3$, the g_n peaks are fairly prominent, but peaks g_5 and g_6 cannot be discerned from the noise. For $n > 8$, the g_n peaks again become apparent.

B. Band B'

As can be seen from the ZEKE portion of the spectrum shown in Figure (7.3), band B' is much less intense than band A'. In addition, the progression is much shorter. Note that while band A' closely matches band A in the photoelectron spectrum, band B' covers a much smaller energy range than band B in the PES. No structure was seen between band B' and 300 nm, even using the partially discriminated cross section mode of the apparatus. Figure (7.6) shows band B' on an expanded scale. Because the signal was so much less for this band, the signal-to-noise ratio is not as good as for band A'.

Again, the members of the progression in this band appear as groups of peaks, but the profiles and relative intensities of groups exhibit irregularity. The first three members of the progression are qualitatively similar in profile to those found in the band A' in that the groups are dominated by a central intense peak, labelled n' , as well as fairly intense side peaks, a_n' and b_n' , found to higher photon energy and a less intense side peak, g_n' , at lower photon energy. The central peaks n' in the first three groups seem to form a short, $300 \pm 6 \text{ cm}^{-1}$ progression. However, the profiles of the fourth and fifth groups are quite different. There is no peak at the correct position in the fourth group to be a part of the 300 cm^{-1} progression, although the average position of the two intense peaks labelled a_3' and f_3' is just where peak 3' would be expected. In the fifth group, peak 4', while apparently part of the main 300 cm^{-1} progression, is noticeably less intense than the peaks to either side. Peak 5' can barely be discerned from the noise. Peak positions and spacings for band B' can be found in Table (7.3).

C. Band C'

We were restricted to examining this band using the partially discriminated cross section mode of the apparatus due to very low photoelectron signal. The low signal is due to small

photodetachment cross section near threshold for this state and lower photodetachment laser power.

The broad features of band C' shown in Figure (7.3) are roughly 200 cm^{-1} wide and are separated by approximately 430 cm^{-1} peak to peak. The broad peaks are not perfectly symmetric; there are probably many sequence bands (as were seen for the higher resolution sections of the spectrum) and/or combination features contributing to the profile of these features.

IV. Analysis and Discussion

According to Rohlfing and Raghavachari,⁴ the ${}^2\text{B}_{2g}$ anion ground state has the valence orbital configuration $\dots(\text{b}_{3g})^2(\text{b}_{3u})^2(\text{a}_g)^2(\text{b}_{1u})^2(\text{b}_{2g})^1$. Electrons removed from either the b_{1u} or the b_{3u} orbitals can depart via s-wave photodetachment, while this is not the case for the b_{2g} or a_g orbitals.²² Therefore, according to the assignment of the Si_4^- PES in Ref. (4), [see band labels on Figure (7.1)] we would expect to see bands A and C in the ZEKE spectrum, which we do, since these states result from the removal of an electron from the b_{1u} and b_{3u} orbitals, respectively. Band X in the PES is *not* seen in the ZEKE spectrum, which is consistent with its assignment to the ${}^1\text{A}_g + e^- \leftarrow {}^2\text{B}_{2g}$ transition. This transition involves removing the b_{2g} electron, which would depart as a p-wave. Band B seen in the PES was assigned to the ${}^3\text{B}_g + e^- \leftarrow {}^2\text{B}_{2g}$ transition,⁴ corresponding to removal of an a_g electron. This transition, therefore, should *not* be apparent in the ZEKE spectrum, but we do observe band B' which corresponds to the rising edge of band B in the PES. As discussed below, we believe band B is due to overlapping electronic transitions, one of which can occur by s-wave detachment. We now consider all three bands in the ZEKE spectrum in more detail.

A. Band A'

The energy of band A' and the fact that we observe it in the ZEKE spectrum is consistent with the *ab initio* assignment of this band to the ${}^3\text{B}_{3u} + e^- \leftarrow {}^2\text{B}_{2g}$ transition.⁴ The progression of the central peaks [peaks n in Figure (7.4)] can be fit with the harmonic frequency $\omega_e = 312 \pm 1 \text{ cm}^{-1}$ and a very small anharmonic constant $\omega_e x_e = 0.3 \pm 0.1 \text{ cm}^{-1}$. The harmonic frequency is very close to the *ab initio* value of 306 cm^{-1} for the ν_2 (a_g) mode in the $\text{Si}_4 {}^3\text{B}_{3u}$ state. Moreover, the *ab initio* geometries for Si_4^- and the ${}^3\text{B}_{3u}$ state of Si_4 , which are shown in Figure (7.7) along with the ν_2 and ν_1 (a_g) normal modes of the ${}^3\text{B}_{3u}$ neutral (the force constants for determining the normal modes were obtained from our own *ab initio* calculations on Si_4) suggest a large displacement along the ν_2 normal coordinate upon photodetachment, but almost no displacement along the higher frequency ν_1 normal coordinate. Hence, the ν_2 mode should be the only active vibration in the ZEKE spectrum. We therefore assign peaks n to the 2_0^0 progression.

Although the assignment of the 2_0^0 progression is straightforward, locating the origin is somewhat more ambiguous. Peak 0, located at 415.27 nm, appears to be the lowest energy peak in the 312 cm^{-1} progression, but one could argue that there is a small peak buried under noise at 312 cm^{-1} lower in energy (420.68 nm), or even 624 cm^{-1} to the red of peak 0 (426.28 nm) where no detectable electron signal was seen.

We attempted to determine the location of the origin and the actual normal mode displacement by performing a single mode (ν_2) Franck-Condon simulation of the spectrum. Simulations performed assuming the origin was at 415.27 nm (with ΔQ of $0.219 \pm 0.008 \text{ \AA(amu)}^{1/2}$), 420.68 nm ($\Delta Q \sim 0.235 \pm 0.008 \text{ \AA(amu)}^{1/2}$) or 426.28 nm ($\Delta Q \sim 0.259 \pm 0.008 \text{ \AA(amu)}^{1/2}$) all satisfactorily matched the experimental progression. However, based on the *ab initio* geometries and force constants, we can calculate the ν_2 normal mode displacement

between the anion and neutral. We find this to be $0.208 \text{ \AA}(\text{amu})^{1/2}$, which is in best agreement with the normal coordinate displacement assumed for the simulation with the origin at 415.27 nm. We therefore take this to be the origin. The excitation energy of the $^3\text{B}_{3u}$ state is then $0.815 \pm 0.010 \text{ eV}$ [listed in Table (7.4)] which is in good agreement with the 0.85 eV excitation energy calculated by Rohlfing and Raghavachari.⁴

We next consider the set of peaks g_n , each of which is located 53 cm^{-1} to the red of the corresponding central peak n . The bimodal intensity distribution of these peaks, passing through a minimum at $n = 5 - 6$, can be explained by assigning them to a "hot-band" progression in the the ν_2 mode originating from the $\nu_2 = 1$ level of the anion, i.e. a 2_1^{v+1} progression. The intensity minimum can be qualitatively understood by referring to Figure (7.8), which shows anion and neutral harmonic potential energy curves displaced along the Q_2 coordinate by $0.219 \text{ \AA}(\text{amu})^{1/2}$, the displacement that best reproduced the intensity distribution of the main progression (peaks n). This displacement is such that a node in the neutral $\nu_2 = 6$ wave function coincides with one of the the maxima of the anion $\nu_2 = 1$ wave function, causing the overlap to be close to zero. Based on this assignment, the ν_2 frequency in the anion is 365 cm^{-1} , quite close to the *ab initio* frequency of 383 cm^{-1} .⁴ The intensity distribution of peaks n and g_n can be satisfactorily reproduced in a one-dimensional simulation (not shown) where the vibrational temperature of the anions is assumed to be 200 K.

The large geometry change and fairly large frequency change in the ν_2 mode between the anion and neutral can be explained by considering the orbital from which the electron is removed in the neutral $\leftarrow$ anion transition. The b_{1u} orbital is formed by the (in-plane) p_z orbitals [see Figure (7.7)] which effectively bonds the silicon atoms labelled 1 and 3. Removal of an electron from this orbital will weaken this bond, resulting in the longer bond distance and lower ν_2 frequency in the neutral, since this mode primarily involves the stretching of r_D .

We next consider the other vibrational features in band A', peaks $a_n - f_n$. As mentioned earlier, these peaks originate from vibrationally excited levels in the anion, and we assign them to sequence bands in modes other than the ν_2 mode, that is, $2_0^0m_1^1$, $2_0^0m_2^2$, etc. transitions. There are five other normal modes of $\text{Si}_4/\text{Si}_4^-$ that could be contributing to this structure. However, using a vibrational temperature of 200 K as a guideline, significant population is expected only in the four lowest frequency modes of the anion. In order of increasing frequency, these are calculated⁴ to be the ν_6 (165 cm^{-1}), ν_5 (295 cm^{-1}), ν_2 (383 cm^{-1}), and ν_3 (390 cm^{-1}) modes. The normal modes are shown in Figure (7.7).

The ν_2 mode has already been accounted for. The f_n peaks, each of which lies 25 cm^{-1} to the blue of the main peak n , are of comparable intensity to the most intense g_n peaks, and likely originate from the $\nu = 1$ level of a mode close in frequency to the ν_2 mode. According to the *ab initio* results, the most likely candidate is the ν_3 mode, and we therefore assign peaks f_n to the $2_0^0\alpha_1^1$ progression. Although we cannot directly extract the ν_3 anion and neutral frequencies from the peak positions, they do yield the *difference* between the anion and neutral frequencies, and show that the ν_3 mode is 25 cm^{-1} lower in the neutral. This is consistent with the *ab initio* results, which give $\nu_3 = 367\text{ cm}^{-1}$ in the neutral, 23 cm^{-1} less than the calculated anion frequency. As discussed earlier, peaks $a_n - e_n$ to the red of peak n appear to be sequence bands composed of two overlapping progressions. The presence of sequence bands to the red of the central peak means that the vibrational modes involved have higher frequencies in the neutral than in the anion. This is at odds with the *ab initio* results,⁴ for which *all* of the frequencies for the $\text{Si}_4\text{ }^3\text{B}_{3u}$ state are lower than in the anion. Since the leading members of these progressions, peaks a_n and b_n , are quite intense, these progressions most likely involve the two lowest frequencies of the anion, the ν_5 and ν_6 modes. From the positions of peaks a_n and b_n relative to peak n , the frequencies of one of these modes is 27 cm^{-1} higher in the neutral than in the anion, while the other is 52 cm^{-1} higher in the neutral. In contrast, the *ab initio*

calculations predict the ν_5 and ν_6 frequencies to be higher in the anion by 118 cm^{-1} and 8 cm^{-1} , respectively.

We therefore have two possible assignments for these peaks. In one assignment, peak a_n is the $2_0^06_1^1$ transition and peak b_n is primarily the $2_0^05_1^1$ transition (with some contribution from the $2_0^06_2^2$ transition). These assignments and those of peaks $c_n - e_n$ are listed in Table (7.2). In the other assignment, ν_5 and ν_6 are switched. In order to better choose between these assignments, we can simulate the spectrum using the four modes considered above ($\nu_2, \nu_3, \nu_5, \nu_6$). We do this first for the assignment in Table (7.2). For the ν_5 and ν_6 modes, we need to assume values for the neutral frequencies, and these will fix the anion frequencies. If we choose the *ab initio* values for the neutral frequencies, the anion frequencies are those given in Table (7.5). We obtain the simulation shown in Figure (7.9) using 200 K as the vibrational temperature for the ν_2 mode and slightly different vibrational temperatures for the other three modes [listed in Table (7.5)]. The temperatures were fit paying closest attention to peak groups with $n = 3$ and 4, since our data is best for these [see inset, Figure (7.9)].

The reasonable fit between the simulated and experimental spectrum using vibrational temperatures close to 200 K for all four modes offers indirect support both for the assignment of peaks $a_n - e_n$ and for using the *ab initio* frequencies for the neutral. While different modes have different cooling efficiencies in a free jet expansion, we would expect the temperatures of the remaining modes to be in the neighborhood of 200 K, the appropriate temperature for the ν_2 mode, particularly if they have similar or lower frequencies. If we use the alternate assignment proposed above, with the ν_5 and ν_6 modes switched from Table (7.2), and use the *ab initio* values for the neutral frequencies, then the anion frequencies are $\nu_5 = 150\text{ cm}^{-1}$ and $\nu_6 = 107\text{ cm}^{-1}$, and the required vibrational temperatures are 380 K and 107 K, respectively [these values are included parenthetically in Table (7.5)]. This is a noticeably larger deviation from 200 K than

the values obtained using the former assignment, and makes this assignment somewhat less desirable.

Another option is to use the *ab initio* ν_5 and ν_6 frequencies for the anion [see Table (7.5)], and fix the neutral frequencies accordingly. Using the peak assignments in Table (7.2), we require vibrational temperatures of 650 K and 450 K for the ν_5 and ν_6 modes, respectively. These temperatures for the lowest frequency modes seem unreasonably large compared to the 200 K temperature for the ν_2 mode. A similarly large deviation is obtained using the alternate assignment assuming the *ab initio* anion frequencies.

Overall, the peak assignments in Table (7.2) and the frequencies listed in Table (7.5) seem the most reasonable of all the possibilities considered. The small frequency change in the ν_6 mode upon photodetachment to the $^3B_{3u}$ state is sensible as it is an out-of-plane vibration whereas the b_{1u} orbital is primarily in the plane of the molecule. The increase in the ν_5 frequency upon photodetachment is more difficult to rationalize on the basis of molecular orbital considerations.

The spectra support the *ab initio* geometries for Si_4^- and the Si_4 excited state, as well as the *ab initio* frequencies for the anion and neutral ν_2 and ν_3 modes. However, the spectra are inconsistent with the *ab initio* ν_5 and ν_6 frequencies. The ν_5 frequency for the anion is particularly suspect, since it lies well above the predicted neutral frequency, whereas our spectrum shows it should be less than the neutral frequency. Moreover, a high vibrational temperature for the ν_5 mode is always needed to simulate the spectrum if the *ab initio* value is used. It is possible that the large discrepancy between the *ab initio* Si_4/Si_4^- ν_5 frequency difference and the observed frequency difference is due to an incorrect assignment of the b_n peaks. For instance, b_n could be due to a combination band; if b_n were due to the $2\sigma_g^{-1}5\sigma_g^2$ transition, its position would be in fairly good agreement with the calculated ν_5 frequency. However, were this the case, peak b_0 (found 50 cm^{-1} from the origin) would not appear in the

spectrum. Also, the intensity of the b_n peaks is too high for a $\Delta v = 2$ transition in a non-totally symmetric mode. Thus, we believe our assignment of the b_n peaks to sequence band transitions is correct. In any case, independent measurements of either the anion or neutral v_5 and v_6 frequencies would result in a more complete understanding of the ZEKE spectrum.

B. Band B'

Rohlfing and Raghavachari assigned band B shown on the PES [Figure (7.1)] to the ${}^3B_g + e^- \leftarrow {}^2B_{2g}$ transition,⁴ where the 3B_g state has a C_{2h} structure resulting from a slight distortion of the ${}^3B_{2g}$ (D_{2h}) state. They pointed out that the irregular spacings of the band may be due to contributions from the nearby ${}^3B_{1g}$, ${}^1B_{2g}$ and ${}^1B_{3u}$ states. However, only the ${}^1B_{3u}$ state is accessible from the anion by s-wave detachment. This suggests that band B' in the ZEKE spectrum and the leading edge of band B in the photoelectron spectrum are due to the ${}^1B_{3u} + e^- \leftarrow {}^2B_{2g}$ transition. The ${}^1B_{3u}$ state is the singlet counterpart of the ${}^3B_{3u}$ state responsible for band A', so the apparent origin of band B' at 349.90 nm implies a singlet-triplet splitting of 0.558 eV for the B_{3u} state. This is lower than the calculated splitting, 1.04 eV, but the disagreement is not so unreasonable considering the degree of difficulty in accurately calculating singlet-triplet splittings in complex molecules.

The profile of band B' is very different from band A', with the intensity of band B' falling off after only a few peaks. Moreover, the vibrational structure in band B' is irregular. As mentioned in Sec. III, the first three groups of peaks in this band [Figure (7.5)] are similar to the peak groups in the band A'. The spacing of the central peaks 0' - 2' is $300 \pm 8 \text{ cm}^{-1}$, and the fairly intense sequence bands occurring to the red of these features (g_n) are spaced such that the anion frequency is approximately $365 \pm 5 \text{ cm}^{-1}$. Thus, the n' peaks appear to be a progression in the v_2 mode of the neutral ${}^1B_{1u}$ state, with a frequency 12 cm^{-1} lower than the v_2

mode in the $^3B_{1u}$ state. The fourth group of peaks is very different; it is an intense doublet separated by approximately 38 cm^{-1} . These peaks, f_3 and a_3 , are separated by 279 cm^{-1} and 317 cm^{-1} from the peak $2'$, so it seems that the 300 cm^{-1} progression stops at peak $2'$. It is true that the signal-to-noise ratio of this band is not very good and the spacings between either f_3 or a_3 and peak $2'$ fall almost within the experimental uncertainty of the 300 cm^{-1} progression. However, the a_3 and f_3 peaks are well resolved from each other, while the peaks $2'$, $1'$ and $0'$ are poorly resolved from the adjacent transitions. Thus, the pattern of transitions in the fourth group is clearly different from the lower energy groups of peaks.

Since the band B' does not span the energetic extent of band B in the PES, there must be at least one "dark" state lying close to the $^1B_{3u}$ state. By this, we mean a Si_4 electronic state which is not accessible by s-wave detachment and therefore is seen in the PES but not the ZEKE spectrum; this includes all three of the other electronic states predicted to occur in the vicinity of band B. Hence, a possible explanation for the vibrational irregularity of band B' is that the higher vibrational levels of the $^1B_{3u}$ state are vibronically coupled to one of these "dark" states.

As examples of possible vibronic coupling schemes, any totally symmetric vibrational level of the $^1B_{3u}$ state could be coupled with odd vibrational levels in a b_{1u} mode of the $^1B_{2g}$ state, odd b_{2u} levels of the $^3B_{1g}$ state, or odd b_u levels of the 3B_g state. Given that the three candidate states for vibronic coupling are all predicted to lie within 0.3 eV of where we observe the $^1B_{3u}$ state, one might expect the dominant coupling to be with the $^1B_{2g}$ state, as this is the only nearby state with the same spin multiplicity.

The peak pattern for the fourth group is what one might expect under the following circumstances. Suppose a $v_4 = \text{odd level}$ [b_{1u} vibrational symmetry-see Figure (7.7)] of the $^1B_{2g}$ state were accidentally degenerate with the $v_2 = 3$ level of the $^1B_{3u}$ state, at the energy where peak $3'$ would normally occur. The two vibronically coupled levels will mix and repel one

another, and a 38 cm^{-1} splitting via this interaction would yield peaks a_3 and f_3 . Peak a_3 then consists of two overlapped transitions—one due to the higher energy transition resulting from the vibronic coupling interaction, and the other from the transition analogous to peaks a_0 - a_2 (see below). Clearly, such a mechanism must be regarded as speculative, but it is certainly not unreasonable given the large number of nearby electronic states.

The $4'$ group is most likely affected in a similar manner, but due to the poor S/N, it is difficult to get a precise idea of what could be happening with it. The chance of vibronic coupling only increases at higher energies due to presence of more combination bands with the appropriate vibronic character, so we would only expect it to be increasingly difficult to analyze these higher energy peaks.

There remain several other issues regarding this band. It has been mentioned that the profiles of the first three groups of peaks in the B' band are qualitatively similar to those in the A' band, but not exactly. For example, the spacing between peaks a_n and n' in band B' is slightly smaller than between peaks a_n and n in band A' . If the a_n peaks are due to sequence bands in the ν_6 mode, a difference between the neutral singlet and triplet ν_6 frequencies of about 5 to 10 cm^{-1} (the triplet frequency being higher) would account for this. Also, the origin of this band has not been definitively identified, although we assign it to peak $0'$, the central peak of the lowest energy group identified with band B' . However, the lower signal to noise associated with band B' may cause the actual origin to be obscured. The excitation energy of the $^1B_{3u}$ state assuming peak $0'$ to be the origin is $1.37 \pm 0.010\text{ eV}$ [see Table (7.4)]. While we cannot determine the origins of the $^1B_{2g}$, 3B_g or $^3B_{1g}$ states, our vibronic coupling hypothesis requires at least one of them to lie quite close to the $^1B_{3u}$ state.

C. Band C'

While not much information can be extracted from the broad features comprising band C', a few words on its assignment are warranted. This band, which was assigned to the $^3\text{B}_{1u} + e^- \leftarrow ^2\text{B}_{2g}$ transition, lies approximately 1.2 eV above band A'. This raises the possibility that band C' is due to the transition to the $^1\text{B}_{3u}$ state (the singlet-triplet splitting for B_{3u} was calculated to be 1.04 eV) and that band B' is the $^3\text{B}_{1u} + e^- \leftarrow ^2\text{B}_{2g}$ transition. However, this possibility is unlikely for the following reason. From the *ab initio* geometries, the ν_1 mode should be active in transitions to the $^3\text{B}_{1u}$ state. The ν_1 frequencies of all of the excited $\text{D}_{2h} \text{Si}_4$ states are around 400 cm^{-1} or greater. The B' progression is approximately 300 cm^{-1} , while the peak spacing in band C' is roughly 430 cm^{-1} , consistent with a ν_1 progression. We therefore believe that the assignment of band C' made by Rohlfing and Raghavachari is correct.⁴

V. Conclusion

The results presented here represent a far more detailed experimental probe of the vibrational and electronic structure of silicon tetramer than our previous photoelectron spectroscopy study. We have obtained several vibrational frequencies for the anion and various electronic states of the neutral, particularly the $^3\text{B}_{3u}$ excited state, as well as excitation energies for several electronic states.

Our results also emphasize the interaction between theory and experiment in understanding the spectroscopy of clusters. The role of *ab initio* calculations in interpreting these spectra cannot be overemphasized. In the absence of experimental force constants for Si_4 , *ab initio* calculations are needed to perform any reasonable assignment of the observed vibrational progressions. Moreover, given the complex electronic structure of a species such as

Si₄, the assignment of electronic bands to specific neutral $\leftarrow$ anion transitions also requires some *ab initio* input.

Our experimental results provide a detailed comparison with the calculations. We find from band A' that the excitation energy for the Si₄ ³B_{3u} state is in excellent agreement, as are the vibrational frequencies for the ν_2 mode in the anion and this state of the neutral. The sequence band structure in band A' is consistent with the *ab initio* values for the ν_3 mode in the anion and neutral, but not with the *ab initio* values for the ν_5 and ν_6 modes. Our results also show that band B in the Si₄⁻ photoelectron spectrum is due to transitions to overlapping electronic states, as suggested in the calculations, but the ZEKE spectrum implies that the lowest energy of these is the Si₄ ¹B_{3u} state, whereas the calculations predict this to be about 0.5 eV higher than where we observe it. Finally, on the basis of the observed vibrational progression, we find the *ab initio* assignment of band C to the transition to the Si₄ ³B_{1u} state to be reasonable.

We feel that these comparisons between experiment and theory will become even more essential as we begin to study the larger Si clusters via threshold photodetachment spectroscopy. Many of these are predicted to exhibit several low-lying structures with very different geometries. A comparison of experimental and theoretical vibrational frequencies and electronic excitation energies will facilitate sorting out these possible cluster structures.

Acknowledgements

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Table (7.1) Positions, spacings and tentative assignments for the main peaks in the A' band of Si_4^-

Peak	Position (nm)	Spacing (cm^{-1}) ^a	Tentative Assignment ^b
0	415.27(14)	314	Origin
1	409.93(13)	311	2_0^1
2	404.77(13)	308	2_0^2
3	399.78(13)	313	2_0^3
4	394.84(12)	310	2_0^4
5	390.06(12)	311	2_0^5
6	385.39(12)	308	2_0^6
7	380.87(12)	308	2_0^7
8	376.46(11)	308	2_0^8
9	372.15(11)	305	2_0^9
10	367.98(11)	310	2_0^{10}
11	363.83(11)	306	2_0^{11}
12	359.83(10)	303	2_0^{12}
13	355.95(10)		2_0^{13}

^aError for each spacing is $\pm 11 \text{ cm}^{-1}$

^bBased on peak 0 being the origin

Table (7.2) Positions, relative spacings, and tentative assignment of sequence bands found around peaks 3 and 4 in the A' band of Si_4^- .

Peak	Position (nm)	Spacing from main feature (cm^{-1}) ^a	Tentative assignment
g ₃	400.74(13)	-59	2 ₁ ⁴
f ₃	400.13(13)	-21	2 ₀ ³ 3 ₁ ¹
3	399.78(13)	0	2₀³
a ₃	399.40(13)	24	2 ₀ ³ 6 ₁ ¹
b ₃	398.94(13)	53	2 ₀ ³ 5 ₁ ¹
c ₃	398.56(13)	74	2 ₀ ³ 5 ₁ ¹ 6 ₁ ¹
d ₃	398.09(13)	107	2 ₀ ³ 5 ₂ ²
e ₃	397.34(13)	154	2 ₀ ³ 5 ₃ ³
g ₄	395.56(12)	-46	2 ₁ ⁵
f ₄	395.19(12)	-22	2 ₀ ⁴ 3 ₁ ¹
4	394.84(12)	0	2₀⁴
a ₄	394.39(12)	29	2 ₀ ⁴ 6 ₁ ¹
b ₄	393.99(12)	55	2 ₀ ⁴ 5 ₁ ¹
c ₄	393.64(12)	77	2 ₀ ⁴ 5 ₁ ¹ 6 ₁ ¹
d ₄	393.29(12)	100	2 ₀ ⁴ 5 ₂ ²

^aError for each spacing is $\pm 11 \text{ cm}^{-1}$

Table (7.3) Positions and relative spacings of the peaks found in the B' band of Si₄⁻.

Peak	Position (nm)	Relative spacing (cm ⁻¹) ^a
0'	349.90(12)	0
a _{0'}	349.70(12)	16
b _{0'}	349.35(12)	45
g _{1'}	347.0(12)	239
1'	346.20(12)	305
a _{1'}	345.86(12)	334
b _{1'}	345.40(14)	372
g _{2'}	343.61(12)	529
2'	342.69(12)	602
a _{2'}	342.41(12)	625
b _{2'}	342.13(14)	649
g _{3'}	340.22(12)	814
f _{3'}	339.45(8)	880
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a _{3'}	339.00(8)	918
b _{3'}	338.60(11)	954
g _{4'}	337.21(17)	1076
f _{4'}	336.26(11)	1160
4'?	336.96(11)	1186
a _{4'}	335.61(15)	1217
5'	332.71(11)	1477

^aError for spacing is $\pm 14 \text{ cm}^{-1}$

Table (7.4) Excitation energies for several of the low-lying states of Si_4 .

State of Si_4	T_e (eV)
$^3B_{1u}$	2.01 ± 0.02
$^1B_{3u}$	1.37 ± 0.01
$^3B_{3u}$	0.815 ± 0.010
1A_g	0 (E.A.= 2.17 ± 0.01)

Table (7.5) Si_4 neutral and anion frequencies along with anion vibrational temperature assumed for the spectral simulation shown in Figure (7.7). The alternative interpretation of the spectrum for ν_5 and ν_6 is shown in parenthesis. Also included are calculated anion frequencies.

Mode	Neutral frequency (cm^{-1})	Anion frequency (cm^{-1})	Temperature (K)	Calc'd ^b Anion freq. (cm^{-1})
ν_2	312 ^a	365	200	383
ν_3	367	392	270	390
ν_5	177	125(150)	170(380)	295
ν_6	159	132(107)	290(120)	165

^aCalculated neutral frequency for ν_2 is 306 cm^{-1} .

^bRef. (4)

Figure (7.1) Photoelectron spectra of Si_4^- [Ref. (17)] obtained using 3.493 eV photon energy (top panel) and 4.66 eV photon energy (bottom panel) with the assignments of Rohlfing and Raghavachari [Ref. (4)].

