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PROGRESS REPORT AND RENEWAL PROPOSAL
ION DIP SPECTROSCOPY OF COLD MOLECULES AND IONS

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Abstract

A research program is underway with the objective of developing techniques of high resolution multiphoton spectroscopy for selective, ultrasensitive molecular detection. Methods under study include various forms of ion dip spectroscopy and new methods of ion fragmentation spectroscopy. The studies are providing a new understanding of the fundamental spectroscopy and photophysics of large molecular ions. Dimer and cluster ions of polynuclear aromatics and related species are also being investigated, with potential detection applications.

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TABLE OF CONTENTS

Introduction	1
Progress	
Upward Ion Dip Spectroscopy	4
Ion Fragmentation Spectroscopy	5
Proposal for Second Year	9
Direct Multiphoton Fragmentation	
Dimer and Cluster Fragmentation	11
Conclusion	12
References	14
Figures	15
Appendix	26
Reprint	27
Preprints	29

PROGRESS REPORT AND RENEWAL PROPOSAL
ION DIP SPECTROSCOPY OF COLD MOLECULES AND IONS

John Wessel, The Aerospace Corporation

Introduction.

Currently, we are at the midpoint of the two year research program on ion dip spectroscopy of cold molecules and ions. The objective of the effort is to develop new techniques of high resolution multiphoton spectroscopy. The new approaches provide the potential for outstanding spectral selectivity, combined with sensitivities that approach the single molecule detection limit. Direct optical detection methods fall far short of the selectivity desired for single molecule detection applications. Emphasis is being given to approaches that provide enhanced selectivity for ultrasensitive molecular detection by photoionization methods. The primary potential application is direct optical detection of potentially carcinogenic aromatic hydrocarbon vapors. A major goal is to provide discrimination between closely related species, such as structural isomers of alkyl substituted aromatic compounds. Currently, supersonic jet techniques provide a principal tool for fundamental studies of chemical reaction dynamics due to the state selectivity of the method [1,2]. In one phase of the proposed studies, described below, we are applying supersonic beam techniques to investigate ion spectroscopy and fragmentation processes in aromatic species. In another part of the program we are investigating ion cluster spectroscopy and fragmentation processes. In this document we review progress achieved during the last year and propose investigations for the following year of the program.

Spectral broadening, caused by thermal excitation of vibrational and rotational degrees of freedom, presents a major problem for application of ultrasensitive laser techniques to practical molecular detection problems. Supersonic beam cooling techniques and multiresonance excitation processes provide immense increases in spectral selectivity for detection applications. Low temperature spectroscopic techniques clearly have the potential to differentiate between geometrical isomers at sub-parts-per-trillion concentrations, and to do this without requiring chemical separation procedures. Therefore, the new techniques may be ideal for the most demanding environmental applications. The major emphasis of this proposed research program is to investigate and develop new spectroscopic techniques that can be used in conjunction with photoionization spectroscopy and supersonic cooling in order to increase selectivity. At the present stage of development, we need to know if the fundamental physical processes that form the basis of the new methods are generally applicable to molecules of interest, and we need to know if the models developed in our recent research apply to broad classes of molecules.

It is convenient to describe the different detection methods described here as being related forms of ion dip spectroscopy. They include downward ion dip spectroscopy, shown in Figure 1, which has been used in past scientific studies [3 -6], but up to now has not achieved its high potential selectivity. This method provides high resolution spectra of ground state vibrational energy levels with the high sensitivity of photoionization detection. Extensive information available about ground state vibrational energies of molecules (infrared and Raman spectra) provides a strong motivation to develop this method for detection applications. The method should be generally applicable to

molecules with stable upper excited electronic states.

The closely related approach of upward ion dip spectroscopy is less developed than the downward method. Using current experimental techniques, the upward method provides signals superior to those obtained for the downward method. The generality of upward ion dip spectroscopy has not been investigated, however it is clear that it can provide a wealth of scientific information concerning highly excited molecular states [7].

Multiphoton ionization-fragmentation spectroscopy [8], described in Figure 2, is a totally different type of ion dip spectroscopy. The fragmenting process is sensed as a dip in the parent ion signal when parent ions are converted into lighter fragments. This technique has the potential for high resolution ion spectroscopy, thereby providing a separate manifold of ion states useful for molecular identification. Prior studies of ion fragmentation processes lead to the conclusion that stepwise resonant multiphoton transitions of ions are broadened far beyond simple expectations based on the discrete 1-photon absorption spectra of the ion. Currently we are investigating this phenomenon and pursuing approaches that promise to overcome the power broadening and homogeneous broadening limitations. We are also exploring alternatives to multiphoton ion fragmentation, including 1-photon ultraviolet induced ion fragmentation and 1-photon near infrared induced cluster ion fragmentation.