Figure (7.2) Diagram of the tunable photodetachment apparatus: (x) interaction region; (1) detachment laser windows; (2) extraction plates and apertures; (3) magnetic shielding; (4) electron einzel lens; (5) ion detector (6) electron detector (above the plane).

Figure (7.3) The ZEKE spectrum of Si_4^- (solid lines) is superimposed onto the energy scale of the PES of Si_4^- obtained using 4.66eV photon energy (dotted line).

Figure (7.4) Expanded-scale, finer-step scan of the A' band.

Figure (7.5) Expanded-scale, finer-step scan of peaks 3 and 4 of the A' band.

Figure (7.6) Expanded-scale scan of the B' band.

Figure (7.7) Calculated geometries of the ground $^2B_{2g}$ anion state and the neutral $^3B_{3u}$ state [Ref. (4)], the orbital from which an electron is removed in the transition between the two states, and the normal coordinates of the $^3B_{3u}$ state of Si_4 .

Figure (7.8) One-dimensional potential energy curves for the anion and neutral ν_2 modes. The anion potential is displaced by the amount determined in the simulation of band A' .

Figure (7.9) Four mode Franck-Condon simulation (solid line) of the A' band (circles). The inset shows an expanded scale view of the simulation. Those peaks labelled explicitly by n or g_n are due to excitations in the v_2 mode of the anion and/or neutral.

Chapter 8. Study of the low-lying states of Ge_2 and Ge_2^- using negative ion ZEKE spectroscopy

Abstract

The properties of the low-lying states of Ge_2 and Ge_2^- are probed using negative ion zero electron kinetic energy (ZEKE) spectroscopy. The ZEKE spectrum of Ge_2^- yields an electron affinity of 2.035 ± 0.001 eV for Ge_2 , as well as term energies and vibrational frequencies for the low-lying states of Ge_2^- and Ge_2 . The anion has a $^2\Pi_u$ (3/2) ground state ($\omega = 309 \pm 5$ cm^{-1}) and a $^2\Sigma_g^+$ ($\omega = 326 \pm 10$ cm^{-1}) at $T_e = 279 \pm 10$ cm^{-1} . The neutral has a $^2\Sigma_g^+$ ground state ($\omega = 286 \pm 5$ cm^{-1}) exhibiting a 114 ± 5 cm^{-1} zero field splitting between the $X0_g^+$ and 1_g components. The $^3\Pi_u$ first excited state [$T_e = 694$ cm^{-1} , $\omega = 308.0$ cm^{-1} from Li, Van Zee, and Weltner, J. Chem. Phys. **100**, 7079 (1994)] has a spin-coupling constant, A , of approximately 484 cm^{-1} , with the 2_u , 1_u , and $0_u^\pm$ components not symmetrically spaced. The manifold of low-lying singlet states was also probed, yielding $T_e = 3308 \pm 5$ cm^{-1} for the $^1\Delta_g$ state ($\omega = 276 \pm 3$ cm^{-1}), $T_e = 4941 \pm 5$ cm^{-1} for the $^1\Sigma_g^+$ state ($\omega = 204 \pm 5$ cm^{-1}) and $T_e \approx 4943 \pm 10$ cm^{-1} for the $^1\Pi_u$ state ($\omega = 303 \pm 5$ cm^{-1}).

I. Introduction

The ongoing effort to characterize the geometries and electronic structures of small elemental semiconductor clusters has been fueled by theoretical studies for at least ten years. However, experiments on these elusive species have proven extremely difficult, primarily due to the lack of mass-specificity of most cluster sources. For instance, only recently has a fairly complete understanding of the electronic structure of Si_2 been experimentally obtained using negative ion photodetachment techniques,¹ in contrast to the 14 years of partially successful *ab initio* study,² which is surprising in light of its believed role in CVD processes.³ The presence of many low-lying states inaccessible from the neutral ground state further contributed to the difficulty in completely characterizing the electronic structure of the smallest silicon cluster. To date, most spectroscopic information on small metal,⁴ carbon,⁵ and semiconductor clusters^{6,7,8} has been accrued from mass-selective experiments, such as negative ion photodetachment.

As an extension of our previous work on Si_2^- , this paper presents the zero electron kinetic energy, or ZEKE spectrum of Ge_2^- which, when compared with the previously obtained anion photoelectron spectrum (PES)⁹ and matrix studies performed by Li, Van Zee, and Weltner,¹⁰ gives an accurate map of the five lowest-lying states of Ge_2 and the two low-lying states of Ge_2^- . The germanium dimer has been predicted to be electronically very similar to silicon dimer, with a $^3\Sigma_g^-$ ($\dots 2\sigma_g^2 1\pi_u^2$) ground state and a very low-lying $^3\Pi_u$ ($\dots 2\sigma_g^1 1\pi_u^3$) first excited state having a calculated term energy (T_e) ranging from 50 to 800 cm^{-1} .^{11,12,13,14} There are also four singlet states resulting from these same orbital occupancies along with the ($\dots 1\pi_u^4$) occupancy predicted to lie within 1.5 eV of the ground state, as with Si_2 . On the other hand, relativistic effects are expected to be more important in Ge_2 than Si_2 . With Ge_2 approaching Hund's case (c), Λ and Σ are no longer good quantum numbers (states having different Λ and Σ but the same Ω can mix)^{15,16} with Ω remaining good, and the spin-orbit components of the $^3\Pi_u$ state may be better described as 0_u^+ , 0_u^- , 1_u and 2_u states (2_u being the lowest-lying), and the

$^3\Sigma_g^-$ state better described as $X0_g^+$ and 1_g states. The energy splitting between the various Ω components of Ge_2^- should be substantially larger than the spin-orbit splitting in Si_2^- , for which the splitting between the $^3\Pi_0$ and $^3\Pi_2$ states (24) is 145 cm^{-1} , and the splitting between the $X0_g^+$ and 1_g components of the $^3\Sigma_g^-$ state (24) is 2.6 cm^{-1} .¹⁰

The $^3\Pi_u [1_u (v' = 0, 1, 2, 3)] \leftarrow ^3\Sigma_g^- (X0_g^+)$ transition was observed in Weltner's matrix absorption studies, giving a term energy of 694 cm^{-1} (711 cm^{-1} between ground vibrational levels of the two states) and a 308 cm^{-1} vibrational frequency for the 1_u component of the $^3\Pi_u$ excited state. Transitions to the other Ω components of the $^3\Pi_u$ state are not allowed from the $^3\Sigma_g^- (X0_g^+)$ state. A vibrational frequency assigned to the $^3\Sigma_g^- (X0_g^+)$ state in a matrix was observed in Raman/fluorescence studies.¹⁷ To our knowledge, no spectroscopic information on the low-lying singlet states has until now been obtained.

The low-lying singlet states, however, can be accessed using negative ion photodetachment techniques. While the more common anion PES sometimes cannot resolve close-lying or overlapping electronic transitions, negative ion ZEKE spectroscopy is particularly well suited toward small cluster study, as it combines mass-selection with good spectroscopic resolution. Anion ZEKE is most powerful when used in tandem with fixed-frequency photoelectron spectroscopy (PES) which, with its less-restrictive selection rules, is sensitive to more electronic transitions.

No *ab initio* results are presently available for Ge_2^- , but if it is electronically similar to Si_2^- , it has two close-lying $^2\Pi_u$ and $^2\Sigma_g^+$ states (the $^2\Sigma_g^+$ state was the ground state of Si_2^- , and the $^2\Pi_u$ state was approximately $250 \pm 80\text{ cm}^{-1}$ higher in energy). All of the low-lying triplet and singlet valence states of Ge_2 can in principle be accessed in the PES by photodetaching an electron from the valence orbitals of at least one of the anion states. Figure (8.1) shows a schematic of the low-lying neutral and anion electronic states including the various Ω components, and the one-electron transitions between them. For reference, the transition observed by Weltner is also shown as the darker arrow connecting the $^3\Sigma_g^- (X0_g^+)$ and $^3\Pi_u (1_u)$

neutral levels. Two-electron transitions are generally too weak to be observed using our particular photodetachment techniques. For instance, the transition from the $2\Sigma_g^+ (\sigma_g^2 \pi_u^4)$ anion state to either component of the $3\Sigma_g^- (\sigma_g^2 \pi_u^2)$ neutral would require both electron detachment and rearrangement, and will be too weak to be observed in either the PES or ZEKE spectrum.

While any of the 1-electron transitions in Figure (8.1) can be observed in the PES, the selection rules in ZEKE spectroscopy are more restrictive due to the Wigner threshold law.¹⁸ For atomic systems, this dictates that near threshold, the detachment cross section goes as:

$$\sigma \propto \sigma_0 (E_{kv} - E_{\text{threshold}})^{\ell+1/2}, \quad \text{Eqn. (8.1)}$$

where $(E_{kv} - E_{\text{threshold}})$ and ℓ are the kinetic energy and angular momentum of the ejected electron, respectively. Geltman and coworkers extended the threshold law to diatomics with the same result.¹⁹ From Eqn. (8.1) it can be seen that the cross section rises sharply above threshold *only* for $\ell = 0$, or s-wave electrons. As ZEKE spectroscopy relies on detecting electrons near a detachment threshold, it is sensitive only to s-wave transitions. Given the angular momentum of orbitals in a homonuclear diatomic, the end result is that *only* transitions involving the detachment from π_u or σ_u orbitals yield s-wave photoelectrons. On Figure (8.1), those $\ell > 0$ transitions that cannot be observed using ZEKE are indicated as dotted lines.

While at times inconvenient, the more restrictive ZEKE selection rules can be useful in the situation where the PES is congested by overlapping transitions, as is the case with both Si_2^- and Ge_2^- . In addition, it effectively reveals the orbital from which an electron is ejected in a particular transition, which greatly facilitates spectral assignment. From the Ge_2^- PES and ZEKE spectrum, the splittings (or term energies) between the Ω components are resolved for both the $3\Sigma_g^-$ and $3\Pi_u$ states, and the term energies for the $1\Delta_g$, $(1)^1\Sigma_g^+$ and $1\Pi_u$ states are extracted. Vibrational frequencies for all of these states are determined from the ZEKE

spectrum. Additionally, the relative energies and vibrational frequencies of the $^2\Gamma_u$ (3/2) and the $^2\Sigma_g^+$ anion states are also determined.

II. Experimental

The apparatus used to obtain the ZEKE spectrum of Ge_2^- has been described in detail elsewhere, but the basic operation is as follows. A beam of cold germanium clusters is generated in a molecular beam source similar to that developed by Smalley.²⁰ The surface of a rotating and translating germanium rod is ablated using 6 mJ/pulse of the second harmonic output of a Nd:YAG laser operated at a 20 Hz repetition rate. The resulting plasma is then entrained in a pulse of 90% Ne/10% He carrier gas from a piezoelectric valve,²¹ typically with a backing pressure of 60 to 70 psi. In order to generate sufficient quantities of Ge_2^- , the source was run under conditions that generally produce vibrationally hot ions (e.g., lower beam pulse duration, earlier rod ablation relative to carrier gas entrainment), as the colder conditions tend to skew the mass distribution to higher mass. The negatively charged species in the subsequent expansion that pass through a 2 mm skimmer are colinearly accelerated to 1 keV, and mass-selected using time-of-flight.²²

The mass-separated anions then enter a detector region where they are selectively photodetached using an excimer-pumped tunable dye laser. As the dye laser is scanned through the detachment continuum of the ion of interest, only those photoelectrons ejected with nearly zero kinetic energy (ZEKE's) in the frame of the molecular beam are collected as a function of detachment energy. The resulting spectrum is therefore peaked at the thresholds of transitions from anion to neutral levels. This selective detection of threshold electrons, based on techniques developed by Müller-Dethlefs *et al.*²³ for the photoionization of neutrals, yields an energy resolution of 3 cm^{-1} .

The electron signal for the ZEKE spectrum of Ge_2^+ was signal averaged for 1500 shots/point, and normalized to the ion current and detachment laser power. The dyes used were Rhodamine 610, Rhodamine 590, Coumarin 540A, Coumarin 503, Coumarin 480, and Coumarin 450.

III. Results

The PES of Ge_2^+ obtained using 2.98 eV photon energy (416 nm) and at two laser polarizations is shown in Figure (8.2) (dotted lines). Photoelectrons ejected from different orbitals will generally have different angular distributions, and by comparing the two different laser polarizations, the extent of the overlapping transitions congesting the PES can be seen. Moreover, by comparing how the peak intensities change with the detachment laser polarization, a first-order idea of which transitions involve p-wave detachment can be obtained; in the similarly obtained PES of Si_2^+ , the p-wave transitions tended to be more intense in the $\theta = 0^\circ$ (electron detection parallel to the electric field vector of the detachment laser) spectrum. For instance, peaks C_Ω and peak F are particularly intense in the $\theta = 0^\circ$ spectrum, suggesting they involve p-wave detachment. The group of peaks at the lower-energy end of the spectrum are comprised of transitions to the lowest-lying triplet states of the neutral, and the group of peaks on the high-energy end are the transitions to the higher-lying singlet neutral states. The Ge_2^+ ZEKE spectrum (solid line) has been superimposed onto the $\theta = 90^\circ$ PES. Note that the PES have been placed on the ZEKE binding energy (cm^{-1}) scale.

The upper, solid trace in Figure (8.3) shows the triplet band of the ZEKE spectrum on an expanded scale. The peak labeling convention is based on the assignments that will be discussed in detail later. Briefly, different letters correspond to different electronic bands, and where there are two subscripts, the first denotes the value of Ω of the neutral state, and the second is the vibrational quanta in the neutral state (in the singlet band, only the neutral

vibrational quanta is denoted in the peak label subscripts). The triplet band is dominated by a progression of doublets labeled $A_{0,v}$ and $A_{1,v}$ ($v = 0, 1, 2, 3$) which have an average splitting of $117 \pm 5 \text{ cm}^{-1}$. The centers of the doublets are spaced by $286 \pm 5 \text{ cm}^{-1}$; this is presumably a vibrational progression. The lower-intensity peaks $a_{0,0}$ and $a_{1,0}$ appear to be transitions from the fundamental of the anion (hot bands), and are found $309 \pm 5 \text{ cm}^{-1}$ to lower photon energy of peaks $A_{0,0}$ and $A_{1,0}$, respectively. In addition to these features, there are lower intensity peaks spaced irregularly among the 286 cm^{-1} progression. The most distinct of these is $B_{2,0}$ found $58 \pm 7 \text{ cm}^{-1}$ to higher photon energy of $A_{0,0}$. Peak $b_{2,0}$ also appears to be a hot band spaced $326 \pm 10 \text{ cm}^{-1}$ to lower photon energy of peak $B_{2,0}$. There are also shoulders on both sides of peak $A_{1,1}$ found 308 ± 10 and $374 \pm 10 \text{ cm}^{-1}$ ($B_{2,1}$ and $B_{1,0}$, respectively) to higher photon energy of peak $B_{2,0}$. Peaks $B_{0,-0}$ and $B_{0+,0}$, while appearing to be a part of the $A_{0,v}$ and $A_{1,v}$ progression, are actually spaced $340 \pm 10 \text{ cm}^{-1}$ rather than 286 cm^{-1} from peaks $A_{0,2}$ and $A_{1,2}$ (peak $A_{0,3}$ found 80 cm^{-1} to lower photon energy of peak $B_{0,-0}$, is the tail of the $A_{0,v}$ progression). There are several transitions that are apparent in the PES [Figure (8.2)] that are absent in this energy region of the ZEKE spectrum. All of the peaks labeled " C_x " in the upper panel of Figure (8.2) should be found within 100 cm^{-1} of $17\,100 \text{ cm}^{-1}$ (C_{2u}), $17\,460 \text{ cm}^{-1}$ (C_{1u}), and $18\,050 \text{ cm}^{-1}$ (C_{0u}). Peak positions and relative energies are summarized in Table (8.1). The peak positions generally have an uncertainty of $\pm 5 \text{ cm}^{-1}$, and so the relative energies are generally good to $\pm 7 \text{ cm}^{-1}$.

The ZEKE spectrum of the singlet band of Ge_2^- is shown on an expanded scale as the solid trace in Figure (8.4). There appear to be three electronic transitions contributing to the structure in this region. The lowest energy is a $276 \pm 3 \text{ cm}^{-1}$ progression labeled D_v ($v = 0, \dots, 4$). The origin, D_0 , which is actually a partially-resolved doublet, is found 3314 cm^{-1} above peak $A_{0,0}$ in the singlet band. Peak d_0 appears to be a hot band, and is found $307 \pm 7 \text{ cm}^{-1}$ to lower photon energy of D_0 . E_0 indicates the origin of a second electronic transition found 4664 cm^{-1} to higher photon energy of peak $A_{0,0}$. Peak G_0 is spaced approximately 220 cm^{-1} to higher

photon energy of peak E_0 , which could reasonably be a vibrational spacing. However, peak E_2 , which is found $607 \pm 7 \text{ cm}^{-1}$ from E_0 , is much less intense than would be expected if E_0 , G_0 and E_2 formed a progression. On the other hand, peak G_0 is broad, and it is feasible that two transitions are contributing to G_0 : the fundamental of E_0 , and yet another electronic transition for which G_1 is the fundamental. This gives a frequency of $303 \pm 5 \text{ cm}^{-1}$ for the neutral state accessed by the E transition, and $204 \pm 7 \text{ cm}^{-1}$ for the state accessed by the G transition. Peak e_0 , another hot band, is $329 \pm 7 \text{ cm}^{-1}$ from E_0 . Peaks g_1 and g_2 are spaced approximately 100 cm^{-1} to lower photon energy of G_0 and G_1 , respectively. As the anion frequencies so far have been either approximately 309 cm^{-1} or 326 cm^{-1} , peaks g_1 and g_2 are spaced appropriately to be the $v' = 1 \leftarrow v'' = 1$ and $v' = 2 \leftarrow v'' = 1$ sequence and hot band transitions, respectively, between an anion state and the neutral state responsible for G_0 . Again, Table (8.1) summarizes peak positions and relative energies.

By comparing the singlet bands in the ZEKE and PES spectra, there appears to be a one to one correspondence between the transitions in both spectra. However, as mentioned above, peak F in the PES appears to be a p-wave transition based on its polarization dependence. Upon close inspection of peak F in the lower panel of Figure (8.1), the overlapping ZEKE peak (G_0) falls on the higher-energy side. It therefore seems likely that peak F is composed of two transitions, one of which proceeds via s-wave, and the other via p-wave.

IV. Analysis and Discussion

The assignment and subsequent analysis of the spectra requires consideration of both the ZEKE spectra and the PES. The approach taken below is to first analyze the triplet band of the PES and ZEKE spectrum considering the higher-resolution spectroscopic information from Weltner's matrix studies. From this, the spectroscopic constants of the anion states will be

extracted. With more information about the anion states, the analysis of the singlet band then proceeds in a more straightforward manner.

A. Triplet band

Figure (8.1) illustrates the three one-electron transitions between the doublet anion states and the lowest-lying triplet neutral states, two of which should be observed in the ZEKE spectrum [Figure (8.3)]: the ${}^3\Sigma_g^- (1_g, X0_g^+) \leftarrow {}^2\Pi_u (3/2)$ transition and the ${}^3\Pi_u (0^+, 0^-, 1_u, 2_u) \leftarrow {}^2\Sigma_g^+$ transitions. We can immediately assign peaks $A_{\Omega,v}$ to the former. As pointed out by Weltner,¹⁰ the zero field splitting (ZFS) between the $X0_g^+$ and 1_g components of the neutral ${}^3\Sigma_g^-$ state of Ge_2 is expected to be approximately 100 cm^{-1} based on the square of the relative spin-orbit splittings in the Ge and Si atoms ($\text{SO}_{\text{Ge}}/\text{SO}_{\text{Si}} = 6.3$) as well as the ZFS in Si_2 (2.6 cm^{-1}).²⁴ It therefore seems reasonable to associate the $A_{0,v} - A_{1,v}$ doublet structure with the average 117 cm^{-1} spacing with the ZFS between the $X0_g^+$ and 1_g components of the neutral ${}^3\Sigma_g^-$ state. This splitting has contributions from both first order spin-spin interaction and second order spin-orbit interaction, but as the former is generally on the order of less than 1 cm^{-1} ,²⁵ 117 cm^{-1} can be taken as the second-order spin-orbit constant (conventionally, $2\lambda^{SO}$).¹⁶ The 286 cm^{-1} vibrational frequency characteristic of the $A_{\Omega,v}$ progression is slightly higher than the $277 (\pm 10; \text{error bars were not included in the spectral analysis}) \text{ cm}^{-1}$ ground state frequency determined from Raman matrix studies.¹⁷ From the position of the hot bands (peaks $a_{0,0}$ and $a_{1,0}$) we determine that the frequency of the ${}^2\Pi_u$ anion is 309 cm^{-1} . From the Si_2^- ZEKE spectrum, we were also able to determine the 122 cm^{-1} spin-orbit splitting in the ${}^2\Pi_u$ anion,¹ as the $\Omega = 1/2$ level was sufficiently populated in the beam in order to observe both the ${}^3\Sigma_g^- \leftarrow {}^2\Pi_u (3/2)$ and the ${}^3\Sigma_g^- \leftarrow {}^2\Pi_u (1/2)$ transitions. However, since the Ge_2^- spin-orbit splitting is expected to be roughly 700 to 800 cm^{-1} , the population of spin-orbit excited anions in the beam is likely to be very small, and we only observe transitions from the $\Omega = 3/2$ component.

We can simulate the vibrational structure in the $^3\Sigma_g^- (0_g^+, 1_g) \leftarrow ^2\Pi_u (3/2)$ transitions within the Franck-Condon approximation. In the simulation, we assume that the intensity of individual vibronic transitions within an electronic band are proportional to their Franck-Condon factors (FCF's),

$$\text{Intensity} \propto |\langle v' | v'' \rangle|^2. \quad \text{Eqn. (8.2)}$$

The vibrational wave functions of the neutral and anion, v' and v'' , respectively, are taken to be harmonic (or Morse) oscillators with the frequencies determined from the spectra. The relative bond distances of the anion and neutral are then varied until the extension of the simulated progression matches the observed progression.

The simulation of the $^3\Sigma_g^- (0_g^+, 1_g) \leftarrow ^2\Pi_u (3/2)$ transitions is shown as the lighter dashed trace on the lower part of Figure (8.3). Harmonic oscillator wave functions with 309 and 286 cm^{-1} frequencies were used for the anion and neutral, respectively. A bond distance difference of $0.059 \pm 0.003 \text{ \AA}$ was required to reproduce the extension of the progression, and while the direction of the bond length change cannot be determined from the simulation (using harmonic oscillators) the anion bond length should be shorter than the neutral, as the transition involves removing a bonding electron. An anion vibrational temperature of 350 K was required to match the hot band intensity; this temperature is fairly typical for our cluster source given this vibrational frequency.

Given the $^3\Sigma_g^- (0_g^+, 1_g) \leftarrow ^2\Pi_u (3/2)$ assignment and the term energy of the $^3\Pi_u (1_u)$ state from Weltner's matrix studies, we would expect the $^3\Pi_u (1_u) \leftarrow ^2\Pi_u (3/2)$ transition to lie approximately 700 cm^{-1} above the $^3\Sigma_g^- (X0_g^+) \leftarrow ^2\Pi_u (3/2)$ transition, and to be observed only in the PES as it involves the removal of a σ_g electron. In the upper panel of Figure (8.2), peak C_{1u} lies $670 \pm 50 \text{ cm}^{-1}$ to higher energy than peak A. We therefore assign peak C_{1u} in the PES to the $^3\Pi_u (1_u) \leftarrow ^2\Pi_u (3/2)$ transition. It then follows that peak C_{2u} , found 360 cm^{-1} to lower

energy, is the ${}^3\Pi_u(2_u) \leftarrow {}^2\Pi_u(3/2)$ transition. From the PES, it is not clear which of the lower-intensity transitions to slightly higher energy are the ${}^3\Pi_u(0_u^-) \leftarrow {}^2\Pi_u(3/2)$ and ${}^3\Pi_u(0_u^+) \leftarrow {}^2\Pi_u(3/2)$ transitions.

We can now apply what is known about the ${}^3\Pi_u(2_u - 1_u)$ splitting to interpret the remaining structure in the triplet region of the ZEKE spectrum that has not been accounted for by the ${}^3\Sigma_g^-(X0_g^+, 1_g) \leftarrow {}^2\Pi_u(3/2)$ transition. Peaks $B_{\Omega,v}$ must result from the ${}^3\Pi_u(0_u^+, 0_u^-, 1_u, 2_u) \leftarrow {}^2\Sigma_g^+$ transitions, the only others that proceed *via* s-wave detachment in this energy region. By comparing the dotted trace of the simulation with the ZEKE spectrum, the lower-intensity peaks and shoulders labeled $B_{\Omega,v}$ stand out more clearly as a second set of electronic transitions. The most distinct of these peaks is $B_{2,0}$. The shoulder $B_{1,0}$ is found 374 cm^{-1} to higher photon energy, which is close to the ${}^3\Pi_u(2_u - 1_u)$ splitting observed in the PES. Moreover, $B_{2,1}$ and $B_{1,1}$ are found approximately 308 cm^{-1} to higher photon energy of $B_{2,0}$ and $B_{1,0}$, respectively, which is the vibrational frequency of the ${}^3\Pi_u(1_u)$ state determined by Weltner. We therefore assign peak $B_{2,0}$ to the ${}^3\Pi_u(2_u) \leftarrow {}^2\Sigma_g^+$ transition, and $B_{1,0}$ to the ${}^3\Pi_u(1_u) \leftarrow {}^2\Sigma_g^+$ transition. Peaks $B_{2,1}$ and $B_{1,1}$ are transitions to the fundamental levels of the ${}^3\Pi_u(2_u)$ and ${}^3\Pi_u(1_u)$ states, respectively.

From the position of the ${}^3\Pi_u(1_u) \leftarrow {}^2\Sigma_g^+$ transition (peak $B_{1,0}$), the relative energy of the ${}^2\Sigma_g^+$ and ${}^2\Pi_u(3/2)$ anion states can be determined. The ${}^3\Pi_u(1_u) \leftarrow {}^2\Sigma_g^+$ transition is $432 \pm 10\text{ cm}^{-1}$ higher in energy than the ${}^3\Sigma_g^-(X0_g^+) \leftarrow {}^2\Pi_u(3/2)$ transition, but from Weltner's work, the ${}^3\Pi_u(1_u)$ neutral zero point level is known to lie $711 \pm 3\text{ cm}^{-1}$ above the ${}^3\Sigma_g^-(X0_g^+)$ zero point level.¹⁰ This gives that for the anion, the ${}^2\Pi_u(3/2)$ level is $279 \pm 11\text{ cm}^{-1}$ below the ${}^2\Sigma_g^+$ level (by using Weltner's value, the energy splitting we determine for the anion states is more accurate than what we would have determined from comparing the position of peak C_{2u} in the PES and peak $B_{2,0}$ in the ZEKE spectrum, which would have yielded $240 \pm 80\text{ cm}^{-1}$). The relative weakness of the B transitions likely results from their originating from an excited anion level. Given the expected spin-orbit splitting in the ${}^2\Pi$ state of Ge_2^- , the ${}^2\Pi_u(1/2)$ excited level

may be roughly 400 to 500 cm^{-1} above the $2\Sigma_g^+$ state. The frequency of the $2\Sigma_g^+$ can be extracted from the position of the $b_{2,0}$ hot band, which is found 326 cm^{-1} to lower photon energy of peak $B_{2,0}$. This is slightly higher than the 309 cm^{-1} frequency determined for the $2\Pi_u$ (3/2) state.

So far, peaks $B_{0-,0}$ and $B_{0+,0}$ have not been addressed. These are approximately half the intensity of peak $B_{2,0}$, and they are spaced 856 and 968 cm^{-1} , respectively, to higher photon energy. As there are no other electronic transitions that should be observed in this region of the spectrum, we tentatively assign them to the $3\Pi_u$ (0_u^-) $\leftarrow 2\Sigma_g^+$ and $3\Pi_u$ (0_u^+) $\leftarrow 2\Sigma_g^+$ transitions. It should be noted again that although the spacing between peaks $B_{0+,0}$ and $B_{0-,0}$ is very close to the $A_{0,v} - A_{1,v}$ splitting, peaks $B_{0+,0}$ and $B_{0-,0}$ do not energetically fall in the $A_{0,v} - A_{1,v}$ vibrational progression, and perturbation of this progression spacing is unlikely given the absence of any other close-lying gerade states. If these peaks do represent the $3\Pi_u$ ($0_u^\pm$) $\leftarrow 2\Sigma_g^+$ transitions, the spin coupling constant, A , for the $3\Pi_u$ state is between $856/2 = 428$ to $968/2 = 484$ cm^{-1} , which is higher than the 1_u-2_u splitting (374 cm^{-1}). The asymmetric arrangement of the $3\Pi_u$ ($0_u^\pm$) and $3\Pi_u$ (2_u) states about the $3\Pi_u$ (1_u) state was also observed for the Si_2 $3\Pi_u$ state in Weltner's studies, and is due to the mixing of the $\Omega = 1$ level with the higher-lying $1\Pi_u$ state. This mixing will be further addressed in the next section where the term energy of the $1\Pi_u$ state is discussed.

The $3\Pi_u$ (0_u^+) level is always higher-lying than the $3\Pi_u$ (0_u^-) level due to the form of the (off-diagonal) spin-spin interaction.¹⁵ The splitting effectively arises because the $3\Pi_u$ (0_u^-) state correlates to the Ge ($2P_{3/2}$) + Ge ($2P_{3/2}$) dissociation asymptote, while the higher-lying $3\Pi_u$ (0_u^+) level correlates to the Ge ($2P_{1/2}$) + Ge ($2P_{3/2}$) asymptote. Moreover, the $3\Pi_u$ (0_u^+) potential necessarily crosses the $3\Sigma_u^+$ (0_u^-) and $3\Sigma_u^-$ (0_u^+) potentials near the dissociation continuum, which can give rise to further electronic coupling. The magnitude of this splitting in any diatomic is rarely measured, since transitions to only one of the levels is generally allowed from a particular state. However, calculations on In_2 give a $0_u^+-0_u^-$ splitting of 231 cm^{-1} with a

calculated $2A$ of 1397 cm^{-1} , and for Sn_2 , the $0_u^+ - 0_u^-$ splitting is calculated to be 108 cm^{-1} with $2A =$ approximately 2715 cm^{-1} .¹¹ While our measure $0_u^+ - 0_u^-$ splitting seems relatively large by comparison to the calculated $0_u^+ - 0_u^-$ splitting for isoelectronic Sn_2 , the order of magnitude seems reasonable. Nonetheless, the similarity between the Ge_2 $0_u^+ - 0_u^-$ and $\text{XO}_g^+ - 1_g$ splittings compels us view this whole issue with some caution.

As can be seen in the lower half of Figure (8.3), a spectral simulation was also performed for the ${}^3\Pi_u (0_u^+, 0_u^-, 1_u, 2_u) \leftarrow {}^2\Sigma_g^+$ transitions (heavier dashed line). The neutral frequency assumed for all four components was 308 cm^{-1} , per Weltner,¹⁰ and the anion frequency was assumed to be 326 cm^{-1} . The transitions to the ${}^3\Pi_u (0_u^\pm)$ states were assumed to be half the intensity of the transitions to the ${}^3\Pi_u (1_u)$ and ${}^3\Pi_u (2_u)$ states, which were in turn scaled to have 0.25 the intensity of the ${}^3\Sigma_g^- (\text{XO}_g^+) \leftarrow {}^2\Pi_u (3/2)$ transition in order to best match the spectrum. A bond length difference of $0.04\text{ \AA}$ between the anion and neutral was assumed to match the extension of the vibrational progression, and again, the anion should have the shorter bond distance.

Geometry calculations on the lowest-lying neutral states predict the bond length of the ${}^3\Pi_u$ excited state to be $0.1\text{ \AA}$ shorter than the ${}^3\Sigma_g^-$ state,^{11,12,13,14} which, considering the bond length differences determined from the spectra, suggests that the anion ${}^2\Pi_u$ state is approximately $0.08\text{ \AA}$ longer than the ${}^2\Sigma_g^+$ state (calculations yield values from 2.42 to $2.46\text{ \AA}$ for the ${}^3\Sigma_g^-$ state and 2.33 to $2.39\text{ \AA}$ for the ${}^3\Pi_u$ state). Thus, shifting an electron from the σ_g to the π_u orbital results in shortening the bond by nearly $0.1\text{ \AA}$ in both the anion and neutral. The relative bond distances between the anion and neutral states are startlingly similar to those found for Si_2 and Si_2^- . The anion states were found to be different by $0.09\text{ \AA}$ with the ${}^2\Pi_u$ state being longer, and the neutral states were known to be different by $0.09\text{ \AA}$ with the ${}^3\Sigma_g^-$ state being longer. Moreover, spectral simulations of the ZEKE spectrum of Si_2^- gave bond length differences on the order of $0.04\text{ \AA}$ in both ZEKE transitions. This interesting similarity between

the response of the bond lengths of Ge_2 and Si_2 to the shifting of valence electrons within the triplet manifold further reflects the electronic similarity between these two species.

Table (8.1) summarizes the peak assignments discussed in this section, and Table (8.2) summarizes the spectroscopic constants extracted from the spectrum and used in the spectral simulations, including the term energies of the $^3\Pi_u$ (0_u^+ , 0_u^- , 1_u , 2_u) states applied in the spectral simulation.

B. Singlet band

From electronic state calculations,¹¹ transitions to the $^1\Delta_g$, $(1)^1\Sigma_g^+$ and $^1\Pi_u$ neutral states lie roughly 0.5 - 0.7 eV above the ground state should result in the structure observed to higher energy in both the PES. In Table (8.2), the *ab initio* term energies of these three states are listed. Figure (8.1) shows the four 1-electron transitions between the two anion states and these three neutral states. An additional $(2)^1\Sigma_g^+$ state is predicted to lie approximately 1.3 eV above the ground state; the $(2)^1\Sigma_g^+ \leftarrow ^2\Sigma_g^+$ (p-wave) transition is not observed in the PES obtained using 2.98 eV photon energy, but in the PES obtained using 4.66 eV photon energy, it was found to lie (with lower accuracy) $9300 \pm 100 \text{ cm}^{-1}$ (1.15 eV) above the $^3\Sigma_g^- \leftarrow ^2\Pi_u$ (3/2) transition. Adding the term energy of the $^2\Sigma_g^+$ anion state yields $T_e = 9580 \text{ cm}^{-1}$ for the $(2)^1\Sigma_g^+$ state. There are three transitions expected to be observed in the ZEKE spectrum: $^1\Delta_g \leftarrow ^2\Pi_u$ (3/2), $(1)^1\Sigma_g^+ \leftarrow ^2\Pi_u$ (3/2), and $^1\Pi_u \leftarrow ^2\Sigma_g^+$.

Since the $^1\Delta_g$ state is predicted to be the lowest-lying of the singlet states, peaks D_v ($v = 0, \dots, 4$) are assigned to the $^1\Delta_g$ ($v' = 0, \dots, 4$) $\leftarrow ^2\Pi_u$ (3/2) transition. The $276 \pm 3 \text{ cm}^{-1}$ ($\omega_e x_e = 1.2 \pm 0.6 \text{ cm}^{-1}$) progression is the most extended of all the progressions. This is consistent with calculated geometries, which predict the $^1\Delta_g$ state to have the longest bond distance of all the low-lying states. The position of the hot band, d_0 , gives an anion frequency of approximately 308 cm^{-1} , which further supports that this is a transition from the $^2\Pi_u$ (3/2) anion state. The

energy spacing between peak D_0 and $A_{0,0}$ directly gives the term energy of the ${}^1\Delta_g$ state: $3314 \pm 7 \text{ cm}^{-1}$.

As with the triplet band, the Franck-Condon simulation gives an approximate bond length difference between the anion and neutral. The total simulation of the singlet band is shown as the dashed line in Figure (8.4). In the case of the transition to the ${}^1\Delta_g$ state, the bond length difference is determined to be $0.095 \pm 0.005 \text{ \AA}$. This further suggests that the bond distance in the ${}^1\Delta_g$ state is $0.036 \text{ \AA}$ longer than that in the ${}^3\Sigma_g^- (X0_g^+)$ state. This is in qualitative agreement with the calculated bond distance between these two states, $0.06 \text{ \AA}$.¹¹

Again referring to the calculated frequencies of the singlet states [Table (8.2)], the $(1) {}^1\Sigma_g^+$ state has a substantially lower frequency than the other singlet states. We therefore assign the $G_0 - G_1$ progression to the $(1) {}^1\Sigma_g^+ \leftarrow {}^2\Pi_u (3/2)$ transition, as it exhibits the smallest vibrational spacing, 204 cm^{-1} . From the average spacing of the sequence bands, g_1 and g_2 , the anion frequency in this transition is approximately 305 cm^{-1} , which is close to the previously determined ${}^2\Pi_u (3/2)$ frequency, further supporting the assignment. As above, the term energy of this state can be extracted from the energy spacing between peaks G_0 and $A_{0,0}$: 4941 cm^{-1} . In the simulation shown, a bond length difference of $0.045 \pm 0.005 \text{ \AA}$ was found to satisfactorily fit the progression. This is $0.014 \text{ \AA}$ less than that used in the ${}^3\Sigma_g^- (X0_g^+) \leftarrow {}^2\Pi_u (3/2)$ fit, suggesting that the bond distances of the ground ${}^3\Sigma_g^- (X0_g^+)$ and excited $(1) {}^1\Sigma_g^+$ states have nearly identical bond distances. While this is counterintuitive given the lower frequency in the excited singlet state, geometry calculations do predict these two states to have nearly identical bond lengths, presumably because the $(1) {}^1\Sigma_g^+$ is a mixture of both the $1\pi_u^4$ and $2\sigma_g^2 1\pi_u^2$ configurations, and population in the $1\pi_u$ orbital results in a shorter bond distance.^{11,12,13,14}

The remaining vibrational progression in the ZEKE spectrum, E_v , can be assigned by elimination to the ${}^1\Pi_u \leftarrow {}^2\Sigma_g^+$ transition. The position of the hot band, e_0 , gives an anion frequency of $329 \pm 5 \text{ cm}^{-1}$, which is in agreement with the $326 \pm 5 \text{ cm}^{-1}$ determined for the ${}^2\Sigma_g^+$

anion state determined from the triplet band. In the fit shown, the neutral frequency was chosen as $304 \pm 5 \text{ cm}^{-1}$ with a bond length change between the anion and neutral of $0.05 \pm 0.005 \text{ \AA}$.

In order to determine the term energy of the $^1\Pi_u$ state, we must add the term energy of the $^2\Sigma_g^+$ anion state to the energy separation between peak E_0 and $A_{0,0}$, which gives a value of 4943 cm^{-1} . Within the error bars of the experiment, we cannot assert which of the $(1)^1\Sigma_g^+$ and $^1\Pi_u$ states is higher lying, and calculations do not give a strong indication; the $(1)^1\Sigma_g^+$ and the $^1\Pi_u$ states are predicted to close-lying, with Balasubramanian¹¹ and Facchioni¹³ predicting the $^1\Pi_u$ state to be higher-lying than the $(1)^1\Sigma_g^+$ state, and Kingcade *et al.*¹⁴ predicting the $^1\Pi_u$ state to be lower. While it may seem too remarkable a coincidence that these state are nearly degenerate, it is further supported by the sole p-wave transition observed in the singlet band of the PES [Figure (8.1)]. Peak F in the PES, which can only be the $^1\Pi_u \leftarrow ^2\Pi_u$ (3/2) transition, energetically coincides with peak G_0 in the ZEKE spectrum, which, in addition to irrefutably being an s-wave transition, has been definitively assigned to the $(1)^1\Sigma_g^+ \leftarrow ^2\Pi_u$ (3/2) transition. As the coincident transitions originate from the same anion state, the neutral states must coincide energetically.

Given the term energy of the $(1)^1\Sigma_g^+$ state and the ZFS between the $X0_g^+$ and 1_g levels of the $^3\Sigma_g^-$ state, an approximate value for the spin coupling constant, A , in the $^3\Pi_u$ state can be calculated with,¹⁶

$$2\lambda^{SO} = 117 \text{ cm}^{-1} \approx \frac{4A^2}{E(^1\Sigma_g^+) - E(^3\Sigma_g^-)} \quad \text{Eqn. (8.2)}$$

Adjusting the T_e of the $(1)^1\Sigma_g^+$ state to account for the 117 cm^{-1} repulsion "felt" by both the $(1)^1\Sigma_g^+$ and $X0_g^+$ levels, $2A$ determined from Eqn. (8.2) is 742 cm^{-1} , which is fairly close to the observed splitting, 484 cm^{-1} .

The extent of the asymmetry between the $^3\Pi_u$ ($2_u, 1_u, 0_u^\pm$) levels similarly is due to the repulsion between the $^1\Pi_u$ and $^3\Pi_u$ (1_u) levels, and can be calculated given the term energy of the $^1\Pi_u$ state. The shift to both states is given by¹⁶ $A^2/2K$, where $2K$ is the deperturbed splitting between the $^3\Pi_u$ (1_u) and $^1\Pi_u$ levels [i.e., the $(^3\Pi_u - ^1\Pi_u)$ exchange integral]. Assuming $A = 484 \text{ cm}^{-1}$ from half the $B_{0+,0} - B_{2,0}$ splitting, and 4000 cm^{-1} for the deperturbed exchange, $A^2/2K$ is 60 cm^{-1} . This is smaller than what is observed, but considering the splitting between the $^3\Pi_u$ ($0_u^\pm$) levels is not considered in the calculation, it seems quite close.

V. Conclusion

The work presented here again shows how the combination of anion PES and ZEKE spectroscopy provides a powerful probe of electronically complicated species. The term energies and vibrational frequencies obtained for the five lowest-lying neutral triplet and singlet states of Ge_2 were found to be consistent with ab initio values. Moreover, with Weltner's term energy for the $^3\Pi_u$ (1_u) state, we were able to determine the energy splitting between the $^2\Pi_u$ ($3/2$) and $^2\Sigma_g^+$ states of the anion with less uncertainty than would have been afforded by the PES and ZEKE spectrum alone.

From the triplet band of the ZEKE spectrum, the zero field splitting between the $X0_g^+$ and 1_g components of the $^3\Sigma_g^-$ neutral state was determined to be $114 \pm 5 \text{ cm}^{-1}$, both components having a $286 \pm 5 \text{ cm}^{-1}$ vibrational frequency. The term energies of the $2_u, 1_u, 0_u^-$ and 0_u^+ components of the $^3\Pi_u$ state, with their 308 cm^{-1} vibrational frequency (per Weltner¹⁰) were found to be $337, 711, 1193, \text{ and } 1305 \pm 14 \text{ cm}^{-1}$, respectively. These energies are taken with respect to the zero-point energies. It was also determined that the $^2\Sigma_g^+$ ($\omega_e = 326 \pm 10 \text{ cm}^{-1}$) anion state lies $279 \pm 10 \text{ cm}^{-1}$ above the $^2\Pi_u$ ($3/2$) ($\omega_e = 309 \pm 5 \text{ cm}^{-1}$) level.

From the singlet band, term energies for the $^1\Delta_g$, (1) $^1\Sigma_g^+$, and $^1\Pi_u$ states were determined. The $^1\Delta_g$ ($\omega_e = 276 \pm 3 \text{ cm}^{-1}$), as predicted, was found to be the lowest-lying with T_e

$\approx 3308 \pm 7 \text{ cm}^{-1}$. The $(1)^1\Sigma_g^+$ ($\omega_e = 204 \pm 7 \text{ cm}^{-1}$) and $^1\Pi_u$ ($\omega_e = 304 \pm 10 \text{ cm}^{-1}$) states are nearly degenerate, with T_e 's around $4942 \pm 7 \text{ cm}^{-1}$.

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Table (8.1) Peak positions, relative energies and assignments in both the PES and ZEKE spectra. The asterisk (*) indicates that the peak was observed only in the PES. In the case where peaks are observed in both spectra, the detachment energy obtained from the ZEKE spectrum is used. It should be noted that 2_u , 1_u , 0_u^- and 0_u^+ refer to the Ω components of the $^3\Pi_u$ neutral state, and 0_g^+ and 1_g are the components of the $^3\Sigma_g^-$ neutral state.

Peak	Binding Energy (cm ⁻¹)	Relative Energy (cm ⁻¹)	Assignment neutral + e ⁻ (eKE = 0) ← anion
$a_{0,0}$	16 409	-318	$0_g^+ (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 1)$
$b_{2,0}$	16 451	-268	$2_u (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 1)$
$a_{1,0}$	16 534	-193	$1_g (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 1)$
$A_{0,0}$	16 727	0	$0_g^+ (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{2,0}$	16 785	58	$2_u (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$A_{1,0}$	16 840	113	$1_g (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
*C _{2u}		-280	$2_u (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$A_{0,1}$	17 009	282	$0_g^+ (v' = 1) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{2,1}$	17 103	376	$2_u (v' = 1) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$A_{1,1}$	17 129	402	$1_g (v' = 1) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{1,0}$	17 159	432	$1_u (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$A_{0,2}$	17 300	573	$0_g^+ (v' = 2) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
*C _{1u}		-670	$1_u (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$A_{1,2}$	17 417	690	$1_g (v' = 2) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{1,1}$	17 467	740	$1_u (v' = 1) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$A_{0,3}$	17 580	853	$0_g^+ (v' = 3) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{0-,0}$	17 641	914	$0_u^- (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$B_{0+,0}$	17 753	1026	$0_u^+ (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
*C _{0u}		-1200	$0_u^- (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
$B_{0-,1}$	17 966	1239	$0_u^- (v' = 1) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
$B_{0+,1}$	18 067	1340	$0_u^+ (v' = 1) \leftarrow ^2\Sigma_g^+ (v'' = 0)$
<hr/>			
d_0	19 734	3007	$1\Delta_g (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 1)$
	19 861	3134	?
Π_0	20 035 / 20 046	3308/3319	$1\Delta_g (v' = 0) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
D_1	20 312	3585	$1\Delta_g (v' = 1) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
D_2	20 586	3859	$1\Delta_g (v' = 2) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
D_3	20 846	4119	$1\Delta_g (v' = 3) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
e_0	21 062	4335	$1\Pi_u (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 1)$
D_4	21 119	4392	$1\Delta_g (v' = 4) \leftarrow ^2\Pi_{u,3/2} (v'' = 0)$
E_0	21 390	4664	$1\Pi_u (v' = 0) \leftarrow ^2\Sigma_g^+ (v'' = 0)$

g_1	21 552	4825	$(1) \ ^1\Sigma_o^+ (v' = 1) \leftarrow \ ^2\Pi_{u,3/2} (v'' = 1)$
*F		-4940	$\ ^1\Pi_u (v' = 0) \leftarrow \ ^2\Pi_{u,3/2} (v'' = 0)$
G_0	21 668 / 21 690	4941/4963	$(1) \ ^1\Sigma_o^+ (v' = 0) \leftarrow \ ^2\Pi_{u,3/2} (v'' = 0);$ $\ ^1\Pi_u (v' = 1) \leftarrow \ ^2\Sigma_o^+ (v'' = 0)$
g_2	21 784	5057	$(1) \ ^1\Sigma_o^+ (v' = 2) \leftarrow \ ^2\Pi_{u,3/2} (v'' = 1)$
G_1	21 872	5145	$(1) \ ^1\Sigma_o^+ (v' = 1) \leftarrow \ ^2\Pi_{u,3/2} (v'' = 0)$
E_2	21 997	5271	$\ ^1\Pi_u (v' = 2) \leftarrow \ ^2\Sigma_o^+ (v'' = 0)$

Table (8.2) Spectroscopic constants of the low-lying electronic states of Ge_2 and Ge_2^- .

State	Orbital occupancy ¹¹	T_e (cm^{-1})	ω_e (cm^{-1})	r_e (Å)	<i>ab initio</i> T_e/ω_e ¹¹
$(2)^1\Sigma_g^+$	$1\pi^4$ (51%) $2\sigma_g^2 1\pi_u^2$ (17%) $1\pi_u^2 1\pi_g^2$ (14%)	9578*	-----	-----	10840/258
$^1\Pi_u$	$2\sigma_g 1\pi_u^3$ (80%)	4943	303 ± 5	y + 0.05	5794/269
$(1)^1\Sigma_g^+$	$2\sigma_g^2 1\pi_u^2$ (63%) $1\pi^4$ (17%)	4941	204 ± 7	x + 0.045	5521/192
$1\Delta_g$	$2\sigma_g^2 1\pi_u^2$ (83%)	3308	276 ± 3	x + 0.095	3982/255
Ge_2	$^3\Pi_u$ 0_u^+	$2\sigma_g 1\pi_u^3$ (80%)	1305	y +	767/251
	0_u^-		1193	0.04	
	1_u		711 ¹⁰		
	2_u		337		
	$^3\Sigma_g^-$ 1_g	$2\sigma_g^2 1\pi_u^2$ (85%)	114	x +	0/259
	0_g			0.059	
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Ge_2^-	$^2\Sigma_g^+$	$2\sigma_g 1\pi_u^4$	279 ± 10	326 ± 10	y
	$^2\Pi_{u,3/2}$	$2\sigma_g^2 1\pi_u^3$	0	309 ± 5	x

*value obtained from 4.66 eV PES of Ge_2^- with $\pm 100 \text{ cm}^{-1}$ uncertainty

Figure (8.1) One-electron allowed transitions between the two anion and five neutral states discussed in the text. S-wave transitions are indicated by solid lines, and p-wave by dashed lines. The left-most transition indicated by (*) is that observed by Weltner [Ref. (10)] in matrix absorption studies.

Figure (8.2) Photoelectron spectra of Ge_2^- obtained using 2.98 eV photon energy at two different laser polarizations (dotted lines) and the ZEKE spectrum of Ge_2^- (solid line).

Figure (8.3) Triplet band of ZEKE spectrum of Ge_2^- (solid line, upper trace) and simulations of the two electronic transitions responsible for structure (below; lighter line indicates the $^3\Sigma_g^+ (1_g, 0_g^+) \leftarrow ^2\Pi_u (3/2)$ transitions, heavier dashed line indicates the $^3\Pi_u (0_u^\pm, 1_u, 2_u) \leftarrow ^2\Sigma_g^-$ transitions).

Figure (8.4) Singlet band of ZEKE spectrum of Ge_2^- (solid line) and spectral simulations (dotted line, see text).

Chapter 9. Study of $\text{In}_2\text{P}/\text{In}_2\text{P}^-$ and $\text{InP}_2/\text{InP}_2^-$ using negative ion zero electron kinetic energy spectroscopy

Abstract

The zero electron kinetic energy (ZEKE) spectra of In_2P^- and InP_2^- are presented and compared to their previously obtained photoelectron spectra (PES) as well as *ab initio* calculations on analogous species. The threshold spectra, which give high accuracy electron affinities of 2.400 ± 0.001 eV for In_2P and 1.617 ± 0.001 eV for InP_2 , show well-resolved vibrational structure in the transitions from the ground anion states to the various neutral states. The ZEKE spectrum of In_2P^- exhibits a fairly extended, 47 cm^{-1} progression that we assign to the symmetric bend (ν_2) in the ground $^2\text{B}_1$ neutral state. There is also a 204 cm^{-1} progression that we assign to the symmetric stretch. The InP_2^- ZEKE spectrum shows transitions to two electronic states of the neutral. For the ground state, the symmetric stretch mode is the most active in the spectrum, while in the excited state, the symmetric bend mode is most active. The InP_2 ground state symmetric stretch frequency is 190 cm^{-1} , and the excited state symmetric bend frequency is 287 cm^{-1} . An anion ground state frequency is determined to be 227 cm^{-1} . The term energy of the excited state is determined to be 1.280 ± 0.001 eV. Based on molecular orbital arguments, these frequencies suggest a $^2\text{B}_2$ ground InP_2 state, a $^2\text{A}_1$ first excited state, and a $^1\text{A}_1$ anion ground state.

I. Introduction

A considerable experimental and theoretical effort has been focused on the study of very small clusters in the hope that, by understanding the bonding in these species, insight toward the evolution of matter between the atomic and bulk scales will be gained. Clusters of pure semiconductor materials such as silicon have been of particular interest, owing to their potential technological importance. Mixed semiconductors are also important materials in circuit components as well as more exotic devices such as infrared light detectors and semiconductor injection lasers.¹ On the whole, spectroscopic investigations of pure semiconductor clusters have tended to lag behind the calculations, due to the dual requirements of size-selectivity and spectral resolution in cluster spectroscopy experiments. For instance, only recently have ground and excited state frequencies been determined for Si_n ($n = 3, 4, 6, 7$),^{2,3,4,5} while calculations have been ongoing for almost ten years.⁶

Mixed semiconductor clusters present the same experimental challenges, and are also more of a challenge from a theoretical standpoint because of the wider range of structural permutations available in a binary system. Several calculations on small GaAs, InSb, and AlP clusters^{7,8,9,10,11} have determined that multiple structural permutations possible for these species can in fact be close-lying in energy. In addition, each close-lying permutation may be congested with close-lying electronic states due to dangling bonds and, in some cases, open shells. The molecular geometries of small clusters are very different from bulk structures. Some of the compelling experimental questions regarding these small species, therefore, revolve around how the bonding in small clusters compare between clusters of similar atoms (i.e. the various III-V semiconductors) and how the bonding changes in clusters of different stoichiometries. The experimental work so far on mixed clusters leaves these questions largely unanswered. For example, while the electronic spectroscopy of several small GaAs and InP

clusters has been studied by photoelectron and photodissociation spectroscopy, vibrational frequencies have only been measured for the diatomic and some of the triatomic species.¹²

In this paper, we present zero electron kinetic energy (ZEKE) studies on In_2P^- and InP_2^- which, along with our previously obtained negative ion photoelectron spectra (PES),¹³ were in part motivated by the experimental work on small indium phosphide clusters done by Mandich and coworkers. By using resonant one-color and two-color photodissociation spectroscopy, Mandich mapped out the absorption of several clusters between 0.84 and 1.84 eV.¹⁴ One of the interesting findings of Mandich's studies was that the energy of the HOMO-LUMO gap (or, more accurately, the lowest-energy transition allowed from the ground state) for the clusters, both stoichiometric and non-stoichiometric, was very near the band gap of bulk InP, although the odd-numbered clusters in her studies exhibited stronger absorption at lower energies. The PES studies of In_xP_y^- mentioned above were complementary to Mandich's experiments; the clusters we investigated were in general smaller than those studied by Mandich, and more of the neutral states were accessed in our studies, but we observed size-dependent electronic structural trends similar to those revealed by Mandich. The only other work to date on small InP clusters is the infrared matrix isolation study by Weltner which yielded the InP diatomic frequency and the ν_3 frequency for In_2P .¹²

Both the work of Mandich and our PES data yielded some electronic structure for several mass-determined InP clusters, but no vibrational structure was resolved. The types of infrared or electronic absorption experiments that could determine vibrational frequencies are in general complicated by the presence of multiple species generated by most cluster sources. On the other hand, negative ion ZEKE spectroscopy is particularly well suited toward small cluster study, as it combines both mass selection and spectral resolution as high as $2\text{-}3\text{ cm}^{-1}$ (compared to $60\text{-}100\text{ cm}^{-1}$ for anion PES). Thus far, we have applied this technique toward the investigation of C_5^- ,¹⁵ C_6^- ,¹⁶ and Si_n^- ($n = 2, 3, \text{ and } 4$)^{4,5} and have been able to resolve the low-frequency modes and closely-spaced sequence band structure characteristic of these species.

The negative ion ZEKE spectra of In_2P^- and InP_2^- presented below show rich electronic and vibrational structure that was unresolved in the PES, yielding detailed information on both the anion and neutral species. The In_2P^- ZEKE spectrum shows transitions to vibrational levels in at least two modes of the ground state of the neutral. The InP_2^- spectrum exhibits transitions to two electronic states of the neutral: the ground state and a low-lying excited state. The ZEKE spectra are compared with the corresponding PES,¹³ as well with the calculations on the analogous In_xSb_y and Ga_xAs_y triatomics by Balasubramanian⁷ and the $\text{GaAs}_2/\text{GaAs}_2^-$ anion calculations by Meier.⁹ To aid in our analysis of InP_2^- , we have also performed our own *ab initio* calculations for frequencies and geometries at the MP2 level using an effective core potential basis set. The interesting frequency trends predicted for the two lowest-lying states of InP_2 are born out well in our spectra. While we have not performed any frequency calculations for In_2P , the vibrational structure observed in the In_2P^- spectrum is consistent with the calculated ground electronic states of Ga_2As and In_2Sb .

The ZEKE spectra strongly indicate that the anions and neutrals for both species have C_{2v} geometries. In the In_2P neutral ground state, the bonding between the phosphorous atom and the indium atoms is much stronger than the bonding between the indium atoms, which is at most very weak. The anion exhibits stronger bonding among all of the atoms. For the InP_2 neutral ground state, the bonding between the two phosphorous atoms appears to be a strong, double covalent bond, with single bonds connecting each phosphorous to the indium atom. This is in contrast to the first excited state, which has comparatively weakened P-P bonding and stronger In-P bonding. The bonding properties in the InP_2^- ground state appear to lie between the two neutral states. These observations can be explained with reference to the molecular orbitals for the valence electrons.

II. Experiment

The threshold photodetachment apparatus used in these studies has been discussed in detail elsewhere,¹⁷ but will be described briefly here. Figure (9.1) shows a schematic diagram of the apparatus employed in these experiments. A beam of cold indium phosphide cluster anions is generated in a laser vaporization/pulsed-molecular beam source similar to that developed by Smalley and coworkers.¹⁸ The surface of a rotating, translating rod of InP is vaporized using 2 to 4 mJ/pulse of the 2nd harmonic output of a Nd:YAG operated at 20 Hz repetition rate. The resulting plasma is entrained in a pulse of He carrier gas from the molecular beam into a clustering channel. The gas then expands into the source chamber, and those negative ions passing through a 2 mm skimmer are colinearly accelerated to 1 keV and mass-selected using *time-of-flight*. The cluster of interest is then selectively photodetached using a (pulsed) excimer-pumped tunable dye laser. Only the electrons detached with nearly zero kinetic energy in the anion beam frame are collected as a function of photon energy. This selective detection of threshold electrons, based on the techniques developed by Müller-Dethlefs *et al.* for photoionization of neutrals,¹⁹ gives an energy resolution of 3 cm⁻¹.

For both molecules, the spectra were first obtained using the cluster source configuration that produced the coldest Si₄⁻ spectrum;⁴ a piezoelectric molecular beam valve used in conjunction with a 0.2" long, 0.15" inner diameter clustering channel terminated with a 0.1" exit slit. This generates clusters with a vibrational temperature of approximately 200 K (higher frequency modes generally are hotter, while lower frequency modes are usually more efficiently cooled). After obtaining spectra of ions generated with the piezoelectric valve source, portions of the spectra were retaken using a new source incorporating a liquid nitrogen-cooled clustering channel. This N₂(l)-cooled source, shown in the inset of Figure (9.1), is comprised of

a Vespel piece attached to the pulsed valve, and the copper clustering channel. Laser vaporization and molecular beam entrainment occurs in the Vespel piece, which serves to thermally insulate the pulsed valve from the cold clustering channel. The clustering channel is 1.25" long with an inner bore of 0.10". A terminal exit slit on the clustering channel was also required for the most effective cooling in this source configuration; it is also made of copper, and has an inner diameter of 0.05". A 1/8" copper tube carrying liquid nitrogen is fastened directly to the outside of the channel. Even with the insulating Vespel piece, some cooling of the pulsed valve occurred. We found the General Valve solenoid-type molecular beam valve to be more reliable with this source configuration as the valve plunger tip was less sensitive to temperature than the O-ring tip used in the piezoelectric valve. By retaking a portion of the Si_4^- spectrum, we determined that the use of the cooled clustering channel further enhanced cluster cooling to a vibrational temperature of approximately 100 - 130 K.

For In_2P^- , the photodetachment cross section was unusually large, and the signal was averaged for only 800 shots/point for the 200 K spectrum and 600 shots/point for the $\text{N}_{2(l)}$ portion of the spectrum. The dyes used for the spectrum were Coumarin 503, Coumarin 480, and Coumarin 450. For In^+_{22} , the spectrum was signal averaged for 1500 shots/point for the 200K spectrum, and 800 shots/point for the $\text{N}_{2(l)}$ portion. The dyes used for InP_2^- were Rhodamine 800, LDS 722, LDS 698, Nile Blue 690, DCM, Rhodamine 640, Coumarin 440, Exalite 416, DPS and QUI.

III. Results

A. In_2P^-

Figure (9.2) shows the ZEKE spectrum of In_2P^- (solid line) plotted vs. detachment wavelength. This is superimposed onto the previously obtained PES obtained with 4.66 eV

photon energy (dotted line).¹³ For the energy scale of the PES, shown on the upper x - axis, the electron kinetic energy (eKE) is given by

$$\text{eKE} = h\nu - \text{EA} - E_{\text{int}}, \quad \text{Eqn. (9.1)}$$

where $h\nu$ is the photon energy (4.66 eV), EA is the electron affinity of the neutral cluster, and E_{int} is the internal energy (vibrational, electronic, etc.) of the final neutral state. The PES shows two bands labeled **X** and **A**, which are 0.1 to 0.15 eV wide, respectively, and spaced by 0.23 eV. These correspond to transitions to two electronic states of the In_2P : the ground state (**X**) and a low-lying state (**A**). The ZEKE spectrum in the energy region of band **X** shows extensive vibrational structure spaced by 47 cm^{-1} which was unresolved in the PES. It is also apparent from the superimposed spectra that band **A** in the PES is absent in the ZEKE spectrum.

A detailed look at the ZEKE spectrum of band **X** is shown in Figure (9.3), in which the upper trace was obtained from In_2P^- generated using the $\text{N}_{2(d)}$ -cooled channel in cluster production, and the center trace was obtained using the room temperature source. The peaks in both spectra are 8 cm^{-1} full width, half maximum (FWHM). The signal to noise is clearly better in the upper trace, the baseline is better-resolved between 510 and 515 nm, and several of the smaller peaks are less intense in the upper spectrum. All of these effects are consistent with colder ions in the upper spectrum and aid in identifying hot band transitions from vibrationally excited anions, such as the peak indicated with an asterisk (*) which is more intense in the center spectrum than in the upper spectrum.

The spectra show several vibrational progressions indicated by the combs in Figure (9.3). The characteristic spacing in each progression is $47.0 \pm 0.3 \text{ cm}^{-1}$. Peak 0 is the apparent origin of the most intense progression, labeled the $2_0^+ 1_0^0$ progression, and is the lowest energy peak originating from the anion ground vibrational state. This yields an electron affinity of $2.400 \pm 0.001 \text{ eV}$ for In_2P . Three less intense progressions, labeled $2_0^+ 1_0^n$ ($n = 1 - 3$), are found to the

blue of the 2_0^v progression, and the origins of the four progressions are spaced by $204 \pm 2 \text{ cm}^{-1}$. We are therefore observing vibrational progressions in two vibrational modes (ν_1 and ν_2) of neutral In_2P . The assignments of these modes will be discussed in detail in the next section, but for the purpose of presenting the data, the combs will serve as peak labels. There is also a peak found at 304 cm^{-1} from the most intense 2_0^2 peak indicated with an arrow ($\downarrow$). It is approximately at the right position to be the $2_0^0 1_0^2$ transition, but based on the patterns in the spectrum, it is anomalously intense. In the upper spectrum, there is a progression, labeled $2_0^v 3_1^1$, in which each peak is 27 cm^{-1} to the blue of a peak in the 2_0^v progression. The $2_0^v 3_1^1$ progression is better resolved in the upper spectrum than in the center spectrum, but the $2_0^v 3_1^1$ signal in the center spectrum overall seems to have more intensity. This structure appears to be a sequence band originating from vibrationally excited anions (with $\nu_3 = 1$) and will be discussed in detail below.

In the $\text{N}_{2(l)}$ -cooled configuration, we also scanned the laser to lower photon energy and found the low-intensity hot bands between 519 and 525 nm (approximately 300 cm^{-1} to the red of the 2_0^v progression). This group of peaks has a characteristic spacing of around one half the 47 cm^{-1} spacing of the 2_0^v progression. These features, along with the $2_0^v 3_1^1$ progression, appear to be the only progressions attributable to transitions from vibrationally excited anions.

Peak positions and relative energies for the ZEKE spectrum of In_2P^- are summarized in Table (9.1).

B. InP_2^-

The PES of InP_2^- obtained using a photon energy of 4.66 eV^{13} is shown in the bottom panel of Figure (9.4). As with In_2P , this spectrum shows transitions to two electronic states of the neutral, labeled bands **X** and **A**. The two upper panels in Figure (9.4) show the ZEKE spectra of InP_2^- plotted against detachment wavelength superimposed onto the vibrationally

resolved PES obtained using two lower photon energies; the 355 nm spectrum of band A (the higher eKE region of the 355 nm spectrum was truncated to show only band A) shows a 280 cm^{-1} progression, and the 532 nm spectrum shows a partially resolved 190 cm^{-1} progression band X. More vibrational structure appears in the upper spectra because the resolution improves with lower eKE. In contrast to the In_2P^+ spectrum, the two bands in the InP_2^+ spectrum are 0.3 eV wide and spaced by approximately 1.28 eV . ZEKE spectra are observed for both bands, although in both cases, the intensity profile of the structure in the ZEKE spectra does not appear to match the profiles of the bands observed in the PES. More detailed views of the ZEKE spectra of band X and band A are found in Figures (9.5) and (9.6), respectively. Again, spectra obtained under the two source conditions are presented, with the "colder" data presented in the upper panel, and the data acquired using the room temperature cluster source in the center panel.

1) Band X

The ZEKE spectrum of band X shown in Figure (9.5) is dominated by a $190.0 \pm 0.2\text{ cm}^{-1}$ progression, with progression members indicated on the 2_0^0 comb. Because of the extension of the progression, the origin transition will have very low intensity, and may in fact be obscured by the noise. The 2_0^0 peak corresponds to the lowest energy peak observed in this progression. We therefore take it as the origin, yielding an electron affinity for InP_2 of $1.617 \pm 0.001\text{ eV}$.

At higher photon energy, there is another, somewhat less intense progression with a characteristic spacing of 190 cm^{-1} indicated with the $1_0^1 2_0^0$ comb. In the center spectrum, the $1_0^1 2_0^4$ is the most intense member of the $1_0^1 2_0^0$ progression, peak 2_0^4 is the most intense of the 2_0^0 progression, and the two peaks are spaced by 479 cm^{-1} , suggesting a 479 cm^{-1} frequency for a second neutral (ν_1) mode. This frequency is not entirely definitive from the spectrum, since the determination of the origin of the $1_0^1 2_0^0$ progression is made ambiguous by the sequence band progression, $2_0^0 3_1^1$, which overlaps somewhat with the $1_0^1 2_0^0$ progression. Each peak in the $2_0^0 3_1^1$ progression is approximately 78 cm^{-1} to the red of a 2_0^0 transition, while the $1_0^1 2_0^0$ transitions are

approximately 92 cm^{-1} to the red of the $2_0^{v=3}$ transitions. While this difference in spacing allows us to discern unambiguously between the two progressions near the origin (where there are no $1_0^1 2_0^v$ transitions) and at higher photon energies (where the $1_0^1 2_0^v$ transitions will dominate) the first few members of the $1_0^1 2_0^v$ progression are small and overlap with the more intense part of the $2_0^{v=3,1}$ progression, giving rise to the possibility that the ν_1 frequency is actually $(479 + 190)\text{ cm}^{-1}$ or $(479 - 190)\text{ cm}^{-1}$. However, the 479 cm^{-1} frequency is supported by our *ab initio* calculations presented below.

There is another progression, the $2_1^{v=1}$ progression, displaced 37 cm^{-1} to lower photon energy from the 2_0^v progression and assigned to a hot band progression originating from the anion $\nu_2 = 1$ level. The intensity profile of this progression differs somewhat from the others in that it peaks earlier. While the intensities of the $2_1^{v=1}$ progression are not uniformly less intense in the upper spectrum than in the center spectrum, the intensities in the center spectrum appear to be complicated by the overall congestion and lack of baseline between peaks. The 2_{11}^3 , 2_1^4 , and 2_1^5 transitions, however, are less intense in the upper spectrum. Another progression, labeled $1_0^1 2_0^{v=1}$ and displaced 37 cm^{-1} to the red of the $1_0^1 2_0^v$ progression, similarly peaks earlier than the $1_0^1 2_0^v$ progression.

Peak positions and relative energies for band X are summarized in Table (9.2).

2) Band A

Band A shown in Figure (9.6) is dominated by a single progression with a $287 \pm 1\text{ cm}^{-1}$ characteristic spacing indicated by the 2_0^v comb. The origin of this progression appears to be at 428.09 nm . The energy difference between the origins of band X and band A gives a term energy of $1.280 \pm 0.001\text{ eV}$ for the excited state. While there appears to be only one active mode in the spectrum, there are two additional progressions displaced approximately 60 and 75 cm^{-1} to the blue of the 2_0^v progression; these are labeled the $2_1^{v=1}$ and $2_0^v 3_1^1$ progressions respectively, and have been assigned to transitions from singly excited anions. There are also several lower-intensity peaks apparently due to transitions from doubly excited anion vibrational

levels. The main 2_0^v progression in the ZEKE spectrum [Figure (9.6)] not only fails to span the width of band A in the PES [Figure (9.4)] but the progression members broaden noticeably for $v > 2$.

While the profile of the 2_0^v progression is clearly perturbed, it can still be seen that the relative intensities of peaks in the hot band 2_1^{v+1} progression compared to the 2_0^v peaks depend on v ; for $v = 0$ and 1, the hot band intensities are greater than the corresponding transitions from the cold ions, while for $v = 2$, the hot band has less than half the intensity of the cold transition. In contrast, the intensity distribution in the $2_0^v 3_1^1$ progression approximately follows that of the 2_0^v progression.

A summary of the peak positions and relative energies for band A can be found in Table (9.3).

3) *Ab initio* results

Previous *ab initio* calculations^{7,9} on both GaAs₂ and InSb₂ predict a 2B_2 ground state and low-lying 2A_1 excited state, and a 1A_1 ground state for GaAs₂⁻ (no calculations on InSb₂⁻ have yet been published). Using the Gaussian 92 software package,²⁰ geometry and frequency calculations at the MP2 level using the LANL2Z (Los Alamos National Laboratory double zeta) effective core potential were performed for the two isovalent neutral states of InP₂ as well as the corresponding 1A_1 InP₂⁻ anion state.

The geometries, frequencies, and normal coordinates for these states in InP₂ as determined by the MP2 calculation are shown in Figure (9.7). There are striking differences between the geometries and vibrational modes of the two neutral states. For instance, compared to the ground 2B_2 neutral state, the excited 2A_1 state has a shorter In-P bond by 0.34 Å and a 0.3 Å longer P-P bond. The dramatic differences between the vibrational frequencies are also reflected in the disparate normal coordinates, as shown in Figure (9.7). The term energy for the 2A_1 neutral state was calculated to be 1.139 eV. The 1A_1 anion ground state has

both intermediate bonding relative to the two neutral states, and, except for ν_1 , intermediate vibrational frequencies.

While our calculations are not as sophisticated as those performed by Balasubramanian⁷ and Meier,⁹ we will see that the vibrational frequencies, geometry changes, and InP_2 excited state energy are consistent with the two bands in the InP_2^- ZEKE spectrum. In assigning features in the ZEKE spectrum, it is therefore reasonable to assume that the InP_2 ground and excited states and the InP_2^- ground state are indeed the 2B_2 , 2A_1 , and 1A_1 states, respectively, with properties close to those shown in Figure (9.7). This assignment will be considered in more detail in the Discussion section.

IV. Analysis

In order to understand the vibrational structure in the ZEKE spectra, it is useful to have a reasonable idea of the likely anion and neutral geometries. Without any *a priori* knowledge about these molecules, we are unable to determine the point group of either based on the spectra alone. For $\text{In}_2\text{P}^+/\text{In}_2\text{P}$ and $\text{InP}_2^-/\text{InP}_2$, there are four possible geometries that these species can assume: C_{2v} , $D_{\infty h}$, $C_{\infty v}$, and C_s . Balasubramanian's calculations on analogous neutrals⁷ suggested that the $C_{\infty v}$ (i.e., Ga-As-As) and C_s structures are unstable with respect to rearrangement to C_{2v} structures. Our *ab initio* results on InP_2^- and InP_2 states presented in the previous section are on C_{2v} species, but as we made no attempt to establish the universal minimal anion and neutral geometries, we rely on the *ab initio* calculations by Meier *et al.*⁹ who predicted that the linear structures for the analogous GaAs_2^- and GaAs_2 were much higher in energy than the bent structures. Very acute bond angles ($<50^\circ$) are predicted for the ground states of InSb_2 , GaAs_2 and GaAs_2^- , and the low-lying excited states of InSb_2 and GaAs_2 are also predicted to be strongly bent.⁷ If the predicted trends hold for InP_2 , then one would expect

the InP_2^- ZEKE spectrum to represent transitions between C_{2v} anion and neutral structures we have calculated.

The Ga_2As and In_2Sb ground states are predicted to have an obtuse geometries with bond angles of 109.5° and 104° , respectively,⁷ but no calculations on the anions analogous to In_2P^- have been performed. However, the progressions in the ZEKE spectrum are relatively short, indicating a fairly small change in geometry between anion and neutral. Thus, if neutral In_2P is an obtuse C_{2v} structure with a bond angle in the range of 100 - 110° , then the anion most likely has an obtuse C_{2v} structure as well. On the other hand, the calculations predict low-lying linear ($D_{\infty h}$) excited states for both Ga_2As and In_2Sb , so we must consider the possibility that these are in fact the ground states and that we are observing transitions from linear or nearly linear In_2P^- and linear In_2P .

A. $\text{In}_2\text{P}^-/\text{In}_2\text{P}$

1) Band X vibrational structure and peak assignments

Given the above discussion, the geometries of both the neutral and anion can be inferred with reasonable certainty considering several points. First, the In_2P^- ZEKE spectrum exhibits a substantial amount of activation in two modes of the neutral, with the 47 cm^{-1} mode being more active than the 204 cm^{-1} mode. In electronic spectroscopy, one typically observes progressions only in totally symmetric vibrational modes. The presence of two active modes therefore argues against a linear $\leftarrow$ linear transition, as this would show significant activation in the sole totally symmetric mode with possibly a small amount of activation in double quanta of the degenerate bend and/or the antisymmetric stretch. Moreover, if the neutral were linear, spin-orbit splitting effects would be obvious in the spectra since there is at least one unpaired electron in In_2P ; no such effects are observed. From Balasubramanian's calculations, the lowest-lying linear state is a $^2\Pi_u$ state, but even if it were a $^2\Sigma$ state, the zero field splitting should be on the order of several hundred wave numbers (for In_2 , the energy splitting between

the components of the lowest-lying $^3\Sigma$ state was calculated to be on the order of 0.1 eV²¹). The overall appearance of the spectrum thus suggests a C_{2v} ground state for In_2P , consistent with the ground states predicted for isovalent Ga_2As and In_2Sb ground states. As mentioned above, this means that In_2P^- most likely has a C_{2v} geometry as well.

We now consider the modes to which the two observed frequencies correspond. The $\omega_1 = 204 \text{ cm}^{-1}$ frequency is close to the InP diatomic frequency of 257.9 cm^{-1} determined by Weltner¹² by infrared spectroscopy of InP isolated in rare-gas matrices, so it is most likely due to relative In-P motion, namely the symmetric stretch. The $\omega_2 = 47 \text{ cm}^{-1}$ frequency then must correspond to the bend vibration. The low frequency for this mode suggests it is primarily due to relative In-In motion. In fact, this frequency is considerably lower than the calculated In_2 ground state frequency,²¹ $\sim 100 \text{ cm}^{-1}$, suggesting very weak bonding between the two indium atoms in In_2P . Weltner also observed an infrared transition at 249.3 cm^{-1} which was assigned to the ν_3 antisymmetric stretch mode of In_2P . In a triatomic C_{2v} molecule with weak binding between the end atoms, the antisymmetric stretch frequency is typically higher than the symmetric stretch, so our assignment of the ν_1 mode and Weltner's assignment of the ν_3 mode appear consistent.

While it is straightforward to assign the main progressions and determine neutral vibrational frequencies for the active modes, it is more difficult to determine the anion frequencies and assign the sequence and hot band progressions. To do so, it is useful to simulate the spectrum for an assumed set of anion and neutral frequencies. This is done within the Franck-Condon approximation, where the intensity of a transition between vibrational levels v'' and v' of the anion and neutral, respectively, is assumed proportional to the Franck-Condon factors:

$$I(v' \leftarrow v'') \propto |\langle \chi' | \chi'' \rangle|. \quad \text{Eqn. (9.2)}$$

The vibrational wave functions, χ , are taken to be a product of a Morse oscillator wave function corresponding to the symmetric stretch, and two harmonic oscillator wave functions corresponding to the symmetric bend and antisymmetric stretch normal modes. The anion and neutral symmetric mode wave functions are displaced from one another along their corresponding normal coordinates until the observed peak intensities are matched. Our simulations assume that the vibrational modes in the anion and neutral are separable and parallel. These are certainly reasonable approximations since we are not trying to extract detailed geometric displacements from our analysis.

In the simulations shown as the bottom trace in Figure (9.3), the following frequencies were used: $\omega_1'' = 295 \text{ cm}^{-1}$, $\omega_1' = 207 \text{ cm}^{-1}$ ($\omega_1\chi_1' = 3 \text{ cm}^{-1}$), $T_1 = 150 \text{ K}$; $\omega_2'' = 100 \text{ cm}^{-1}$, $\omega_2' = 47 \text{ cm}^{-1}$, $T_2 = 70 \text{ K}$; $\omega_3'' = 223 \text{ cm}^{-1}$, $\omega_3' = 249.3 \text{ cm}^{-1}$ (Weltner's tentative value from matrix work¹²) $T_3 = 140 \text{ K}$. The simulation matches the experimental peak spacings quite well (the peak indicated with the arrow has not been fit in the simulation). The peak assignments indicated on the combs in Figure (9.3) were determined by this simulation, where ν corresponds to ν_2' . Most of the structure observed in the spectrum are attributed to transitions from vibrationally cold anions. The individual peak assignments are listed explicitly in Table (9.1).

Since there were relatively few intense peaks originating from vibrationally excited anion levels, choosing the anion frequencies for the simulation and assigning the hot band and sequence band structure was not straightforward. The anion symmetric stretch frequency ($\omega_1'' = 295 \text{ cm}^{-1}$) was chosen such that the hot band positions between 519 to 525 nm could be reasonably matched, treating them as the $2_0^0 1_1^0$ hot band progression. It is not a uniquely determined frequency, as the spectrum could have been fit satisfactorily using 270 or 317 cm^{-1} (i.e., displaced by $\pm$ one half of a bend quantum) for ω_1'' . Overall, however, this is the most reasonable assignment for these transitions. The frequency of 295 cm^{-1} is too high for these transitions to originate from the $\nu_2'' = 1$ anion level, and transitions of the type $2_0^0 3_1^0$ are not allowed because the ν_3 mode is not totally symmetric.

We next consider the progression assigned as the $2_0^v 3_1^1$ sequence band progression. This progression is displaced 27 cm^{-1} to the blue of the 2_0^v progression, indicating that the anion frequency in the mode responsible for this structure is 27 cm^{-1} less than the neutral frequency, so our assignment implies that $\omega_3'' - \omega_3' = -27\text{ cm}^{-1}$. Using Weltner's value for ω_3' yields $\omega_3'' = 223\text{ cm}^{-1}$. This number is uncertain, however, because the origin of the $2_0^v 3_1^1$ progression is difficult to pinpoint. If, for example, the true origin is 20 cm^{-1} to the red of the 2_0^v progression instead of 27 cm^{-1} to the blue, this would mean that $\omega_3'' - \omega_3' = 20\text{ cm}^{-1}$ and that $\omega_3'' = 269\text{ cm}^{-1}$. We prefer the lower value but acknowledge it may be incorrect.

The alternate assignment of this progression as the 2_1^{v+1} hot band progression was rejected for the following reason. We found that the profile of the 2_0^v progression was best fit assuming a much greater anion ω_2'' frequency than the 47 cm^{-1} neutral frequency. When we attempted to fit the spectrum assuming comparable frequencies, the simulated progression was considerably more extended than the observed spectrum. For example, the normal coordinate displacement could be adjusted until the simulated 2_0^2 peak was the most intense of the 2_0^v progression, as in the spectrum, but the simulated 2_0^1 and 2_0^3 transitions were much more intense relative to the 2_0^2 transition than what is observed. However, using a much greater anion frequency, i.e. a narrower anion bend potential, the anion wave function is more localized, causing it to have good overlap with fewer neutral wave functions. This yields a narrower progression. The anion frequency in the simulation had to be at least 100 cm^{-1} in order to reproduce the experimental intensity distribution, implying considerably stronger bonding between the indium atoms.

Given this, it seems surprising that there is no obvious hot band structure that we can attribute to ν_2 . However, we found that when the anion symmetric bend frequency was chosen to be a near multiple of the neutral frequency, such as 100 cm^{-1} , the simulation would show no distinct sequence or hot bands in ν_2 (except for possibly the peak indicated with the asterisk, which is fit as a 2_1^1 sequence band in the fit presented). The 100 cm^{-1} anion ν_2 frequency we

chose for the presented spectrum cannot be considered definitive; the spectral profile could also be fit satisfactorily assuming $\omega_2'' = 150 \text{ cm}^{-1}$.

Our overall assignments thus indicate that the symmetric stretch and bend frequencies are higher in the anion than the neutral, with the biggest change occurring in the ν_2 mode. If our assignments are correct, they imply considerably stronger bonding between the two indium atoms in the anion as compared to the neutral. In the Discussion section it will be shown that this is consistent with the expected anion and neutral molecular orbital occupancies.

2) Approximation of the geometry differences between the anion and neutral

Since we do not know the exact form of the normal coordinates or the geometries for either the anion or the neutral, we cannot quantitatively determine the geometry differences between them. We can, however, obtain an estimate of the change in In-In bond distance between the anion and neutral, assuming the ν_2 mode is primarily an In-In relative motion, which seems likely given the low frequency. The 2_0^+ progression was fit using an In diatomic, with a neutral frequency of 47 cm^{-1} and an anion frequency of 100 cm^{-1} , and an absolute bond length difference of approximately $0.2 \text{ \AA}$ (the In-In distance is presumably smaller in the anion). This is a small change, considering that the calculated In-In bond distance in In_2Sb is $4.6 \text{ \AA}$. Assuming an In-P bond distance $0.1 \text{ \AA}$ greater than the bulk bond distance of $2.54 \text{ \AA}$ (the In-Sb bond distance in In_2Sb is calculated to be approximately $0.1 \text{ \AA}$ greater than the bulk bond distance) and a neutral In-In bond distance of $4.6 \text{ \AA}$, this corresponds to a bond angle change from 112° in the anion to 120° in the neutral. This is, however, a crude approximation, and should be treated with appropriate caution.

B. $\text{InP}_2^-/\text{InP}_2$

Based on the discussion at the beginning of this section, we expect InP_2^- and InP_2 to have C_{2v} symmetry. Therefore, we will only discuss the InP_2^- ZEKE spectrum in terms of $C_{2v} \leftarrow$

C_{2v} transitions. Both bands in the InP_2^- spectrum are much more congested and complicated than band X in the In_2P^- spectrum, and spectral simulations of both bands X and A in the InP_2^- spectrum have proven unsatisfactory since the intensity profiles of both bands appear anomalous. Nonetheless, the simulations have aided in sorting through the numerous sequence bands and combination bands observed in the spectra, and will now be discussed in some detail.

1) Band X vibrational structure and peak assignments

As discussed in the results section, one can extract two vibrational frequencies for the X state of neutral InP_2 from the ZEKE spectrum in Figure (9.5): $\omega_1' = 478 \text{ cm}^{-1}$ and $\omega_2' = 190 \text{ cm}^{-1}$. The frequency for the ν_2 mode is comparable to the In-P symmetric stretch frequency in In_2P (204 cm^{-1}) and the diatomic InP frequency (253 cm^{-1}) and is in good agreement with the calculated 182 cm^{-1} ν_2 value for the $^2\text{B}_2$ neutral state (Sec. III.B). It is therefore reasonable to assign the ν_2 mode to the InP_2 symmetric stretch and to expect this mode to consist primarily of In-P relative motion, as is consistent with the calculated normal coordinate for this mode. The ν_1 frequency, higher than but comparable to the calculated ν_1 frequency, is approximately two thirds of the P_2 triple-bonded ground state ($^1\Sigma_g^+$) frequency, 780 cm^{-1} , suggesting that this mode consists primarily of P-P relative motion between two doubly bonded phosphorous atoms. The frequencies therefore suggest a bonding scheme in which the indium atom is singly bonded to each P atom, and this costs one bond between the two P atoms. This is also consistent with the calculated geometry for the $^2\text{B}_2$ ground neutral state, in which the P-P bond distance, $2.16 \text{ \AA}$, is slightly longer than the P_2 ground state ($^1\Sigma_g^+$) bond distance, $1.89 \text{ \AA}$, but is comparable to the bond distance of the P_2 first excited state ($^1\Sigma_u^+$), $2.12 \text{ \AA}$.

Band X of the InP_2^- ZEKE spectrum was simulated using Eqn. (9.2) with the above values for ω_1' and ω_2' ; the remaining anion and neutral frequencies are discussed below. The simulation, shown in the bottom panel of Figure (9.5), appears to reasonably fits the main

features of band X in the center panel, namely the 2_0^v and $1_0^1 2_0^v$ progressions. The simulation also includes the $1_0^2 2_0^v$ progression, not labeled in Figure (9.5), which overlaps the higher energy peaks in the 2_0^v progression. The ν_2 mode clearly shows the most activity, suggesting that the biggest geometry change between the anion and neutral is in the In-P bond length.

The simulations also helped identify two hot band progressions, the 2_1^{v+1} and $1_0^1 2_1^{v+1}$ progressions, and the $2_0^v 3_1^1$ sequence band progression. This assignment of the two hot band progressions yields $\omega_2'' = 227 \text{ cm}^{-1}$ for the anion, which is in qualitative agreement with the calculated value, 192 cm^{-1} . Based on this, the origin of the 2_1^{v+1} progression, namely the 2_1^0 transition, should appear 227 cm^{-1} to lower photon energy of the 2_0^v origin. However, we found that when we scanned to lower photon energy (under the $\text{N}_2(\lambda)$ -cooled source conditions) the S/N in this energy region was such that no additional structure was observed. The 2_1^{v+1} assignment is based on the intensity distribution of the 2_1^{v+1} progression, which differs from the main 2_0^v progression in that it peaks earlier (at $v = 3$) and dies off much more rapidly. Such a difference is expected for a hot band because there is a node in the $\nu_2'' = 1$ wave function where the $\nu_2'' = 0$ wave function is a maximum. Hence the Franck-Condon factors for the two anion levels are quite different. In principle, the intensity distribution in an extended hot band progression should be bimodal. This is seen in the simulated progressions, in which the intensity distribution peaks on both sides of the minimum at $\nu_2' \approx 5$. However, the experimental progression does not rise again at higher ν_2' ; this may be related to the whole progression dying out at lower energy than is observed in the PES [see Figure (9.4)], or to the various approximations in our Franck-Condon analysis.

The remaining sequence band progression was assigned to the $2_0^v 3_1^1$ progression rather than the $2_0^v 1_1^1$ progression based on the results of the *ab initio* frequency calculations (Sec. III.B). The calculations predict that the anion ν_3 frequency is on the order of 200 cm^{-1} lower than the ν_1 frequency. This means that the anion $\nu_3 = 1$ level should be more populated than the $\nu_1 = 1$ level, so the sequence band in the ν_3 mode should be more intense. Since the $2_0^v 3_1^1$

progression is displaced 75 cm⁻¹ to the red of the 2₀^v progression, we have $\omega_3'' - \omega_3' = 75 \text{ cm}^{-1}$, which is in qualitative agreement with the calculated difference, 126 cm⁻¹.

2) Band A vibrational structure and peak assignments

By comparing the spectra of band A obtained under different source conditions [top and middle panels of Figure (9.6)], there appears to be only one progression originating from the anion ground state with a peak spacing of 287 cm⁻¹. The neutral vibrational mode associated with this progression cannot be determined based on comparison with the *ab initio* frequencies calculated for the 2A₁ excited state, as 287 cm⁻¹ is equally close to both of the calculated symmetric frequencies [see Figure (9.7)]. However, the relative geometries calculated for the anion and the 2A₁ neutral state suggest that the ν_2 bend, in which the P-P bond elongates while the In-P bond contracts (and vice versa), should be more active than the ν_1 stretch, in which both bonds elongate (or contract). Therefore, the progression has been assigned to 2₀^v transitions, with $\omega_2' = 287 \text{ cm}^{-1}$. It is also interesting to note from Figure (9.7) that in the ground state, ν_1 is primarily a P-P stretch and ν_2 an In-P stretch, while in the 2A₁ state, ν_1 and ν_2 are better described as the symmetric stretch and bend, respectively, and both modes involve the relative motion of all three atoms.

The Franck-Condon simulation in Figure (9.6) shows that one can account for most of the structure in addition to the main progression with two more progressions, the 2₁^{v+1} hot band progression and the 2₀^v3₁¹ sequence band. Explicit peak assignments are listed in Table (9.3). The 2₁^{v+1} progression was fit assuming $\omega_2'' = 227 \text{ cm}^{-1}$ in the anion, the same value found for the 2₁^{v+1} progression in band X. As in band X, the intensity distribution peaks earlier for 2₁^{v+1} progression than for the 2₀^v progression. The 2₀^v3₁¹ sequence bands were so assigned by the same arguments given in the previous section, namely that *ab initio* calculations predict $\omega_1'' > \omega_3''$ for the anion, in which case $\omega_3'' - \omega_3' = -75 \text{ cm}^{-1}$ (the calculated difference is -99 cm⁻¹). Note

this is opposite in sign to $\omega_3'' - \omega_3'$ in band X. In the simulation, the remaining, lower-intensity peaks were fit by the $2_0^v 3_2^2$, $2_1^{v+1} 3_1^1$ and 2_2^{v+2} transitions.

The 287 cm^{-1} ν_2 frequency for this excited state is substantially higher than the 190 cm^{-1} frequency observed for the ground state, suggesting that there is more phosphorous relative motion involved in the excited state ν_2 mode. Based on this, we can infer that the P-P bonding is weaker and the In-P bonding is stronger in this first excited state. This is supported by the calculated geometries for the two neutral states. The 227 cm^{-1} anion ν_2 frequency fits in nicely as having intermediate bonding properties between the two neutral states, suggestive of the orbital occupancies the anion has in common with the two neutral states. The molecular orbital configurations for the anion and two neutral states will be discussed in the following section.

A notable feature of band A is that the peaks in the main progression broaden somewhat for $\nu_2' \geq 3$, suggesting there is a perturbation affecting the neutral state that turns on between peaks 2_0^2 and 2_0^3 . This perturbation is clearly different in nature than the intensity fall-off compared to the photoelectron spectrum that occurs in band X, in which the higher-energy peaks maintained narrow peak widths, and the signal to noise remained quite good. One possibility is that the peak broadening is from dissociation to $\text{In} + \text{P}_2$. The dissociation energy for $\text{InSb}_2 \rightarrow \text{In} + \text{Sb}_2$ is calculated to be only 1.3 eV.⁷ Since T_e for the InP_2 first excited state is 1.280 eV, it is certainly feasible that at least part of band A lies above the dissociation continuum, thereby causing the broadening of peaks at the higher energy end of the band. The ν_2 normal coordinate would appear to facilitate dissociation; a displacement negative of the coordinate shown in Figure (9.7) gives closer phosphorous atoms combined with a longer In-P distance. Assuming that dissociation is occurring, from the position of peak 2_0^3 , which is slightly wider than 2_0^2 , the dissociation energy of InP_2 lies between 1.352 and 1.386 eV.

Another explanation for the peak broadening is suggested by Balasubramanian's calculations on InSb_2 , which predict that the potential energy curves for the first excited (2A_1)

state and ground 2B_2 state cross just above the 2A_1 minimum. These states interact strongly via spin-orbit coupling. If there is a similar curve crossing in InP_2 , one might expect the energy levels of the excited state that lie above the intersection point to be badly perturbed, possibly leading to the broadening seen in band A of our spectrum.

V. Discussion

A. $\text{In}_2\text{P}^+/\text{In}_2\text{P}$ electronic state assignments

From the vibrational analysis of the In_2P^+ ZEKE spectrum, we concluded that the anion bend frequency is higher than the neutral bend frequency, implying that the In-In bond is stronger in the anion than the neutral. Moreover, given the low frequency of the bend mode in In_2P ($\omega_2' \approx 47 \text{ cm}^{-1}$), the 2_0^v progressions in the ZEKE spectrum are quite short, indicating a relatively small displacement along the v_2 normal coordinate between the anion and neutral. One would like to understand these results in terms of the molecular orbital configurations of In_2P and In_2P^+ . While no *ab initio* calculations have been performed on either species, Balasubramanian has determined the dominant molecular orbital configurations for the isovalent neutral In_2Sb and Ga_2As ,⁷ and these serve as a starting point for our discussion.

The ground electronic states of In_2Sb and Ga_2As were calculated to have C_{2v} geometries with a 2B_1 electronic character from the following valence orbital occupancy:

$$1a_1^2 2a_1^2 1b_2^2 2b_2^2 3a_1^2 1b_1^1 (4a_1^0). \quad \text{Eqn. (9.3)}$$

Qualitative pictures of these orbitals are shown in Figure (9.8); these are adapted from the description by Balasubramanian and the pictures of Meier *et al.*⁹ Note that the half-filled $1b_1$ orbital is an out-of-plane orbital with most of its amplitude on the two end atoms. Although

vibrational frequencies were not determined for In_2Sb or Ga_2As , potential energy curves were calculated for the ground and low-lying excited states as a function of bend angle.⁷ The equilibrium bend angles for In_2Sb and Ga_2As were found to be 104° and 109.5° , respectively, and both species calculated to have very broad bend potentials, with fairly weak bonding between the two Group III atoms. This is qualitatively consistent with the low bending frequency seen for the In_2P ground state, and it seems reasonable that the ground state of In_2P is also a $^2\text{B}_1$ state with the valence configuration of Eqn. (9.3).

The anion electronic orbital occupancy may be determined by adding an electron either to the $1b_1$ orbital, resulting in a $^1\text{A}_1$ state, or possibly the $4a_1$ orbital, giving a $^3\text{B}_1$ state. Both of these orbitals are bonding between the two atoms, so in either case one would expect the anion to be more bent and to have a higher bend frequency than the neutral. The $1b_1$ orbital should be less strongly bonding between the In atoms than the $4a_1$ orbital which, given the relatively small geometry change suggested by the short 2_0^+ progression, may favor the $^1\text{A}_1$ state for the anion. This is consistent with Balasubramanian's calculations on the excited states of neutral In_2Sb which predict that states formed by promoting an electron from the $3a_1$ or $2b_2$ orbitals to the $1b_1$ orbital are lower in energy than the quartet states formed by promoting the same electrons to the $4a_1$ orbital. However, that the anion ν_2 frequency is substantially greater than the neutral might suggest the $^3\text{B}_1$ state. We hesitate to make a definite anion state assignment lacking more definitive anion frequencies, especially for the ν_2 mode.

Band A (or lack thereof) Given that In_2P^- is more bent than the neutral ground state, and that in the In_2P^- photoelectron spectrum, the widths of bands X and A are similar, the most likely candidate for the neutral excited state responsible for band A is the $^2\text{B}_2$ state; the $^2\text{B}_2$ state in In_2Sb is predicted to have a bend angle of 80° vs. 104° for the $^2\text{B}_1$ ground state.⁷ A low-lying linear ($^2\Pi_u$) state of In_2Sb is also predicted, but the photodetachment transition to this state should be much more extended than band A due to the large change in bend angle between anion and neutral, so it is a less likely candidate for the upper state in band A.

It still remains unexplained why band A is not present in the ZEKE spectrum. The selection rules for negative ion threshold photodetachment are more restrictive than for PES, due to the Wigner threshold law. For atomic systems, this dictates that the detachment cross section near threshold goes as:²²

$$\sigma \propto \sigma_0 (E_{\text{hv}} - E_{\text{threshold}})^{\ell+1/2}, \quad \text{Eqn. (9.4)}$$

where $(E_{\text{hv}} - E_{\text{threshold}})$ is the energy above threshold (i.e., the kinetic energy of the detached electron) and ℓ is the angular momentum of the ejected electron. The result is that only electrons with $\ell = 0$ (s-wave) have a sharply rising cross section near threshold, a necessary condition to observe a ZEKE transition. This has been applied to polyatomic anions by Reed *et al.*,²³ who point out that only electrons from MO's with the same transformation properties as the x, y, or z body-fixed coordinates can undergo s-wave detachment. In a C_{2v} molecule, all orbitals except those with a_2 symmetry can detach with $\ell = 0$. Hence, from the discussion in the previous section, s-wave detachment is allowed for any one-electron photodetachment transition from a $1\Delta_1$ anion involving the valence orbitals. This would be true if the anion were a $3B_1$ state as well [see Eqn. (9.3)]. In either case one would expect band A in the In_2P^- photoelectron spectrum to appear in the ZEKE spectrum as well.

However, as was pointed out by Reed, the selection rule for s-wave detachment is a necessary but not sufficient condition a sharply rising cross section near threshold. Indeed, our work on Si_3^- showed that several bands in the photoelectron spectrum in which s-wave detachment was allowed did not appear in the ZEKE spectrum.⁴ An important factor here is how much the orbital from which detachment occurs resembles an atomic p-orbital. Of all the orbitals in Figure (9.8), the $1b_1$ appears to have the most atomic p-character, so removal of an electron from this orbital should result in a strong ZEKE signal. In fact, band X gives the most intense ZEKE signal for any molecular anion we have studied thus far, consistent with its

assignment as a ${}^2B_1 \leftarrow {}^1A_1$ (neutral $\leftarrow$ anion) transition. However, it is far from clear that the $1b_2$ orbital deviates from an atomic p-orbital to a sufficient extent that we could not observe ZEKE signal for the transition to the 2B_2 excited state. The determination of conditions sufficient for strong s-wave photodetachment is an interesting and important question for future study as it determines the range of applicability of anion ZEKE spectroscopy.

B. $\text{InP}_2^-/\text{InP}_2$ electronic states

The experimental anion and neutral vibrational frequencies for InP_2 and InP_2^- are, in general, consistent with the calculated properties of the anion and two neutral states shown in Figure (9.7), supporting our identification of the experimentally observed states with the three calculated states. In this section, we compare the properties of these states to the calculated properties of the analogous ground 2B_2 and excited 2A_1 states of GaAs_2 and InSb_2 .^{7,9} as well as the ground 1A_1 state of GaAs_2 .⁹ The calculations on these InP_2 analogs were considerably more sophisticated and complete than our calculations on In_2P and In_2P^- (although no vibrational frequencies were determined in the earlier studies), so they provide a useful framework for understanding the chemical bonding in In_2P and In_2P^- .

The ground 2B_2 electronic state orbital occupancy of InP_2 , GaAs_2 and InSb_2 is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2 2b_1^1 (1a_2^0). \quad \text{Eqn. (9.5)}$$

Two close-lying neutral states, the 2A_1 and 2B_1 states (with calculated T_e 's of 0.67 eV and 1.38 eV, respectively, for InSb_2) are formed by promoting a $4a_1$ and a $1b_1$ electron, respectively, into the $2b_2$ orbital. The ground and first excited electronic orbital occupancies here are those used in the *ab initio* geometry and frequency calculations described in Sec. III.B for InP_2 [Figure (9.7)]. The anion 1A_1 ground state is formed by adding an electron to the $2b_2$ orbital of the 2B_2 state.

The 3B_1 state with unpaired electrons in both the $2b_2$ and $1a_2$ orbitals was found to lie only 0.5 eV higher in energy for $GaAs_2^-$.⁹

Figure (9.7) shows that, compared to the InP_2 2B_2 ground state, the P-P bond distance is longer in the anion and the In-P bond distance is shorter. This reflects the effect the additional electron in the $2b_2$ orbital, which is antibonding between the two phosphorous atoms but bonding between the indium and phosphorous atoms [see Figure (9.8)]. Figure (9.7) shows that the 2A_1 neutral state has a wider bond angle and shorter In-P distance than the neutral ground state; this is consistent with having two electrons in the $2b_2$ orbital but only one in the strongly P-P bonding $4a_1$ orbital.

Our calculated energy separation for the 2B_2 and 2A_1 states of In_2P is 1.139 eV, which is quite close to the observed energy, 1.280 eV. This is approximately twice the calculated term energy for the analogous $GaAs_2$ and $InSb_2$ 2A_1 states.^{7,9} The large difference can be understood by considering how the $2b_2$ and $4a_1$ orbitals correlate to the P_2 diatomic and In atomic orbitals. The $4a_1$ orbital is formed from the $2\pi_u + 5p$ orbitals, while the $2b_2$ orbital correlates to the $2\pi_g + 5p$ orbitals. The energy difference between the $2\pi_u$ and π_g orbitals in P_2 is greater than for As_2 or Sb_2 ,²⁴ causing the $4a_1 - 2b_2$ splitting to be greater in InP_2 than for $GaAs_2$ or $InSb_2$.

An interesting issue in these clusters is the degree of covalent vs. ionic bonding. In bulk InP, the bonding is largely ionic, with excess negative charge on the P atoms. However, there are no P-P bonds in crystalline InP, whereas there is strong P-P bonding in InP_2 , suggesting a covalent bonding picture. On the other hand, Balasubramanian calculated the dipole moments associated with the various electronic states and structural isomers of the GaAs and InSb mixed triatomics.⁷ Dipoles of 1.22 D and 1.64 D were determined for the 2B_2 C_{2v} states of $GaAs_2$ and $InSb_2$, respectively. As the difference in electronegativity between In and P is greater than for Ga and As, or In and Sb, it would follow that the dipole of the 2B_2 state of InP_2 is greater than for $GaAs_2$ or $InSb_2$. This is confirmed by our ab initio calculations, which gave 3.6 D for the 2B_2

state, and 3.55 for the 2A_1 state. Therefore, in spite of the substantial amount of covalent bonding between the two phosphorous atoms in this molecule, the dipole suggests that there is still ionic character along the In-P bond. It is not surprising that the two partially negative phosphorous moieties are so strongly bound in the ground InP_2 state, as P_2^- has been found to be strongly bound ($D_0 = 4.88$ eV) with a bond distance of 1.98 Å,²⁵ which is only 0.09 Å longer than the neutral bond distance.

VI. Conclusions

The ZEKE spectra of the two InP triatomics have shown that these very small clusters are remarkably complex. The two triatomics we have investigated are very different from one another. While both having C_{2v} geometries, the In_2P ground state has very weak In-In bonding, an obtuse bond angle, and a very broad potential, in contrast to the InP_2 ground state, which has very strong P-P bonding, an acute bond angle, and a fairly steep bend potential. The geometry differences between the anions and neutrals seems to be much more dramatic for InP_2 than for In_2P .

The In_2P^- ZEKE spectrum shows progressions in both the 47 cm^{-1} symmetric bend (ν_2) and the 204 cm^{-1} symmetric stretch (ν_1) of the C_{2v} , 2B_1 neutral ground state. From the profile of the progressions and the limited sequence and hot band structure, we can infer that all modes of the anion have higher frequencies than the neutral, which is consistent with the anion having the extra electron in the $1b_1$ orbital. The transition to what we believe is the 2B_2 state observed in the previously obtained PES is not observed in the ZEKE spectrum.

Based on trends in ν_2 frequencies between the two neutral states and the anion, the ground state of InP_2 is determined to have 2B_2 and a 2A_1 first excited electronic state at 1.280 eV above the ground state. This is analogous with the calculated ground and first excited states for InSb_2 and GaAs_2 where the 2B_2 ground state and the 2A_1 first excited state are separated by

less than 1 eV. The anion ground state has appears to be the 1A_1 state. The 2B_2 ground state of InP_2 exhibits much stronger P-P bonding and weaker In-P bonding relative to the first excited 2A_1 state, and the anion has bonding properties intermediate of the two neutral states. It is clear from our analysis of the spectra, which was supported by our *ab initio* calculations, that while the electronic states of this small cluster are fairly close-lying, the vibrational properties are dramatically influenced by simply shifting an electron from the $4a_1$ orbital to the $2b_2$ orbital.

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Table (9.1) Peak positions and assignments for the In_2P^- ZEKE spectrum.

Peak Position (nm)	Energy from origin (cm^{-1})	Assignment ($\nu_1'\nu_2'\nu_3' \leftarrow \nu_1''\nu_2''\nu_3''$)
524.45	-291	
523.85	-269	
523.36	-251	
522.63	-225	
521.97	-200	
521.28	-175	
520.77	-156	
520.09	-131	
519.43	-107	
517.76	-45	010 $\leftarrow$ 010
516.57	0	Origin; EA = 2.400 eV
515.85	27	011 $\leftarrow$ 001
515.34	46	010 $\leftarrow$ 000
514.15	91	020 $\leftarrow$ 000
513.46	118	031 $\leftarrow$ 001
512.90	139	030 $\leftarrow$ 000
512.15	168	041 $\leftarrow$ 001
511.65	187	040 $\leftarrow$ 000
511.26	201	100 $\leftarrow$ 000
510.39	235	050 $\leftarrow$ 000
510.00	250	110 $\leftarrow$ 000
509.25	279	060 $\leftarrow$ 000;121 $\leftarrow$ 001
508.81	296	120 $\leftarrow$ 000
507.63	341	130 $\leftarrow$ 000
506.50	385	140 $\leftarrow$ 000
506.25	395	
505.03	443	
504.48	464	
503.97	485	220 $\leftarrow$ 000
502.82	530	230 $\leftarrow$ 000
501.73	573	240 $\leftarrow$ 000
500.17	635	310 $\leftarrow$ 000

Table (9.2) Peak positions and assignments for band X in the InP_2^- ZEKE spectrum.

Peak Position (nm)	Relative energy (cm^{-1})	Assignment ($\nu_1'\nu_2'\nu_3' \leftarrow \nu_1''\nu_2''\nu_3''$)
771.35	-78	020 $\leftarrow$ 020
769.25	-42	010 $\leftarrow$ 010
766.76	0	origin; EA = 1.617 eV
759.98	116	030 $\leftarrow$ 020; 011 $\leftarrow$ 001
757.68	156	020 $\leftarrow$ 010
755.94	187	010 $\leftarrow$ 000
749.41	302	021 $\leftarrow$ 001; 040 $\leftarrow$ 020
746.96	346	030 $\leftarrow$ 010
745.23	377	020 $\leftarrow$ 000
741.10	451	041 $\leftarrow$ 011
739.06	489	031 $\leftarrow$ 001
736.59	534	040 $\leftarrow$ 010
734.50	573	030 $\leftarrow$ 000
733.3	595	
729.0	675	041 $\leftarrow$ 001
726.3	726	050 $\leftarrow$ 010
724.4	763	040 $\leftarrow$ 000
721.6	816	051 $\leftarrow$ 001; 130 $\leftarrow$ 010
719.2	862	051 $\leftarrow$ 001; 120 $\leftarrow$ 000
716.7	911	060 $\leftarrow$ 010
714.6	952	050 $\leftarrow$ 000
711.6	1011	140 $\leftarrow$ 010
709.8	1046	130 $\leftarrow$ 000
707.1	1100	070 $\leftarrow$ 010
705.1	1140	060 $\leftarrow$ 000
702.1	1201	150 $\leftarrow$ 010
700.2	1240	140 $\leftarrow$ 000
695.80	1330	070 $\leftarrow$ 000
690.00	1451	150 $\leftarrow$ 000
686.70	1520	080 $\leftarrow$ 000
682.10	1619	160 $\leftarrow$ 000
678.11	1705	090 $\leftarrow$ 000; 240 $\leftarrow$ 000
673.56	1804	170 $\leftarrow$ 000
669.37	1897	0 10 0 $\leftarrow$ 000; 250 $\leftarrow$ 000
665.07	1994	180 $\leftarrow$ 000
660.94	2088	0 11 0 $\leftarrow$ 000
656.97	2179	190 $\leftarrow$ 000
652.65	2281	0 12 0 $\leftarrow$ 000
649.0	2366	1 10 0 $\leftarrow$ 000
645.0	2462	0 13 0 $\leftarrow$ 000
641.0	2559	1 11 0 $\leftarrow$ 000
637.0	2657	0 14 0 $\leftarrow$ 000
633.4	2746	1 12 0 $\leftarrow$ 000
629	2856	0 15 0 $\leftarrow$ 000

Table (9.3) Peak positions and assignments for band A in the InP_2^- ZEKE spectrum.

Position (nm)	Relative Energy (cm^{-1})	Assignment ($\nu_1'\nu_2'\nu_3' \leftarrow \nu_1''\nu_2''\nu_3''$)
435.21	-386	
432.20	-226	000 $\leftarrow$ 010
431.00	-161	010 $\leftarrow$ 020
429.84	-99	020 $\leftarrow$ 030
429.49	-80	
428.03	0	origin; $T_e = 1.280$ eV
426.86	64	010 $\leftarrow$ 010
425.86	119	020 $\leftarrow$ 020
425.73	126	
425.49	139	
424.32	204	030 $\leftarrow$ 030
422.79	289	010 $\leftarrow$ 000
421.74	348	020 $\leftarrow$ 010
420.42	423	030 $\leftarrow$ 020
420.14	439	021 $\leftarrow$ 011
419.10	498	040 $\leftarrow$ 030; 031 $\leftarrow$ 021; 022 $\leftarrow$ 011, etc.
417.71	577	020 $\leftarrow$ 000
416.72	634	030 $\leftarrow$ 001
416.37	654	021 $\leftarrow$ 001
415.42	709	040 $\leftarrow$ 020; 031 $\leftarrow$ 011; 022 $\leftarrow$ 002
414.03	790	050 $\leftarrow$ 030; 041 $\leftarrow$ 021; etc.
412.80	862	030 $\leftarrow$ 000
411.62	931	031 $\leftarrow$ 001
410.54	995	050 $\leftarrow$ 020; 041 $\leftarrow$ 011, etc.
408.08	1142	040 $\leftarrow$ 000
403.45	1423	050 $\leftarrow$ 000
399.15	1690	060 $\leftarrow$ 000
394.91	1959	070 $\leftarrow$ 000
390.51	2245	080 $\leftarrow$ 000

Figure (9.1) Threshold photodetachment apparatus. The inset shows a detail of the cluster source in which the InP rod translates and rotates in a slot (1) and is intersected by pulses from the molecular beam (2) and Nd:YAG laser (3) in a Vespel piece (4). The copper clustering channel (5) is cooled by a copper tube carrying N_2 (6).

Figure (9.2) ZEKE spectrum (solid line) superimposed onto the 266 nm (4.66 eV) photoelectron spectrum (dotted line) of In_2P^+ .

Figure (9.3) ZEKE spectrum of In_2P^+ . The upper trace shows data taken using ions generated with the liquid nitrogen-cooled clustering channel, and the center trace with the piezoelectric valve source. The bottom trace is a spectral simulation (see text).

Figure (9.4) Bottom panel: 266 nm (4.66 eV) photoelectron spectrum of InP_2^- . Upper left: ZEKE spectrum of InP_2^- , band A, superimposed onto the 355 nm (3.49 eV) photoelectron spectrum. Upper right: ZEKE spectrum of InP_2^- , band X, superimposed onto the 532 nm (2.33 eV) photoelectron spectrum.

Figure (9.5) ZEKE spectrum of InP_2^- to the neutral ground state (band X) obtained under liquid nitrogen-cooled source conditions (upper panel) and ambient source conditions (middle panel). The Franck-Condon simulation is shown in the bottom panel.

Figure (9.6) ZEKE spectrum of InP_2^- to the first excited neutral state (band A) obtained under liquid nitrogen-cooled source conditions (upper panel) and ambient source conditions (middle panel), and the Franck-Condon simulation (bottom panel).

Figure (9.7) Geometries and normal coordinates of $\text{InP}_2/\text{InP}_2^-$ from MP2/LANL1DZ calculations.

InP_2 $^2\text{B}_2$ ground state:

InP_2 $^2\text{A}_1$ first excited state:

InP_2^- $^1\text{A}_1$ anion ground state:

Figure (9.8) Qualitative representations of the high-lying molecular orbitals of In_2P and InP_2 .

Chapter 10. Study of small gallium arsenide clusters using negative ion photodetachment techniques

Abstract

The electronically resolved anion photoelectron spectra (PES) of Ga_xAs_y^- ($x = 1, 2$; $y = 1, 2, 3$) and the vibrationally-resolved PES of the GaAs diatomic are presented along with the anion zero electron kinetic energy (ZEKE) spectrum of Ga_2As^- . The PES of Ga_xAs_y^- , which show transitions to the ground and low-lying excited states of the neutral clusters, reveal the electronic similarity with the analogous In_xP_y clusters. The higher-resolution PES of GaAs^- shows transitions originating from both the close-lying $^2\Pi$ and $^2\Sigma^+$ anion states to the triplet and low-lying singlet states of the neutral diatomic. The ZEKE spectrum of Ga_2As^- shows two vibrational progressions with characteristic frequencies of 50 cm^{-1} and 47.0 cm^{-1} corresponding to the lowest frequency mode (ν_2) in two states of the neutral. The two neutral states are separated by approximately 160 cm^{-1} , and appear to be the bent and linear components of a Renner-Teller pair.

I. Introduction

In the ongoing effort to experimentally characterize small, pure group IV semiconductor clusters, relatively little attention has been focused on the mixed group III-V clusters. The impetus is certainly there; group III-V semiconductors are important to the fast microelectronics industry, with applications in exotic devices such as IR light detectors and semiconductor injection lasers.¹ The structures and electronic properties of mixed clusters composed of only several atoms present an interesting focus for both experimentalists and theoreticians, as more close-lying structural permutations are available to a binary system than to a pure atomic system. *Ab initio* studies on mixed systems such as small GaAs, InSb, and AlP clusters have predicted that the various structural permutations for a given cluster can be comparable in energy, and each structure can have multiple close-lying electronic states.^{2,3,4,5,6} However, cluster experiments that could test calculations are inherently difficult for several reasons, the most forbidding of which is the lack of mass-specificity of most cluster sources. Because of this, most of the spectroscopic information accrued on small semiconductor clusters has been from mass-selective experiments.^{7,8,9,10,11,12}

As an extension of our previous work on small InP clusters,^{8,9} this paper presents preliminary results obtained on small GaAs clusters using anion photoelectron spectroscopy (PES) as well as the zero electron kinetic energy (or ZEKE) spectrum of Ga₂As⁻. Negative ion photodetachment techniques are particularly well-suited to small cluster study, as ions are intrinsically mass-selectable, thereby eliminating any ambiguity regarding species identification. Moreover, by detaching an electron from a valence orbital of a cluster anion, both the ground and low-lying excited states of the neutral are probed. Anion PES measures the kinetic energy distribution of photoelectrons (eKE) in anion detachment of the type

$$A_xB_y(T_e, v_n') + e^- (eKE) \leftarrow h\nu \text{ (fixed)} + A_xB_y^-(T_e, v_n''), \quad \text{Eqn. (10.1)}$$

and is generally sensitive to all one-electron transitions between anion and neutral levels having term energies, T_e , and vibrational levels, v_n' , accessible with the photon energy. The resolution afforded by our apparatus is approximately 80 cm^{-1} , which is adequate to resolve electronic (and often vibronic) transitions.

Substantially higher resolution (3 cm^{-1}) can be obtained using negative ion ZEKE spectroscopy, which is sensitive to transitions of the type

$$A_x B_y (T_e, v_n') + e^- (eKE = 0, \ell = 0) \leftarrow h\nu (\text{tuned}) + A_x B_y^- (T_e, v_n''), \quad \text{Eqn. (10.2)}$$

where ℓ is the angular momentum of the photoelectron, and is related to the molecular orbital from which it is detached. The requirement of $\ell = 0$ (s-wave electron) is due to the behavior of the photodetachment cross section near detachment threshold which has been explored by Wigner¹³ for atoms and Reed *et al.*¹⁴ for polyatomics. The Wigner threshold law dictates that, near threshold, the cross section goes as

$$\sigma \propto \sigma_o (E_{h\nu} - E_{\text{threshold}})^{\ell+1/2}. \quad \text{Eqn. (10.3)}$$

Therefore, the photodetachment cross section rises sharply at a detachment threshold only for $\ell = 0$, so the ZEKE technique is sensitive only to s-wave electrons. Because not all transitions observed in the lower-resolution PES will be observed in the ZEKE spectrum, the application of both techniques is required for the most complete characterization of these species. We have previously applied the two techniques to the study of small silicon,^{10,11} germanium,¹² and InP ,^{8,9} clusters.

There have been several other experimental studies on small III-V mixed clusters, most of which involve some mass-selectivity. Mandich's photodissociation spectroscopy of In_xP_y ,¹⁵

showed that clusters containing an even number of atoms exhibited absorption similar to the band gap of bulk InP, while the odd-numbered clusters generally absorbed at lower photon energies. Smalley and coworkers obtained the ultraviolet PES of Ga_xAs_y^- ,¹⁶ and the resonant two-photon ionization (R2PI) studies of the GaAs diatomic performed by Morse and coworkers characterized the $X^3\Sigma^-$ and a high-lying (~ 3 eV) $^3\Pi_r$ state.¹⁷ However, even the mass-specific experiments on small GaAs clusters can be confounded because of the proximal masses of Ga and As atoms. Moreover, the two isotopes of Ga (69 and 71 amu) tend to spread out and congest the mass spectra for those clusters containing more than four atoms. For this reason, the UPES of Ga_xAs_y^- by Smalley were mass-resolved only for the total number of atoms in a given cluster, and the electronic structure for any having more than two atoms was not uniquely determined in those studies.¹⁶

In addition to the above experiments are the (not mass-selective) electronic and vibrational absorption work done by Weiner and coworkers on the In(P, As, Sb)¹⁸ and Ga(P, As, Sb)¹⁹ mixed diatomics trapped in rare-gas matrices. The absorption work on GaAs, in particular, determined the vibrational frequency of the $^3\Sigma^-$ ground state of the GaAs diatomic along with several frequencies assigned to the two mixed triatomics. GaAs is isoelectronic with the more recently experimentally characterized Ge_2 and Si_2 ,^{9,10} and has been the subject of several *ab initio* studies by Raghavachari,² Balasubramanian,²⁰ and Bruna and coworkers.²¹ As with the pure Group IV diatomic analogs, a $^3\Pi$ excited state is predicted to be very low-lying, within 2000 cm^{-1} of the $^3\Sigma^-$ state in the case of GaAs. There are also three singlet states expected to lie approximately 0.5 eV to higher energy having $^1\Pi$, $^1\Sigma$, and $^1\Delta$ character, in order of increasing energy. The vibrational frequency of the ground $^3\Sigma^-$ state determined by Morse and coworkers ($\omega_e = 215\text{ cm}^{-1}$, $\omega_e x_e = 3\text{ cm}^{-1}$)¹⁷ and subsequently observed by Weltner in his matrix work¹⁹ are in reasonable agreement with the calculated frequency.²⁰ The several other frequencies observed in Weltner's studies of GaAs trapped in the rare-gas matrices which were

assigned to the mixed triatomics are consistent with the predicted ground state C_{2v} structures predicted for these species,^{3,4} and are further supported by isotopic shift effects.

In this work, we present preliminary electronically-resolved PES of individually mass-resolved $Ga_xAs_y^-$ ($x = 1, 2$; $y = 1, 2, 3$) clusters. The PES apparatus is presently being modified to dramatically enhance the mass resolution, and PES for these and larger clusters with more in-depth analysis of the size-dependent electronic structures of the Ga_xAs_y clusters will be presented at a later time. The band structures of the smaller species presented here are compared to the previously obtained PES of the analogous $In_xP_y^-$ clusters and the *ab initio* calculations available for these species. The vibrationally-resolved PES of the GaAs diatomic, which is isoelectronic germanium dimer, is also discussed. In addition, the substantially higher-resolution anion ZEKE spectrum of Ga_2As^- presented below shows extended, low-frequency ($\sim 50\text{ cm}^{-1}$) vibrational progressions in what appears to be two very close-lying states of the neutral.

II. Experiment

The operation of the PES and the ZEKE spectrometer are similar in principle. In both experiments, an internally cold beam of cluster anions is generated in a laser-vaporization/pulsed-molecular beam source based on that developed by Smalley.²² The negative ions are then mass-selected and photodetached, but the electron detection schemes are different.

A. Photoelectron spectrometer

The negative ion PES has been described in detail elsewhere,²³ but the basic operation is as follows. A beam of cold gallium arsenide anions is generated by vaporizing the surface of

a translating and rotating GaAs rod with 4 - 6 mJ/pulse output of the second harmonic output of a (pulsed) Nd:YAG operated at 20 Hz repetition rate. The resulting plasma is entrained in a pulse of 90% Ne/10% He carrier gas from a Trickle-type²⁴ piezoelectric beam valve, and expanded through a clustering channel into the source vacuum chamber of the apparatus. The cluster anions are extracted into a time-of-flight mass spectrometer where they are accelerated to 1 keV and separate by mass. The ion beam is intersected by a second YAG laser beam, which is timed such that it photodetaches only the cluster ions of interest. A small fraction (approximately 0.4%) of the resulting photoelectrons is detected with a 70 mm diameter microchannel plate detector at the end of a 1 m field-free drift tube that intersects the mass spectrometer drift tube at the interaction region. The photoelectron kinetic energies (eKE) are determined from the electron flight time. The instrumental resolution is eKE-dependent, starting from 8-10 meV for photoelectrons with 0.65 eKE, and degrading as $(\text{eKE})^{3/2}$.

B. ZEKE spectrometer

A detailed description of the anion ZEKE spectrometer can be found elsewhere,²⁵ but briefly, the anions are generated in a similar manner to that described above, except that the clustering channel is cooled using liquid nitrogen, and a General Valve solenoid-type pulsed molecular beam valve is used in lieu of the piezoelectric beam valve. Use of the $\text{N}_2(\text{g})$ -cooled clustering channel was found to enhance the vibrational cooling in both the InP mixed triatomic clusters and Si_4^- .⁹ After the expansion through the clustering channel, those anions passing through a 2 mm skimmer are colinearly accelerated to 1 keV and separate out by mass in a 1 m time-of-flight tube.

The mass separated ions then enter a detector region where they are selectively detached using a (pulsed) excimer-pumped tunable dye laser in a field-free region. The dye laser is scanned through the detachment continuum of the cluster anion of interest,

photoelectrons detached with excess eKE scatter away from the ion bunch, while those with nearly zero kinetic energy (threshold electrons) stay proximal to the remaining ions and neutrals. After several hundred nanoseconds, a weak (typically 2 V/cm) extraction field is applied, and those energetic electrons scattered off the ion beam axis are blocked by a series of apertures between the detachment region and the electron detector. The on-axis energetic electrons and the threshold electrons have different arrival times at the electron detector due to their spatial separation in the extraction field, and the threshold electrons are selectively collected using a gated integration scheme. This selective detection of threshold electrons, based on techniques developed by Müller-Dethlefs for the photoionization of neutrals, yields an energy resolution of as good as 3 cm^{-1} .

The electron signal is normalized to the ion current and detachment laser power, and averaged over 1500 laser shots per point. The dyes used to obtain the ZEKE spectrum of Ga_2As^- were Coumarin 450, Coumarin 480, and Coumarin 501.

III. Results

A. PES of Ga_xAs_y^-

Figure (10.1) shows six PES of Ga_xAs_y^- ($x = 1, 2$; $y = 1, 2, 3$) obtained using a photon energy of 4.657 eV. The eKE is given by

$$\text{eKE} = h\nu - \text{EA} - E^{(0)} - E^{(-)}, \quad \text{Eqr. (10.4)}$$

where $h\nu$ is the photon energy, EA is the electron of the neutral cluster, and $E^{(0)}$ and $E^{(-)}$ are the internal (electronic plus vibrational) energies of the neutral and anion states, respectively. Therefore, the features in the spectra at highest eKE correspond to transitions to the lowest

energy levels of the neutral. Electron affinities for the neutral species were taken to be the onset of the high eKE edge of the highest eKE spectral feature (i.e., low neutral internal energy) which, per Eqn. (10.4), reflects the energy between the ground anion level and the ground neutral level. These values are summarized in Table (10.1). Each of the spectra also show several resolved or partially-resolved peaks, each of which represents an electronic transition from the anion (presumably) ground state to different electronic states of the neutral. Approximate term energies (T_e) for these various states are also included in Table (10.1). None of the spectra show any vibrational structure at this photon energy.

It should be noted that on the Ga_2As^- and Ga_2As_3^- spectra, there are low-intensity peaks at approximately 2.8 eV and 3.0 eV eKE. These peaks have opposite polarization dependencies, and the peak at 2.8 eV happens to be enhanced in the magic angle spectra shown. These features are due to two-photon processes in which fragmentation is followed by detachment of the daughter ion, and are therefore unrelated to the Ga_2As and Ga_2As_3 electron affinities. Very similar features were observed in some of the In_xP_y^- spectra,⁸ and were tentatively assigned to In_2^- detachment, which at first suggests that structure seen here may be due to Ga_2^- detachment. There has been no experimental determination of the electron affinity of Ga_2 , but it has been calculated to be 1.04 eV,²⁶ although this value increases to 1.25 eV when more electrons are included in the calculation.²⁰ This value is low compared to the 1.6 eV detachment energy suggested by the two-photon peak, either implying that the previous assignment is wrong, or that the calculated value is low. The splitting between the two peaks, 0.2 eV, is somewhat higher than the 0.05 eV calculated splitting between the $X^3\Pi_u$ and $^3\Sigma_g^-$ low-lying states in Ga_2 neutral (As with GaAs, the singlet states are predicted to lie 0.5 eV higher than the triplet states, but the predicted anion ground state, $^4\Sigma_g^-$, cannot access the singlet states). However, the EA's of atomic Ga (0.30 ± 0.15 eV) and As (0.81 ± 0.03 eV)²⁷ are even lower than the predicted EA of Ga_2 , and there is no other obvious explanation for the structure.

While the limited range of cluster sizes for which we were able to obtain PES (due to the limitations of the mass spectrometer) precludes our asserting any definite size-dependent trends in the observed electronic band structures, several spectral features are worth being noted. For instance, in the Ga_2As_y^- series, Ga_2As_2 has a much lower electron affinity than both Ga_2As and Ga_2As_3 [see Table (10.1)]. The even-numbered cluster also has a higher T_e than the two odd-numbered clusters. More definitive size-dependent and even-odd trends and how they compare with previously obtained In_xP_y^- PES spectra will be born out in the larger cluster spectra, and will be the subject of a subsequent article.

B. Higher resolution PES of GaAs

The PES of GaAs obtained using a 2.98 eV photon energy (416 nm) and three different laser polarizations is shown in Figure (10.2). Electrons ejected from different orbitals generally have different angular distributions relative to the electric field vector of the detachment laser following²⁸

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 + \beta(E) \left(\frac{3}{2} \cos^2\theta - \frac{1}{2} \right) \right]. \quad \text{Eqn. (10.5)}$$

Therefore, by obtaining spectra at different laser polarizations, overlapping electronic transitions can more easily be discerned.

The spectra appear to be composed of two vibrationally-resolved bands, both of which are composed of multiple electronic transitions. This spectral profile is familiar; the PES of Si_2^- ,¹⁰ Ge_2^- ,¹² and $\text{InP}^{(-8)}$ showed similar band structure due to transitions to the triplet states (lower-lying band) and the singlet states (higher-lying band) from the two close-lying doublet anion states. In all cases, the spacing between the triplet and singlet bands is approximately 0.5 eV. The predicted electronic structure particular to GaAs will be addressed in the discussion

section. The peak positions (eKE, eV) and relative energies (cm^{-1}) are summarized in Table (10.2). Also in Table (10.2), those peaks enhanced in the $\theta = 0^\circ$ are indicated with a dagger ($\dagger$) and those enhanced in the $\theta = 90^\circ$ are indicated with an asterisk (*).

The triplet band is particularly congested, and it is clear that multiple electronic transitions are overlapping. However, by considering the difference between the $\theta = 0^\circ$ and $\theta = 90^\circ$ spectra, there appear to be at least two and possibly three electronic transitions with different polarization dependencies contributing to the observed structure. The first and most obvious band is dominated by peak 1 in the $\theta = 0^\circ$ spectrum; it distinctly stands out as a single intense peak with $\theta = 0^\circ$, while in the $\theta = 90^\circ$ spectrum, it is buried under peak 2. The second band is broader and lies to lower eKE, and is more enhanced in the $\theta = 90^\circ$ spectrum. Most of the intensity of peaks 6 through 15 have appear to be in this second transition; the peaks are not evenly spaced, rather they appear to consist of three transitions separated by 0.06 and 0.07 eV, each having a $240 \pm 40 \text{ cm}^{-1}$ vibrational progression. For instance, in the $\theta = 0^\circ$ spectrum, peaks 11, 8 and 5 appear to be the maxima of three 240 cm^{-1} vibrational progressions, with the spacing between 5 and 8 being -0.06 eV and the spacing between 8 and 11 being -0.07 eV . This might be what one would expect in a transition to a $^3\Pi$ state. A possible third band may contribute to the observed structure and intensity at the higher eKE of the triplet band; at first glance of the $\theta = 90^\circ$ spectrum, there appears to be only one electronic band, but when the $\theta = 90^\circ$ spectrum is subtracted from the $\theta = 0^\circ$ spectrum, there appear to be two bands with slightly different polarization dependencies.

The singlet band is much simpler, and the resolution in eKE = 0.2 to 0.5 eV region is better than for the higher eKE region. It consists of at least four resolved electronic bands, several of which exhibit vibrational progressions: The first is composed of peaks 19 (probable origin), 21, and 23, has a frequency of $285 \pm 20 \text{ cm}^{-1}$, and is enhanced in the $\theta = 0^\circ$ spectrum. Peak 17 appears to be a hot band associated with this progression. The second is composed of peaks 20 (origin), 22, 24 and 25, also has a frequency of $285 \pm 20 \text{ cm}^{-1}$, and is enhanced in the

$\theta = 90^\circ$ spectrum. The peaks in these two progressions are approximately 60 cm^{-1} wide at half the maximum (FWHM). The other two bands are at lower eKE, in a range where peak intensities tend to be less reliable. However, in the PES obtained using 3.49 eV detachment energy (not shown), peaks 28 and 29 emerge definitively as the origins of two electronic transitions having opposite angular dependencies, with peak 28 being enhanced in the $\theta \approx 0^\circ$ spectrum. Peaks 28 and 29 are separated by 280 cm^{-1} , which is comparable to a GaAs vibration. Therefore, part of the intensity of peak 29 may be due to a vibrational progression originating from peak 28. There are several less-intense peaks in the 3.49 eV PES that appear to form a 300 cm^{-1} progression from peak 29. Peaks 27 through 29 are wider (80 to 100 cm^{-1} , FWHM) than the peaks at higher eKE in the singlet band, which could suggest that there are other transitions overlapping.

C. ZEKE spectrum of Ga_2As^-

The ZEKE spectrum of Ga_2As^- is shown as the solid trace in the upper half of Figure (10.3) with the previously discussed PES superimposed (dashed line) on the electron binding energy scale. For future reference, the lower half of Figure (10.3) shows the PES (dotted line) and ZEKE spectrum (solid line) of isoelectronic In_2P^- . Note that only the lowest-lying electronic band in the PES is observed in the ZEKE spectrum, which is the same situation as in the ZEKE spectrum of In_2P^- . The ground electronic state of Ga_2As is predicted to have C_{2v} geometry, and since symmetric modes tend to be the most active in electronic transitions, the a_1 bend (ν_2) and the higher-frequency a_1 symmetric stretch (ν_1) should account for most of the structure observed in the spectrum and described below.

The ZEKE spectrum is shown on an expanded scale in the upper panel of Figure (10.4) as the solid line. It appears to consist of two electronic bands, X and A, having different vibrational contours; band X (the lower energy band) has a narrower profile with a $50 \pm 2\text{ cm}^{-1}$

progression, and band A (the higher-lying band) has a broader profile with a $47.0 \pm 0.2 \text{ cm}^{-1}$ progression. These are presumably neutral bend frequencies. Tentative origins of the two bands are indicated with combs labeled X_2 and A_2 , where the "2" denotes the mode active in the progression, the ν_2 (a_1) symmetric bend, that the comb is indicating. However, these origins, particularly that of band A, cannot be determined definitively. Nonetheless, an approximate electron affinity can be determined from the position of the most intense peak in band X, which yields a 2.452 eV electron binding energy. The peaks in the ZEKE spectrum will be referred to as members of progressions indicated by the combs. For example, peak $X_2(0)$ is the first peak, or origin of the X_2 progression, and peak $A_{12}(3)$ is the fourth peak, or third excited level in the A_{12} progression.

Band X, in addition to the $50 \pm 2 \text{ cm}^{-1}$ progression, has a hot band, x_2' found at 259 cm^{-1} to lower detachment energy of peak $X_2(0)$, which also exhibits a 50 cm^{-1} progression with lower signal to noise. To higher detachment energy, band X overlaps with band A, and it is not immediately obvious which peaks belong to which band.

In addition to the most intense $47.0 \pm 0.2 \text{ cm}^{-1}$ progression (A_2) in band A is a lower-intensity 47 cm^{-1} progression displaced to higher detachment energy. Based on the spacing between the most intense members of each progression, $A_2(2)$ and $A_{12}(2)$, the displacement is 171 cm^{-1} , which is likely the vibrational frequency for the symmetric stretch.

IV. Analysis and Discussion

The approach taken in this section is to first address the Ga_xAs_y^- PES in terms of how they compare to the analogous In_xP_y^- PES. This comparison will be brief, deferring more detailed analysis to the more complete set of Ga_xAs_y^- PES that is forthcoming. The higher-resolution GaAs PES will be discussed in terms of possible transitions between the predicted

anion and neutral states. Finally, the Ga_2As^- ZEKE spectrum will be analyzed and compared to the previously obtained In_2P^- ZEKE spectrum.¹²

A. Electronic structure of Ga_xAs_y

There is a remarkable similarity between the electronic structures observed in several of the PES of Ga_xAs_y^- and their analogous In_xP_y^- clusters.⁸ This is perhaps a little surprising considering the difference in polarity between In-P and Ga-As bonds along with the obvious atomic size differences: Ga and As are comparable in size while In has 1.5 the atomic radius of P. There are also several interesting differences, which along with the similarities, will now be briefly discussed (the GaAs^- and Ga_2As^- spectra will be addressed in sections B and C, respectively).

The PES of GaAs_2^- shows transitions to three electronic states of the neutral. The PES of InP_2^- showed only two electronic transitions in the energy region accessed by the same photon energy, in spite of its having a lower EA (1.61 eV vs. the 1.83 eV EA of GaAs_2).⁸ As was determined from the ZEKE spectrum of InP_2 , the ground $^2\text{B}_2$ (...1b₁²4a₁²2b₂) state of this molecule resembles a doubly bound P_2 diatomic with an In atom loosely attached in C_{2v} geometry. The 1.280 eV excitation to the first excited $^2\text{A}_1$ state was effectively moving an electron from a P-F bonding orbital to a P-P antibonding orbital.⁸ Since the bonding between atoms is stronger for lighter atoms than their heavier counterparts, it would then follow that the T_e of the first excited state in GaAs_2 would be smaller than for InP_2 . This was predicted by Meier *et al.*,⁴ who calculated the $^2\text{B}_2 - ^2\text{A}_1$ splitting in GaAs_2 to be 0.65 eV, which is in reasonable agreement with the observed splitting (the widths of bands X and A in the PES indicates a considerable geometric rearrangement between the anion and both neutral states, so getting a good adiabatic T_e from the PES is not straightforward). Band B is presumably a

transition to the 2B_1 state, but no calculations on the excitation energy for this state are presently available for comparison.

The $GaAs_3^-$ PES spectrum is considerably more congested than the InP_3^- spectrum,⁸ presumably for similar reasons. It seems reasonable that in As-rich GaAs clusters, As-As bonding would dominate (as is the case in $GaAs_2$), simply because As atoms have more valence electrons. Again, since electronic states resulting from As-As bonding schemes should be closer lying than for the states resulting from P-P bonding in P-rich InP clusters, it makes sense that there should be a higher density of states observed in the $GaAs_3^-$ spectrum than in the InP_3^- spectrum.

The profiles of the $Ga_2As_2^-$ and $In_2P_2^-$ PES are very similar.⁸ The differences between the two spectra are subtle; the electronic bands in the $Ga_2As_2^-$ spectrum are broader, suggesting a greater geometry change between the anion and neutral states than for $In_2P_2^-$; the electron affinity of Ga_2As_2 is 0.1 to 0.2 eV higher than the EA of In_2P_2 , and the electronic transitions are slightly closer-lying in the $Ga_2As_2^-$ spectrum. The ground neutral state is predicted to be rhombic, with the As atoms on the shorter axis, and having 1A_g electronic character. This is analogous to the Si_4 neutral ground state.^{11,29} The anion is predicted to have $^2B_{2g}$ character, which also is analogous to the ground state of Si_4^- . Therefore, excited states accessed in the PES are likely similar to the excited states of Si_4 , with band A being the $^3B_{3u} \leftarrow ^2B_{2g}$ transition. The T_e 's for the $^3B_{3u}$ state of Ga_2As_2 and Si_4 are comparable, 0.7 eV for Ga_2As_2 and 0.82 eV for Si_4 . This is not so surprising, however, in light of the similarities between the band structure of GaAs and Si_2 , which is discussed below.

The PES of $Ga_2As_3^-$ and $In_2P_3^-$ again are quite similar. There are presently no calculations available on these larger non-stoichiometric clusters for comparison, but the spectra exemplify how the open-shelled electronic structure of the odd neutral clusters result in higher electron affinities and lower-lying excited electronic states.

B. Electronic structure of GaAs

The GaAs diatomic has been the subject of several non-relativistic *ab initio* studies, all of which conclude that the ground and first excited electronic states are the $^3\Sigma^-$ ($2\sigma^21\pi^2$) and $^3\Pi$ ($2\sigma^31\pi$) states, respectively.^{2,20,21} The ground state was confirmed to be the $^3\Sigma^-$ state by Morse and coworkers in their R2PI studies on the diatomic.¹⁷ A vibrational frequency of 215 cm^{-1} ($\omega_e x_e = 3\text{ cm}^{-1}$) was determined for this state as well. No transitions to the $^3\Pi$ state, to our knowledge, have yet been observed. The corresponding singlet states are predicted to lie approximately 0.7 to 2 eV higher in energy. The $^1\Pi$ ($2\sigma^31\pi$) state is the lowest-lying of these with calculated T_e 's ranging from 0.74 eV to 0.8 eV. The $(1)^1\Sigma^+$ (primarily $1\pi^4$) and $^1\Delta$ ($2\sigma^21\pi^2$) states are predicted to be nearly degenerate at $T_e = 0.9$ to 1.0, with the $(1)^1\Sigma^+$ state slightly lower in energy. Finally, the $(2)^1\Sigma^+$ ($2\sigma^21\pi^2$) state is substantially higher lying, with predicted T_e 's ranging from 1.75 to 2.0 eV. All of these states are analogous to the lowest-lying triplet and singlet states in isoelectronic Si_2 and Ge_2 (except for the ordering of several of the lower singlet states) and likely have similar relativistic effects as those observed in the Ge_2 studies.¹²

The anion has been studied by Balasubramanian,²¹ and, not surprisingly, has similar electronic structure to the anions of silicon and germanium dimers. The ground state is predicted to be the $^2\Sigma^+$ ($2\sigma1\pi^4$) state, with the $^2\Pi$ ($2\sigma^21\pi^3$) state lying approximately 0.1 eV higher in energy (the splitting between the two Ω -components of the $^2\Pi$ state is not taken into account in this calculation). All of the previously mentioned neutral states are accessible by one or both of these anion states via a one-electron transition, and a schematic of these transitions is shown in Figure (10.5). Since the spin-orbit coupling constant, A , in GaAs^- should be roughly 1000 cm^{-1} , the $^2\Pi$ (3/2) level is probably very close to, if not lower than, the $^2\Sigma^+$ level. We may therefore expect both levels to be populated in the molecular beam.

The transition to the $(2)^1\Sigma^+$ state is not shown in Figure (10.5). The $(2)^1\Sigma^+$ state lies up to 1 eV higher than the other singlet states, and it will not be observed in the higher-resolution

PES of GaAs⁻ shown in Figure (10.2) as the 2.98 eV photon energy is not sufficient to access it. However, the 4.66 eV PES shown in Figure (10.1) shows some signal at eKE = 1.0 eV which may be from the $(2)^1\Sigma^+ \leftarrow 2^1\Pi$ transition. A T_e of roughly 1.6 to 1.7 eV for this state can be determined from the splitting between this signal and the high eKE edge of the triplet band.

Since the triplet band of the GaAs⁻ in the PES shown in Figure (10.2) is so congested, we can endeavor to analyze the singlet band first, and then make some qualitative comment on the structure in the triplet band. Attempts to obtain the ZEKE spectrum of GaAs⁻ are presently underway, and the results of that experiment should give more definitive assignments of the structure in the triplet band.

The lowest lying singlet state predicted for GaAs is the $1^1\Pi$ state, which can be accessed from both of the doublet anion states. It therefore seems logical that the two $285 \pm 20 \text{ cm}^{-1}$ progressions (peaks 19-21-23 and peaks 20-22-24) found at the higher eKE end of the singlet band are from the transitions from the two anion states to the $1^1\Pi$ state. The opposite angular dependencies of these two progressions is suggestive; in the similarly obtained PES of Ge₂⁻ and Si₂⁻, transitions involving the ejection of an electron from a π -type orbital (e.g., the $1^1\Pi \leftarrow 2^1\Sigma^+$ transition) were generally enhanced in the $\theta = 90^\circ$ spectrum while ejection of a σ -type orbital (e.g., the $1^1\Pi \leftarrow 2^1\Pi$ transition) were more enhanced in the $\theta = 0^\circ$ spectrum. We therefore assign peaks 19... to the $1^1\Pi \leftarrow 2^1\Pi$ (3/2) transition, and peaks 20... to the $1^1\Pi \leftarrow 2^1\Sigma^+$ transition. Peak 17, as mentioned previously, appears to be a hot band transition associated with the 19-21-23 progression. The spacing between peak 17 and 19 gives a vibrational frequency of 250 cm^{-1} for the $2^1\Pi$ (3/2) anion state. The relative frequencies of the $2^1\Pi$ (3/2) anion and $1^1\Pi$ neutral states are in good agreement with the predicted values [242 cm^{-1} for the anion, 280 cm^{-1} for the neutral from FOCI calculations, Ref. (21)]. The frequency of the $2^1\Sigma^+$ anion state cannot be determined definitively from the spectrum, but it is predicted to be 291 cm^{-1} .²¹

The energy splitting between the origins of these two transitions should give the energy splitting between the $2^1\Sigma^+$ and $2^1\Pi$ (3/2) anion states. If peak 19 is in fact the origin of the $1^1\Pi \leftarrow$

$^2\Pi$ transition and peak 20 the origin of the $^1\Pi \leftarrow ^2\Sigma^+$ transition, the $^2\Pi$ (3/2) anion level lies 10 meV (80 cm^{-1}) above the $^2\Sigma^+$ state. For comparison, in Ge_2^- , the $^2\Pi_u$ (3/2) was found to lie 274 cm^{-1} below the $^2\Sigma_g^+$ anion level, but as the spin-orbit splitting should be on the order of $700\text{--}1000\text{ cm}^{-1}$, the $^2\Pi_u$ (1/2) anion level should be several hundred wave numbers above the $^2\Sigma_g^+$ level, and the center of the $\Omega = 1/2$ and $3/2$ levels (the "deperturbed" level) should also lie above the $^2\Sigma_g^+$ state.¹² The splitting between these two triplet neutral levels for GaAs is predicted to be larger than for Ge_2 neutral,²⁰ so it would follow that the splitting in the anion levels is larger as well, which is consistent with the observed ordering of the anion levels in GaAs^- .

The other two electronic transitions, peaks 28 and 29, could be due to the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition and the $^1\Delta \leftarrow ^2\Pi$ (3/2) transition. Unless the $^1\Delta$ state lies within 80 cm^{-1} of the $^1\Sigma^+$ state, the former transitions should be lower-lying. The vibrational frequency calculated for $^1\Sigma^+$ state is 302 cm^{-1} , while for the $^1\Delta$ state it is 220 cm^{-1} .²⁰ Since there are no peaks observed under 280 cm^{-1} to lower eKE of peak 28, we assign peak 28 to the origin of the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition. This gives that the $^1\Sigma^+$ state is 0.15 eV (1200 cm^{-1}) higher-lying than the $^1\Pi$ state. The remaining transition, peak 29, which is found 280 cm^{-1} to lower eKE of peak 28, could be the $^1\Delta \leftarrow ^2\Pi$ (3/2) transition. However, this assignment is very suspicious since there appears to be no lower-frequency progression extending from peak 29 which would be characteristic of the transition to the $^1\Delta$ state. Upon obtaining the ZEKE spectrum of GaAs , the peak assignments will be made more definitively.

Even with the preceding analysis of the singlet band, the assignment of the structure in the triplet band is far from straightforward. What is expected in the triplet band are two s-wave electronic bands [the $^3\Sigma^+ \leftarrow ^2\Pi$ (3/2) transition and the $^3\Pi$ (2, 1, $0^\pm$) $\leftarrow ^2\Sigma^+$ transition] and one p-wave band [the $^3\Pi$ (2, 1, $0^\pm$) $\leftarrow ^2\Pi$ (3/2) transition]. Only peak 1 in the PES stands out distinctly as a p-wave transition, based on its polarization dependence. Very preliminary work on the ZEKE spectrum indicates that peak 2 is the origin of an extended 260 cm^{-1} vibrational progression, while no ZEKE signal is observed under peak 1. Because 260 cm^{-1} is substantially

higher than the known frequency of the $^3\Sigma^-$ state, peak 2 must be the origin of the $^3\Pi (2) \leftarrow ^2\Sigma^+$ transition. Peak 1 is roughly 0.02 eV from peak 2 (although this splitting has an uncertainty of 100 cm^{-1} given the congestion of the spectrum) which is on the order of the $^2\Sigma^+ - ^2\Pi (3/2)$ splitting in the anion. It therefore seems reasonable to assign peak 1 to the $^3\Pi (2) \leftarrow ^2\Pi (3/2)$ electronic hot band transition.

This preliminary assessment leaves several questions unanswered, however. First, it is not clear from the spectrum where the $^3\Pi (0^\pm \text{ and } 1) \leftarrow ^2\Pi (3/2)$ transitions lie, and why they are not as intense as peak 1. In the Ge_2^- spectrum, the $^3\Pi (0^\pm) \leftarrow ^2\Pi (3/2)$ transitions had less than half the intensity of the $^3\Pi (2) \leftarrow ^2\Pi (3/2)$ transition, but the $^3\Pi (1) \leftarrow ^2\Pi (3/2)$ transition had comparable intensity. Second, the $^3\Sigma^- \leftarrow ^2\Pi (3/2)$ transition is not distinctly observed in the PES. From the work of Morse and Weltner, the vibrational frequency of the $^3\Sigma^-$ state is approximately 210 cm^{-1} . However, there is no 210 cm^{-1} progression observed in the spectrum; most of the spacings are on the order of 240 cm^{-1} or more. Geometry calculations on the $^3\Sigma^-$ and $^2\Pi$ states predict that the difference in bond length between these states is approximately $0.2\text{ \AA}$. A geometry change of this magnitude should excite a fairly extended progression with the third or fourth member being the most intense. Moreover, this progression should lie to lower detachment energy (higher eKE) than the transitions to the $^3\Pi$ state, and very little structure is observed to higher eKE in the PES. However, these issues should be resolved upon obtaining the complete ZEKE spectrum.

C. Analysis of the ZEKE spectrum of Ga_2As^-

The similarity of the PES of Ga_2As^- and In_2P^- [dashed lines, Figure (10.3)] suggests that electronically analogous anion and neutral states are responsible for the two electronic bands in

both spectra. It is therefore surprising that the ZEKE spectra of Ga_2As^- and In_2P^- exhibit such distinct differences. The most obvious difference is that there are two very close-lying electronic bands in the ZEKE spectrum of Ga_2As^- where only one distinct electronic band is observed in the In_2P^- spectrum. The first issue to be addressed is, therefore, whether the two bands reflect transitions from one anion state to two close-lying states in the neutral, or transitions from two close-lying states in the anion to one or two neutral states. Either seems feasible considering the calculated electronic structure of the neutral state.

Ab initio calculations on neutral Ga_2As predict a 2B_1 C_{2v} ground state with the electronic orbital configuration $(1a_1)^2(2a_1)^2(1b_2)^2(2b_2)^2(3a_1)^2(1b_1)^1(4a_1)^0$ and a Ga-As-Ga bond angle of 111° .³ This configuration represents the bent electronic component of a Renner-Teller pair, for which the linear component, in C_{2v} terms, has the $\dots(3a_1)^1(1b_1)^2$ configuration, forming a 2A_1 state, or, the ${}^2\Pi_u$ linear state in the $D_{\infty h}$ point group. The $3a_1$ and $1b_1$ orbitals correlate to the degenerate components of the π_u orbital in the linear molecule, which has the p-orbitals on all three atoms in phase, and in the bent geometry, the $1b_1$ orbital has a nodal plane in the plane of the molecule. The bent and linear components are predicted to be very close-lying, split by only 0.1 to 0.2 eV (800 to 1600 cm^{-1}), with both having very broad and shallow bend potentials. No calculations on the anion state of Ga_2As are yet available, but a possible anion state can be inferred by adding an electron to the distorted, partially-filled $1b_1$ orbital, which results in a 1A_1 state that is isoelectronic with the (predicted) ground state of neutral Ge_3 . The bond angle of the 1A_1 state of Ge_3 is calculated to be approximately 150° , and if the analogous Ga_2As^- state is similarly bent, it could conceivably overlap with the bent and linear components of the neutral Renner-Teller pair, provided all three bend potentials are sufficiently broad.

The analogy between the Ga_2As^- anion and neutral Ge_3 also gives rise to another possible explanation for the two bands in the ZEKE spectrum. Ge_3 is predicted to have a low-lying linear state, having ${}^1\Sigma_g^+$ character (which correlates with the 1A_1 electronic configuration). If the same held for Ga_2As^- , and the ${}^1\Sigma_g^+$ state were only several hundred wave numbers higher

in energy than the 1A_1 state, band X could be an electronic hot band originating from this state, with band A being the $^2B_1 \leftarrow ^1A_1$ transition. This scenario is unattractive for several reasons. First, the excited linear anion state would only overlap with the linear component of the Renner-Teller pair, and transitions to only even quanta in the bend would be allowed. Moreover, very little excitation in the bend would be expected. However, it is possible that the frequency of the linear component of the neutral is 25 cm^{-1} , and that band X is the $^2\Pi_u \leftarrow ^1\Sigma_g^+$ electronic hot band transition. In this case, the splitting between band X and band A would reflect both the splitting between the two anion states and the two neutral states. The other low-lying state predicted for Ge_3 is the $D_{3h} \text{ } ^3A_2'$ state, which correlates to a 3B_2 in C_{2v} geometry. This state cannot impact the spectrum, however, since the electronic configurations of the ground and low-lying neutral states of Ga_2As can be accessed from a Ga_2As^- anion with the 3B_2 configuration.

While these arguments based on *ab initio* geometries of analogous species are fairly compelling, further convincing is desired before making definitive spectral assignments. We can therefore attempt to simulate the spectrum assuming both scenarios. The spectral simulations are performed within the Frank-Condon approximation, in which we assume that the intensities of individual vibronic transitions are proportional to the Franck-Condon factors between the anion and neutral vibrational wave functions. The Ga_2As anion and neutral wave functions are taken to be the product of two harmonic oscillator wave functions corresponding to the ν_1 symmetric stretch (a_1), and the ν_2 symmetric bend (a_1). The ν_3 antisymmetric stretch (b_2) was neglected for simplicity, although it is likely contributing to sequence bands in the observed spectrum.

We perform simulations in two ways. First, we assume two sets of neutral parameters and one set of anion parameters, in order to simulate the first scenario in which the ground anion state is overlapping with both the bent and linear components of the neutral. Second, we assume one set of neutral frequencies and two sets of anion frequencies, in order to simulate

the second scenario in which two bent states of the anion are overlapping with only the bent component of the neutral ground state.

The first simulation attempt with the two sets of neutral parameters is shown as the dashed line in the upper panel of Figure (10.4). The two electronic components comprising the simulation are shown as dashed and solid lines in the lower panel of Figure (10.4). For band X, the following neutral frequencies were used: $\omega_1' = 160 \text{ cm}^{-1}$, $\omega_2' = 51.2 \text{ cm}^{-1}$. For band A, $\omega_1' = 171 \text{ cm}^{-1}$ and $\omega_2' = 47 \text{ cm}^{-1}$. For the anion, $\omega_1'' = 264 \text{ cm}^{-1}$ and $\omega_2'' = 48 \text{ cm}^{-1}$. Of all these frequencies, the ω_2' (band X), ω_2' (band A), ω_1' (band A), and ω_1'' are obvious from the spectrum. The remaining frequencies are chosen to fit other more subtle features in the spectrum. For instance, the ω_1' (band X) was chosen to give appropriate width to the peak labeled as the origin of X_{12} , which overlaps with the A_2 origin.

The ω_2'' (anion) frequency was chosen for consistency with two features in the spectrum. First is the broadness of the 47 cm^{-1} progression in band A. The profile of an extended progression is fairly sensitive to the spatial extent of the wave function of the lower state. Since the 47 cm^{-1} progression in band A is so extended, with five peaks being comparably intense near the maximum intensity of the progression, the anion wave function for this mode must be very broad. In this case, $\omega_2'' = 48 \text{ cm}^{-1}$ adequately fit the observed profile. This is in sharp contrast with the progression observed in the In_2P^- ZEKE spectrum [Figure (10.3)], which has a much narrower profile in spite of its extension. The second feature matched by the anion $\omega_2'' = 48 \text{ cm}^{-1}$ is the hot band found just to lower detachment energy (19729 cm^{-1}) of the X_2 origin. Granted, it is not obvious whether the origin of band X is as it is shown in Figure (10.4) or if it is the peak to 50 cm^{-1} lower detachment energy that has been assigned to a hot band in the preceding simulation. However, the profile of band X could not be matched assuming the latter given $\omega_2'' = 48 \text{ cm}^{-1}$. If the anion frequency were higher, the profile of band X could be fit given the lower energy origin, but the more distinct profile of band A would then not be matched.

While the frequencies chosen for the two neutral states in the preceding simulation are not identical, they are very proximal, which leaves the feasibility that one neutral state is being accessed by two close-lying anion states possible. For the simulation assuming two anion states and one neutral state, the sole neutral frequencies for ν_1 and ν_2 were taken to be 171 cm^{-1} and 47 cm^{-1} , as they are most definitively determined from the less congested progressions in band A. However, no matter how the anion frequencies were chosen, the confinement to one set of neutral parameters would not yield a good fit. First, the band X progression, while exhibiting similar spacing to the band A progression, is not well matched with a 47 cm^{-1} frequency. Second, with $\omega_1' = 171 \text{ cm}^{-1}$, the X_{12} origin falls exactly on the A_2 origin, and no other transitions fill in the several broad peaks where the two bands overlap.

Based on the simulations and the arguments presented at the beginning of this section, we feel confident that the two bands in the ZEKE spectrum are from transitions from one anion state to the two components of the Renner-Teller pair of the neutral. Band X is assigned to the ${}^2B_1 \leftarrow {}^1A_1$ transition, and band A is assigned to the ${}^2A_1 ({}^2\Pi_u) \leftarrow {}^1A_1$ transition. It's not clear that the origins chosen for the simulations are definitive, particularly for the very extended progression in band A, but an approximate value for the Renner-Teller relaxation can be determined from the energy interval between the two bands, which is approximately 160 cm^{-1} . This is substantially less than the predicted value, 800 to 1600 cm^{-1} [Ref. (3)] suggesting that the bond angle of the 2B_1 state may be wider than predicted, which makes it even more feasible that a 150° anion could overlap with both bent and linear components. Moreover, it is possible that the 1A_1 component is only nearly linear or quasi-linear, further facilitating Franck-Condon overlap with a bent anion.

Finally, from Weltner's work on GaAs diatomics and mixed triatomics trapped in rare-gas matrices, a frequency for the antisymmetric stretch of the ground state of Ga_2As was determined to be 204.0 to 205.4 cm^{-1} , depending on the Ga isotopic arrangement.¹⁹ A weaker line at 160 cm^{-1} was noted as a possible candidate for ν_1 . The higher ν_3 frequency is consistent

with the wide-angle C_{2v} molecule, and the 160 cm^{-1} suggested for ν_1 is exactly what we independently determined for the ν_1 frequency in our simulation of band X. This further supports our assignment of band X to the bent $\leftarrow$ bent transition, and since band A has the more extended progression in the bend, the possibility that it is a linear $\leftarrow$ linear transition seems less likely, and the linear $\leftarrow$ bent transition assignment seems further reinforced.

Comparison between the Ga_2As^- and In_2P^- ZEKE spectra. The striking similarity between the band structure in the PES of Ga_2As^- and In_2P^- suggests that these two molecules have the same overall electronic structure in both the anions and neutrals. Because both components of the Renner-Teller pair are observed in the Ga_2As^- spectrum, the anion must have the 1A_1 electronic orbital configuration. Any triplet anion could not access both components *via* a one-electron transition. This then implies that the In_2P^- ground state has the 1A_1 configuration. However, the observation of the two Renner-Teller components in the Ga_2As^- spectrum contrasts sharply with our only observing the bent component in the In_2P^- spectrum. This suggests that the ground anion state of Ga_2As^- is more nearly linear than the ground anion state of In_2P^- . While it is not immediately obvious why this is the case, we can speculate on the differences in bonding between the two species based on a few observations.

First, the ν_2 frequencies in both In_2P and Ga_2As are nearly identical, despite the fact that the reduced mass of Ga_2As is much higher than In_2P . An economical CISD calculation performed using the Gaussian 92 software package gave a 25 cm^{-1} bend frequency for the 2B_1 ground state of In_2P and a reduced mass of 45 amu ,³⁰ and since the calculated frequency is low, either the force constant was underestimated, or the reduced mass was overestimated (or both). On the other hand, the reduced mass of Ga_2As for any mode will be over 69 amu . Therefore, the bend potential for Ga_2As must actually be stiffer than for In_2P , and the Ga atoms, in spite of their lower mass, are not necessarily moving with greater amplitude than the In atoms. The stiffer bending potential in Ga_2As may be due to the better overlap between the p-orbitals of all three atoms in the molecule; for In_2P , the end p-orbitals are much larger than the p-orbital of

the phosphorous atom. The larger p-orbitals in the In atoms may also lend to further Renner-Teller stabilization since the closer the In atoms are, the better the mutual p-orbital overlap. The In_2P molecule does not have to bend as much in order to get some overlap between the end-atom atomic orbitals as does Ga_2As . The In-In bond distance is calculated to be 0.3 Å longer than the Ga-Ga bond distance, while the bulk In-P bond distance is only 0.09 Å longer than the GaAs bulk bond distance. Therefore, it is possible that the electronic character of In_2P is more sensitive to the bend (i.e., stronger Renner-Teller interaction, which subsequently implies a smaller bond angle in the bent component) than does Ga_2As .

Another interesting difference between the two species that can be extracted from the spectra is that the $\text{In}_2\text{P}^+ \nu_2$ frequency was found to be much higher than the neutral ν_2 frequency, while for Ga_2As , the anion and neutral frequencies are comparable. All of this points to the $1b_1$ orbital having more In-In bonding character in In_2P than Ga-Ga bonding in Ga_2As , which is the result of the stronger Renner-Teller interaction for the indium phosphide. Unfortunately, the anion frequencies determined from the spectra are not definitive; they are based to a large extent on progression profiles which could be affected by other things such as mode coupling. Hence, the above arguments should be considered only speculative, and naturally, some higher-level frequency calculations are desired for these complex species.

V. Conclusion

The negative ion photodetachment spectra of small gallium arsenide clusters presented in this paper exhibit the electronic complexity characteristic of small semiconductor clusters. The PES of mass-resolved Ga_xAs_y^- ($x = 1, 2$; $y = 1, 2, 3$) obtained using 4.66 eV photon energy access at least two electronic bands for each cluster, and in the case of Ga_2As^- , the higher-resolution ZEKE spectrum reveals two partially overlapping electronic transitions where only one is observed in the PES. The PES of GaAs_2^- and GaAs_3^- show considerably more structure than

their InP_y^- counterparts, suggesting that the As atoms dominate the bonding in these As-rich species. The Ga_2As_y^- spectra more closely resemble the analogous In_2P_y^- clusters, and the similar electronic structures suggest more equivalent bonding between all of the atoms in the cluster. The Ga_2As_2^- spectrum is even similar to the PES of isoelectronic Si_4^- , further supporting this assessment.

The higher-resolution PES of GaAs^- shows partially-resolved electronic transitions to the low-lying triplet states of neutral GaAs as well as well-resolved transitions to the higher-lying singlet states. Analysis of the singlet band, which lies approximately 0.55 eV higher in energy than the triplet band, indicates that the $^2\Pi$ (3/2) anion state lies 80 cm^{-1} higher than the $^2\Sigma^+$ ground anion state. Also, the $^1\Sigma^+$ excited neutral state lies 1306 cm^{-1} higher than the $^1\Pi$ state, which is the lowest-lying of the neutral states.

The ZEKE spectrum of Ga_2As^- shows two close-lying neutral transitions that appear to be transitions from the 1A_1 anion state to the bent 2B_1 and linear 2A_1 ($^2\Pi_u$) neutral states, which are the two components of a Renner-Teller pair. The two states are approximately 160 cm^{-1} apart, suggesting that the 2B_1 component has a very broad bend angle. Two vibrational modes are active in both bands. For the bent component, the ν_2 bend is $50 \pm 2\text{ cm}^{-1}$, and the ν_1 symmetric stretch is determined to be approximately 160 cm^{-1} from spectral simulations. This is identical to a line observed in GaAs clusters trapped in rare gas matrices that could be attributed to ν_1 of the Ga_2As ground state [Ref. (19)]. In the transition to the linear component, the progression in the $47.0 \pm 0.7\text{ cm}^{-1}$ bend mode is much more extended, and the stretch frequency is 171 cm^{-1} . The anion stretch is determined from a hot band transitions to be 259 cm^{-1} . The ZEKE spectrum of Ga_2As^- differs from the spectrum of In_2P^- in that the In_2P^- spectrum only exhibits one distinct electronic transition. This is counterintuitive based on the remarkable similarity between the respective PES. This suggests that while the electronic structures are similar between these species, the bonding between the constituent atoms, the

group III atoms in particular, is different. This may be due to the differences in the atomic sizes or the disparate polarities along the III-V bonds.

Acknowledgments

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Table (10.1) Adiabatic electron affinities and term energies of the low-lying electronic states of Ga_xAs_y clusters ($x = 1, 2$; $y = 1, 2, 3$). For $y > 1$, values are determined from the 4.657 eV PES and are considered good to ± 0.05 eV. For Ga_2As , the EA is determined from the origin of the ZEKE spectrum, and the $T_e(\text{A})$ is from the 4.657 eV PES. The EA and T_e 's for GaAs are determined from the 2.98 eV PES.

Cluster	Energetics (eV)	Cluster	Energetics (eV)	Cluster	Energetics (eV)
GaAs		GaAs_2	EA = 1.83 $T_e(\text{A}) = 0.74$ $T_e(\text{B}) = 2.01$	GaAs_3	EA = 1.951 $T_e(\text{A}) = 0.43$ $T_e(\text{B}) = 1.06$ $T_e(\text{C}) = 1.87$
Ga_2As	EA = 2.452* $T_e(\text{A}) = 0.30$	Ga_2As_2	EA = 1.87 $T_e(\text{A}) = 0.70$ $T_e(\text{B}) = 1.59$ $T_e(\text{C}) = 2.41$	Ga_2As_3	EA = 2.66 $T_e(\text{A}) = 0.38$

Table (10.2) Peak positions and relative energies for the PES of GaAs⁻ obtained using 2.98 eV photon energy.

Peak	Peak Position, eKE (eV)	Relative energy (cm ⁻¹)	Tentative Assignment
c	1.039	-460	
b	1.022 [†]	-323	
a	1.005 [*]	-186	
1	0.982 ^{††}	0	
2	0.962	161	
3	0.955 [†]	218	
4	0.929 [*]	427	
5	0.896	694	
6	0.871 [*]	895	
7	0.861	976	
8	0.838 [*]	1161	
9	0.806 [*]	1419	
10	0.797 [*]	1492	
11	0.766	1742	
12	0.751 [*]	1863	
13	0.736 [*]	1984	
14	0.708 [*]	2210	
15	0.676 [*]	2468	
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16	0.579 [†]	3250	
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17	0.447 [†]	4315	$^1\Pi (v' = 0) \leftarrow ^2\Pi (3/2) (v'' = 1)$
18	0.434 [†]	4420	
19	0.416 [†]	4565	$^1\Pi (v' = 0) \leftarrow ^2\Pi (3/2) (v'' = 0)$
20	0.406	4645	$^1\Pi (v' = 0) \leftarrow ^2\Sigma^+ (v'' = 0)$
21	0.381	4847	$^1\Pi (v' = 1) \leftarrow ^2\Pi (3/2) (v'' = 0)$
22	0.368 [*]	4952	$^1\Pi (v' = 1) \leftarrow ^2\Sigma^+ (v'' = 0)$
23	0.345 [†]	5137	$^1\Pi (v' = 2) \leftarrow ^2\Pi (3/2) (v'' = 0)$
24	0.335 [*]	5218	$^1\Pi (v' = 2) \leftarrow ^2\Sigma^+ (v'' = 0)$
25	0.305 [*]	5460	
26	0.292 [†]	5565	$^1\Pi (v' = 3) \leftarrow ^2\Sigma^+ (v'' = 0)$
27	0.277	5686	
28	0.254 [†]	5871	$^1\Sigma^+ (v' = 0) \leftarrow ^2\Sigma^+ (v'' = 0)$
29	0.219 [†]	6154	

Table (10.3) Peak positions and relative energies for the ZEKE spectrum of Ga_2As^- .

Peak	Position (cm^{-1})	Relative Energy (cm^{-1})	Tentative Assignment
$x_{\text{D}}'(0)$	19 518	-259	$X(1_1^0)$
$x_{\text{D}}'(1)$	19 551	-226	$X(1_1^0 2_0^1)$
$x_{\text{D}}'(2)$	19 569	-208	$X(1_1^0 2_0^2)$
	19 729	-48	$X(2_0^0)$
$X_{\text{D}}(0)$	19 777	0	Band X origin
$X_{\text{D}}(1)$	19 827	50	$X(2_0^1)$
$X_{\text{D}}(2)$	19 876	96	$X(2_0^2)$
	19 897	120	$A(2_0^0)$
$X_{\text{D}}(3)$	19 922	145	$X(2_0^3)$
$X_{1\text{D}}(0)$	19 938	161	$X(1_0^1)$
$A_{\text{D}}(0)$	19 950	173	Band A origin
$X_{1\text{D}}(1)$	19 975	198	$X(1_0^1 2_0^1)$
$A_{\text{D}}(1)$	19 988	211	$A(2_0^1)$
$A_{\text{D}}(2)$	20 039	262	$A(2_0^2)$
	20 071	294	$A(1_0^1 2_0^1)$
$A_{\text{D}}(3)$	20 085	308	$A(2_0^3)$
$A_{1\text{D}}(0)$	20 114	337	$A(1_0^0)$
$A_{\text{D}}(4)$	20 131	354	$A(2_0^4)$
$A_{1\text{D}}(1)$	20 163	386	$A(1_0^1 2_0^1)$
$A_{\text{D}}(5)$	20 178	401	$A(2_0^5)$
$A_{1\text{D}}(2)$	20 209	432	$A(1_0^1 2_0^2)$
$A_{\text{D}}(6)$	20 229	452	$A(2_0^6)$
$A_{1\text{D}}(3), [A_{\text{D}}(7)]$	20 257 [20 279]	480 [502]	$A(1_0^1 2_0^3), [(2_0^7)]$
$A_{1\text{D}}(4)$	20 306	539	$A(1_0^1 2_0^4), (1_0^2)$
$A_{1\text{D}}(5)$	20 356	579	$A(1_0^1 2_0^5), (1_0^2 2_0^1)$
$A_{1\text{D}}(6)$	20 402	625	$A(1_0^1 2_0^6), (1_0^2 2_0^2)$
$A_{1\text{D}}(7)$	20 450	673	$A(1_0^1 2_0^7), (1_0^2 2_0^3)$
$A_{1\text{D}}(8)$	20 501	724	$A(1_0^1 2_0^8), (1_0^2 2_0^4)$

Figure (10.1) Anion PES of small Ga_xAs_y clusters obtained using 4.66 eV photon energy.

Figure (10.2) Higher resolution PES of GaAs obtained at three different laser polarizations and a photon energy of 2.98 eV.

Figure (10.3) Comparison of 4.66 eV PES (dashed line) and ZEKE spectra (solid line) of Ga_2As^- (upper traces) and isoelectronic In_2P^- (lower traces).

Figure (10.4) ZEKE spectrum of Ga_2As^+ .

Figure 10.5 One-electron transitions between the two low-lying electronic states of GaAs^- and the five lowest-lying electronic states of GaAs .

Chapter 11. The power of negative ion ZEKE Spectroscopy; an aside on the $\text{I}^-\cdot\text{CH}_3\text{I}$ $\text{S}_{\text{N}}2$ reaction complex

Abstract

The negative ion zero electron kinetic energy (ZEKE) spectrum of $\text{I}^-\cdot\text{CH}_3\text{I}$ is presented and discussed. In addition to the high frequency vibrational structure previously seen in the photoelectron spectrum (PES) of $\text{I}^-\cdot\text{CH}_3\text{I}$, the ZEKE spectrum reveals low frequency vibrational structure due to excitation in two van der Waals modes in the ground (**X**) state of the neutral $\text{I}\cdot\text{CH}_3\text{I}$ complex. Of the two other excited states of the neutral complex, the **I** state is not distinctly observed, and no vibrational structure due to van der Waals motion is observed for the **II** state.

I. Introduction

The dynamics of the intermediates of an $X^- + CH_3Y \rightarrow CH_3X + Y^-$ gas phase S_N2 reaction have recently been the focus of considerable investigation, both theoretically and experimentally.^{1,2,3,4,5,6,7,8,9} The ion-dipole stabilized $I^-\cdot CH_3I$ complex, an intermediate in the $I^- + CH_3I$ identity reaction, has been of particular interest. Recently, Cyr *et al.* have combined photoelectron spectroscopy (PES)¹ with photofragmentation studies² to show that charge-transfer excited states of $I^-\cdot CH_3I$, which are believed to be important in the reaction,³ lie near the detachment continuum of the anion complex. The vibrational structure observed in the PES of $I^-\cdot CH_3I$ suggests that the C-I bond in the nominally neutral methyl iodide moiety has an elongated C-I bond, which is likely the result of the ground ion-dipole state mixing with the charge transfer state.¹ This bond elongation has also been predicted in recent calculations by Truhlar.⁴

The experiments Cyr *et al.* are quite striking in that photofragmentation of $I^-\cdot CH_3I$ into an anion and neutral fragment is only observed in the vicinity of the threshold for photodetachment. This situation represents an intra-cluster analogue of the phenomenon recently reported by Chupka and co-workers in which I^- is observed in the multiphoton ionization of CH_3I by dissociative attachment of low energy photoelectrons onto CH_3I .¹⁰ In order to better understand the competition between photofragmentation and photodetachment, it is useful to characterize the neutral $I\cdot CH_3I$ complex formed by photodetachment of the anion to a greater extent than was possible from the photoelectron spectrum alone. In this paper, we present the higher resolution negative ion zero electron kinetic energy, or ZEKE, spectrum of $I^-\cdot CH_3I$ in which we observe that the neutral complex is bound sufficiently strongly to support several van der Waals- type vibrations, at least in the ground spin-orbit state. Van der Waals vibrational structure has also been observed in previously obtained negative ion ZEKE spectra of the similar but simpler ion-neutral complexes, namely $I^-\cdot CO_2$ ¹¹ and several rare-gas halides.¹² The implications of our

results on the $\text{I}^-\text{CH}_3\text{I}$ complex will be discussed in the context of the PES and photofragmentation studies.

II. Experimental

The anion ZEKE apparatus has been described in detail previously,¹³ but the basic operation is as follows. The $\text{I}^-\text{CH}_3\text{I}$ complexes are generated and cooled in a pulsed free jet intersected by a 1 keV electron beam per the methods of Johnson and Lineberger¹⁴ and are mass-selected using time-of-flight. The $\text{I}^-\text{CH}_3\text{I}$ complex is then photodetached using a tunable dye laser, and those electrons detached with nearly zero electron kinetic energy are collected as a function of detachment wavelength. This selective detection of low-kinetic energy electrons, based on methods developed by Müller-Dethlefs *et al.*,¹⁵ yields an energy resolution as good as $\pm 3 \text{ cm}^{-1}$. The electron signal is normalized to laser power and ion current. The dyes used in the scans on $\text{I}^-\text{CH}_3\text{I}$ are DMQ and Coumarin 540. The latter was doubled using a BBO 1 doubling crystal. The spectra were signal averaged for over 3600 shots per point.

III. Results and Discussion

The ZEKE spectrum and the previously obtained PES² of $\text{I}^-\text{CH}_3\text{I}$ are shown in Figure (11.1), where the top panel shows the PES obtained using a detachment wavelength of 4.66 eV, the center panel shows the ZEKE spectrum of band X in the PES, and the lower panel shows the ZEKE spectrum of band II in the PES. Band X in both the ZEKE spectrum and the PES corresponds to the transition to $\text{I} (^2\text{P}_{3/2})\text{-CH}_3\text{I}$ complex from the anion, and band II is the transition to the spin-orbit excited $\text{I} (^2\text{P}_{1/2})\text{-CH}_3\text{I}$ complex. The two bands are separated by $0.955 \pm 0.020 \text{ eV}$ in the ZEKE spectrum, which is very close to the spin-orbit splitting in the bare neutral iodine atom, 0.943 eV. Also, compared to the spectrum of bare I^- , these features are

shifted to higher photon energy by 0.365 ± 0.020 eV, which is fairly close to the enthalpy of formation for the ion dipole complex, $\Delta H_a = -0.39 \pm 0.01$ eV.¹⁶

Both the photoelectron and ZEKE spectra exhibit high-frequency vibrational structure associated with excitation of vibrations in the neutral methyl iodide moiety: nominally the ν_3 C-I stretch in CH_3I . The ν_3 frequency extracted from the position of this 3_0^1 transition in the ZEKE spectrum is approximately 550 ± 20 cm^{-1} , which is very close to the ν_3 frequency of bare CH_3I , 533 cm^{-1} .¹⁷ However, band X in the ZEKE spectrum exhibits further (partially) resolved low-frequency vibrational structure with spacings on the order of tens of wave numbers. This structure, the spacing of which is consistent with motion along a van der Waals bond, shows that this particular state of the neutral-dipole $\text{I}\cdots\text{CH}_3\text{I}$ complex is bound. The noise level in the ZEKE spectrum of band II is such that no definite structure could be unambiguously discerned. Since the van der Waals well for the excited spin-orbit state is almost certainly shallower than that for the ground state,^{11,12} the resulting lower frequency vibrational structure may be too congested to be resolved.

While the quality of the spectrum does not warrant the extensive analysis that we have previously applied to other weakly bound systems,¹¹ there is a definite pattern to the positions of most of the peaks in the origin band. In order to find the simplest possible picture of the vibrational structure, we have performed a simulation within the Franck-Condon approximation, in which transitions between vibrational levels of the anion (ν_n^-) and the neutral (ν_n) are assumed proportional to their Franck-Condon factors, $|\langle \nu_n^- | \nu_n \rangle|^2$. Figure (11.2) shows a simulation (solid trace) superimposed onto the ZEKE data (dotted trace). The simulation includes two low-frequency modes of the neutral, and the neutral vibrational wave function was taken to be the product of a Morse oscillator wave function with $\omega_e = 54.9$ cm^{-1} , $\omega_e x_e = 0.4$ cm^{-1} (mode A) and a harmonic oscillator with $\omega_e = 33$ cm^{-1} (mode B). For a reasonable fit, the anion geometry had to be displaced substantially and comparably along both vibrational coordinates of the neutral. Therefore, the majority of the structure in the simulation is the result of combination

bands (e.g., $A_0^x B_0^y$, $x, y = 1, 2, \dots$) in these two modes. The $A_0^x B_0^1$ progression in the simulation is indicated on the comb in Figure (11.2) to guide the eye.

There is likely to be some excitation of the low frequency anion modes as well, but due to the overall congestion of the ZEKE spectrum, it is difficult to determine which structure is due to hot bands or sequence bands, making the choice of anion frequencies for the simulation somewhat arbitrary. However, we found that if the anion frequency corresponding to mode A is chosen to be approximately 100 cm^{-1} , the width of the simulated progression is in fairly good agreement with the observed progression. Moreover, if the anion frequency of mode B was made to be 53 cm^{-1} (20 cm^{-1} greater than the neutral frequency), the level of congestion due to hot bands, and thus the intensities of peaks in the fit were closer to the experimental peak intensities. The choice of larger frequencies in the anion relative to the neutral is consistent with the stronger $\text{I}^-\cdots(\text{CH}_3\text{I})$ interaction in the ion-dipole complex. For the particular simulation shown in Figure (11.2), the origin was placed at 365.04 nm , the anion wave function was displaced from the neutral wave function substantially and comparably along the coordinates of *both* the 33 cm^{-1} and the 55 cm^{-1} modes, and anion vibrational levels were thermally populated at 50 K . It should be noted that even assuming zero vibrational temperature in the anion, most of the peak positions could be matched simply assuming a large activation in the two neutral frequencies. Including transitions from excited anion levels in the simulation serves primarily to fill in some of the intensity.¹⁸

Truhlar calculated the two lowest frequency modes of the anion to be 64 cm^{-1} and 66 cm^{-1} ; the 100 cm^{-1} anion frequency used in our simulations is substantially higher than either of these. Simulations using Truhlar's anion frequencies gave profiles much more extended than in the experimental spectrum. In particular, when either the 64 cm^{-1} or 66 cm^{-1} frequency modes were taken as the anion mode corresponding to the neutral 55 cm^{-1} mode, the peak of the extended progression could be appropriately simulated, but the simulated structure would tail much further to both the red and blue of the progression maximum than what is observed.

However, because our treatment of what is likely a very complicated system is so simplified, our anion frequencies cannot be considered definitive. On the other hand, the two neutral frequencies are better determined as they correspond to observed peak spacings.

We now consider the electronic states of the anion and neutral, and the observed vibrational structure in terms of these electronic states. The anion electronic structure is fairly straightforward: a closed-shell anion is bound to a closed-shell neutral molecule by both charge-dipole and dipole-induced dipole interactions in addition to some charge-transfer between the I^- and CH_3I .³ The calculations by Truhlar⁴ suggest that the I^-CH_3I complex has C_{3v} symmetry, and the anion electronic state is best described as a 1A_1 state. As mentioned above, Truhlar's vibrational frequency calculations found two low frequency modes involving $I^- - (CH_3I)$ relative motion. The 66 cm^{-1} mode is the $\nu_4(a_1)$ I^-C stretch and the 64 cm^{-1} frequency corresponds to ν_8 , a degenerate (e) rocking mode. The calculated anion frequencies are too close to suggest whether the neutral a_1 or e van der Waals mode should have the higher frequency.

In contrast to the simple closed-shell/closed-shell interaction of the anion, the interaction between an open shell, anisotropic neutral halogen and a closed-shell moiety is complicated by spin-orbit and orientation effects. These considerations have been discussed in our previous work on I^-CO_2 ¹¹ and $Rg-X^-$ ($Rg = Ar, Kr, Xe$; $X = I, Br, Cl$).^{1,19} Figure (11.3) shows a schematic correlation diagram with the three electronic states of the neutral resulting from this interaction. Approximating $I-CH_3I$ as a point dipole (CH_3I) interacting with an iodine atom, the electrostatic interactions cause a splitting of the $2P_{3/2}$ ground spin-orbit level of iodine into an $\Omega = 1/2$ X state, and an $\Omega = 3/2$ I state, where Ω is the projection of the electronic orbital and spin angular momentum onto the C-I axis. In the Hund's case (c) limit, the X state is composed of $1/3 \Pi$ and $2/3 \Sigma$ character, and the I state has only Π character.²⁰ The $2P_{1/2}$ level is not split; the resulting $\Omega = 1/2$ II state has $2/3 \Pi$ and $1/3 \Sigma$ character in the case (c) limit. The well-depth of the X state is the deepest, with the smallest equilibrium internuclear (r_{C-I}) separation, and the I state is the shallowest of the three states with the largest equilibrium internuclear separation.

From the extent of the structure in the $\text{I}^-\text{CH}_3\text{I}$ ZEKE spectrum, we can determine a lower limit of the well depth of the X state of $\text{I-CH}_3\text{I}$ to be 250 cm^{-1} . The true well depth is likely to be considerably larger; the well-depth of the I-CO_2 X state was more rigorously determined to be 359 cm^{-1} ,¹¹ and the $\text{I-CH}_3\text{I}$ well-depth is likely to be greater than this due to the stronger ion-dipole interaction.

The open shell nature of the neutral is also important in considering the vibrational structure associated with the X state. Our analysis shows that at least two van der Waals modes are active, but only one of these (the ν_4 mode) is totally symmetric in the C_{3v} point group. A progression in the degenerate ν_8 mode (with e symmetry) would normally not be expected if both the anion and neutral have C_{3v} symmetry; although transitions in which Δv is even are allowed by symmetry, an extended progression in this mode is highly unlikely based on Franck-Condon factors alone.²¹ Since Π states correlate to degenerate E states in C_{3v} symmetry, the X state (and the other two electronic states) of $\text{I-CH}_3\text{I}$ should possess have some E character. These states can then undergo Jahn-Teller distortion, thereby activating the low-frequency degenerate vibrational mode. This effect is well known in $\text{E} \leftarrow \text{A}$ electronic transitions,²² but is less well-characterized for systems with large spin-orbit coupling such as $\text{I-CH}_3\text{I}$.

The ZEKE spectra of I^-CO_2 and several of rare gas halides show transitions to the I state of the neutral lying quite close to the X band: the X-I splitting varies from 225 cm^{-1} for I-CO_2 ¹¹ to $30\text{-}40\text{ cm}^{-1}$ for rare gas halogen dimers containing Ar or Kr .^{12,19} There is indirect evidence for a close-lying I state in the $\text{I}^-\text{CH}_3\text{I}$ photoelectron spectrum; the peak widths in band X vary with the polarization direction of the photodetachment laser, suggesting they may consist of overlapping electronic transitions. However, no distinct I band is observed in the ZEKE spectrum of $\text{I}^-\text{CH}_3\text{I}$. The likely reason for this is that the potential energy minimum for the van der Waals stretch in the neutral I state lies at a considerably larger internuclear distance than the minimum in the corresponding anion potential. This means that a vertical transition from the anion accesses the repulsive wall of the I state, and resulting broad and featureless band would

be very difficult to observe in the ZEKE spectrum. Two factors favor this explanation. First of all, the dissociation energy of I^-CH_3I is substantially higher than that of I^-CO_2 , 0.39 eV vs. 0.212 eV. Secondly, comparing the neutral complexes, one expects the I atom to interact more strongly with CH_3I than with CO_2 because of the permanent dipole moment in CH_3I . This should result in an increased splitting between the X and I states, along with a larger difference in the equilibrium internuclear distances. Thus, compared to I^-CO_2 , one expects a larger difference in the equilibrium internuclear distances between the anion and I states for I^-CH_3I photodetachment. A preliminary analysis indicates that the I band is missing in the $XeBr^-$ ZEKE spectrum for the same reason.¹⁹

The above discussion offers an explanation of an interesting result observed by Cyr *et al.*² They found that the fast neutral peak resulting from photodetachment of I^-CH_3I at 266 nm was somewhat broader than the parent ion peak, indicating the production of *neutral* $I + CH_3I$ photofragments with *nonzero* relative kinetic energy. These clearly must come from unbound states of the neutral complex that have Franck-Condon overlap with the anion. Transitions to the continuum of the I state could certainly account for their observation. It is also possible that they were observing vibrational predissociation from the $v_3 = 1$ levels of the X and I states.

To summarize, ZEKE spectroscopy of the S_N2 intermediate I^-CH_3I has been used to probe the open shell I^-CH_3I van der Waals complex. The band corresponding to transitions to the X state of the neutral shows vibrational structure from progressions in two low frequency van der Waals modes of the complex. As only one of these is totally symmetric, this suggests that the neutral complex undergoes Jahn-Teller distortion, activating the second (degenerate) mode. Transitions to the I state of the neutral complex were not apparent in the anion ZEKE spectrum. This was attributed to a significantly larger C-I bond distance I state compared to the anion, resulting in transitions to the continuum levels of the I state. The II state is observed, but no vibrational structure is resolved, possibly due to spectral congestion.

Acknowledgments

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¹⁸We also tried to fit the spectrum using displacement along only one of the normal coordinates, with two modes contributing to the *sequence band structure*. However, peak positions could not be as well matched, and the level of congestion we could simulate in this manner did not approach the congestion that is observed.

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Figure (11.1) Previously obtained PES [Ref. (2)] and ZEKE spectrum of $\text{I}^-\text{CH}_3\text{I}$. The PES shown in the upper panel was obtained using 4.66 eV detachment energy. The center and lower panels show the ZEKE spectrum in the energy region of the transition to the ground and excited spin-orbit states, respectively, of the neutral complex.

Figure (11.2) ZEKE spectrum of $\text{I}^-\text{CH}_3\text{I}$ shown on an expanded scale near the origin of band X (dotted line) superimposed onto a spectral fit (solid line, see text).

Figure (11.3) Schematic of the electronic states resulting from the electrostatic interaction between I^- and I with CH_3I .

Appendix I

Publications

- "Study of $\text{In}_2\text{P}/\text{In}_2\text{P}^-$ and $\text{InP}_2/\text{InP}_2^-$ using negative ion threshold photodetachment spectroscopy," Caroline C. Arnold and Daniel M. Neumark, accepted for publication, *Canadian Journal of Physics* (1994).
- "Negative Ion Threshold Photodetachment Spectroscopy of the $\text{I}^--\text{CH}_3\text{I}$ $\text{S}_{\text{N}}2$ Reaction Intermediate," Caroline C. Arnold, Daniel M. Neumark, Donna M. Cyr, and Mark A. Johnson, accepted for publication, *Journal of Physical Chemistry* (1994).
- "Anion Photoelectron Spectroscopy of Small Indium Phosphide Clusters (In_xP_y^- ; $x, y = 1 - 4$)," Cangshan Xu, Esther de Beer, Don W. Arnold, Caroline C. Arnold, and Daniel M. Neumark, *Journal of Chemical Physics*, **101**, 5604 (1994).
- "The study of small carbon and silicon clusters using negative ion photodetachment techniques," Caroline C. Arnold and Daniel M. Neumark, *Advances in Metal and Semiconductor Clusters, Vol. III*, Edited by M. Duncan, JAI Press, Greenwich (1994).
- "Threshold Photodetachment (ZEKE) Spectroscopy of Si_3^- ," Caroline C. Arnold and Daniel M. Neumark, *Journal of Chemical Physics* **100**, 1797 (1994).
- "Study of Si_4 and Si_4^- using Threshold Photodetachment (ZEKE) Spectroscopy," Caroline C. Arnold and Daniel M. Neumark, *Journal of Chemical Physics* **99**, 3353 (1993).
- "Study of C_6^- and C_6 with Threshold Photodetachment Spectroscopy and Autodetachment Spectroscopy- Reply," Caroline C. Arnold and Daniel M. Neumark, *Journal of Chemical Physics* **99**, 1442 (1993).
- "Reassignment of the Si_2^- Photodetachment Spectra," Caroline C. Arnold, Theofanis N. Kitsopoulos and Daniel M. Neumark, *Journal of Chemical Physics* **99**, 766 (1993).
- "Study of the $\text{I}-\text{CO}_2$ van der Waals Complex by Threshold Photodetachment Spectroscopy of $\text{I}-\text{CO}_2^-$," Yuexing X. Zhao, Caroline C. Arnold and Daniel M. Neumark, *Journal of the Chemical Society- Faraday Transactions* **89**, 1449 (1993).
- "Study of C_6^- and C_6 with Threshold Photodetachment Spectroscopy and Autodetachment Spectroscopy," Caroline C. Arnold, Yuexing X. Zhao, Theofanis N. Kitsopoulos and Daniel M. Neumark, *Journal of Chemical Physics* **97**, 6121 (1992).
- "Dielectric Relaxation of Intercalated $\text{Cd}_2\text{P}_2\text{S}_6$," Jeff A. Read, Caroline Chick and Anthony H. Francis, *Journal of Physical Chemistry* **96**, 2010 (1992).

- "Threshold Photodetachment Spectroscopy of C_5^- ," Theofanis N. Kitsopoulos, Caroline J. Chick, Yuexing Zhao and Daniel M. Neumark, *Journal of Chemical Physics* **95**, 5479 (1991).
- "Study of the Low-lying Electronic States of Si_2^- and Si_2^+ Using Negative Ion Photodetachment Techniques," Theofanis N. Kitsopoulos, Caroline J. Chick, Yuexing Zhao and Daniel M. Neumark, *Journal of Chemical Physics* **95**, 1441 (1991).
- "Vibrationally Resolved Photoelectron Spectra of Si_3^- and Si_4^- ," Theofanis N. Kitsopoulos, Caroline J. Chick, Alexandra Weaver and Daniel M. Neumark, *Journal of Chemical Physics* **93**, 6108 (1990).

Submitted for publication or in preparation

- "Study of small gallium arsenide clusters using negative ion photodetachment techniques," Caroline C. Arnold, Cangshan Xu, Gordon R. Burton, and Daniel M. Neumark, in preparation.
- "Study of the low-lying states of Ge_2^- and Ge_2 using negative ion ZEKE spectroscopy," Caroline C. Arnold, Cangshan Xu, Gordon R. Burton, and Daniel M. Neumark, in preparation.
- "Study of the $ArBr^-$, ArI^- , and KrI^- Anions and their Corresponding Neutral van der Waals Complexes by Anion Zero Electron Kinetic Energy Spectroscopy," Yuexing Zhao, Georg Reiser, Ivan Yourshaw, Caroline C. Arnold, and Daniel M. Neumark, submitted to *Journal of Chemical Physics*, May, 1994.

Appendix II

Jahn-Teller interaction code (Fortran)

Program jtchick

```
c This program, written by CCArnold 26 May 93, sets up a matrix for
c a degenerate D3h state (e.g., Si3-) experiencing Jahn-Teller
c distortion. The Matrix, all of the eigenvalues and eigenfunctions
c are put into fort.9, and a shortened version is in fort.8. The
c immediate output gives the matrix elements individually.
c
c format using f77 -O jtchick1.f -o jtchick1 -lnagd
c ndim is 2*(n + 0.5(n-1)) where n is max vib quantum number

Parameter (ndim=420)
implicit double precision (a-h,0-z)
double precision evals (ndim),evecs(ndim,ndim)
double precision wk(ndim)
real*8 PROT(ndim,ndim)

write(9,*)'Chick j-t coupling code output'
write(8,*)'chick short jt output'
write(8,*)'from jtchick.f'
write(9,*)''
write(8,*)''

c puppy is the linear coupling constant,k, as in  $k \exp(i\phi)$ 
c g is the quadratic coupling constant, as in  $g(r^2) \exp(i2\phi)$ 

puppy = 1.9      ←for instance
g = 0.01         ←for instance

write(9,*) 'linear coupling term is',puppy
write(8,*) 'linear coupling term is',puppy
write(9,*) 'quadratic coupling term is',g
write(8,*) 'quadratic coupling term is',g
write(8,*)''

m=0
n=0

c I is the vibrational quantum, k is the ang mom quantum, and ii is
c the sign of the wv fn of the ket. ie, i, k, ii is <n m +/-| in
c the notation of Longuet-Higgins
c aj is the half quantum number
```

```

do 10 i = 1,20
write(*,*) 'i = ' i

do 20 k = i-1, -i+1, -2
do 25 ii = 1, -1, -2
aj = k*1.0 + 0.5*ii
m = m + 1

n=0

c j is the vibrational quantum, l is the ang mom quantum, and ii is
c the sign of the wfn of the bra. ie, j,l,jj is |n m +/->
c bj is the half-quantum number

do 20 j = 1,20
do 40 l=j-1,-j+1,-2
do 45 jj = 1,-1,-2
bj=1*1.0+0.5*jj

n=n+1

c write(*,*) 'm = ',m' n = ',n

if ((i.eq.j).and.(l.eq.(k+1)).and.(aj.eq.bj)) then
PROT(m,n)=i*1.0
endif

c These two terms set up linear coupling
if ((j.eq.(i+1)).and.(l.eq.(k+1)).and.(aj.eq.bj)) then
PROT(m,n)=puppy*sqrt(0.5*(i+k+1)*1.0)
endif

if ((i.eq.(j-1)).and.(k.eq.(l+1)).and.(aj.eq.bj)) then
PROT(m,n)=puppy*sqrt(0.5*(j-1-l)*1.0)
endif

c These three terms set up the quadratic coupling
if ((j.eq.(i+2)).and.(bj.eq.(aj+3.0))) then
PROT(m,n)=0.25*g*sqrt((i+k+1)*(i+k+3)*1.0)
endif

if ((i.eq.(j-2)).and.(aj.eq.(bj+3.0))) then
PROT(m,n)=0.25*g*sqrt((j-1-l)*(j-1-3)*1.0)
endif

if ((j.eq.i).and.(bj.eq.(aj+3.0))) then
PROT(m,n)=0.5*g*sqrt((i+k+1)*(i-k-1)*1.0)
endif

PROT(n,m)=PROT(m,n)

45 continue
40 continue
30 continue
25 continue
20 continue
10 continue

```