PROGRESS

Upward Ion Dip Spectroscopy

Following our discovery last year of prominent upward ion dip transitions in aniline, revealing new highly excited states near the ionization limit of that molecule, this year we discovered unexpected discrete structure in the continuum region of the naphthalene molecule, when probed by 2-color resonance 2-photon ionization. A spectrum is shown in Figure 3, which was recorded by exciting a vibronic intermediate state of the neutral naphthalene molecule with wavelength W1, and then ionizing this state using a second wavelength, W2. The W2 laser source was scanned across the ionization spectrum. Since both W1 and W2 laser sources generated ionization signals by themselves, each individual signal was subtracted from the total signal, leaving the signal due to the combined effect of W1 and W2. An analysis of these unusual transitions led to the conclusion that they arise from Rydberg series associated with vibrationally excited ionization limits. Thus, the total energy is above the lowest ionization threshold, however ionization requires coupling of vibrational and electronic excitation. This involves interaction between a Rydberg state electron, which is weakly bound to the molecules ionic core, and the ionized state, which is tightly bound. It is a weak coupling, thereby accounting for the narrow observed linewidths. The lineshapes were highly asymmetric, and analysis demonstrated that they have the classic Fano profile, which is manifested when a discrete state, carrying oscillator strength, interacts with a continuum state that shares the oscillator strength. The phenomenon provides a highly

characteristic set of relatively discrete transitions, within an ordinarily featureless continuous spectrum. It may prove to be useful for selective detection purposes. The spectra indicate where ionization efficiency can be optimized, that is, at what excitation wavelengths oscillator strengths for discrete and continuum transitions add constructively. From the results, we were able to measure couplings between the Rydberg states and the ion and to accurately estimate lifetimes from linewidth parameters. The work is scheduled to appear in the Journal of Chemical Physics.

Ion Fragmentation Spectroscopy

Multiphoton ionization-fragmentation spectroscopy [8], described in Figure 2, is a totally different type of ion dip spectroscopy. The fragmenting process is sensed as a dip in the parent ion signal when parent ions are converted to lighter fragment ions. This technique has the potential for high resolution ion spectroscopy, thereby providing a separate manifold of ion states for molecular identification, and providing new research opportunities for spectroscopy of ions.

Initially, we anticipated that the mass fragmentation patterns would prove to be highly characteristic of parent PAH molecules. Subsequent work demonstrated that fragmentation processes of the PAH species are described moderately well by statistical models and that detailed information about closely related species, such as spectral structure differentiating geometric isomers, is obscured by the statistical fragmentation processes. As a consequence, we concluded that it was far more promising to seek selectivity by designing detection techniques

based on the highly distinctive absorption spectra of the ions created in multiphoton excitation processes.

Andrews and coworkers [9] discovered that in low temperature solidstate matrices, 1-photon absorption spectra of parent ions are characterized by discrete transitions that can be observed by direct optical absorption. The spectra sensitively reflect molecular properties, such as isomer structure. Therefore, we have investigated the corresponding photofragmentation spectra of ultracold isolated PAH ions in the gas phase. The search for discrete structure was more difficult than anticipated. We discovered that direct multiphoton fragmentation of cold ions typically yields power broadened spectra that obscure information about ion structure. Last year we proposed a model, shown in Figure 4, that could explain the broadening. The multiphoton fragmentation spectra are broadened because the red ion transition is overlapped by transitions based on a lower energy electronic state. The vibronic manifold of the lower energy electronic state that underlies the red states provides a near quasi-continuum of transitions throughout the red region. This furnishes the resonant states needed for efficient ionization far off-resonance from the discrete red transitions. The first absorption step in 2-photon fragmentation is efficiently pumped, even when slightly off-resonance at wavelengths intermediate between the discrete transitions of the red system, whenever intensity is high enough to induce efficient absorption of the second photon during the laser pulse. Simple molecular orbital (MO) energy level calculations predict that this should be a general trend for PAH species.

This year we designed experiments that would take this problem into account. A resulting spectrum, recorded for

2-methylnaphthalene (2MN) is shown in Figure 5. It reproduces the same vibrational structure observed by Andrews in solidstate media. The observed power dependence of the fragmentation spectra, shown in Figure 5, followed predictions of our model. There was clear evidence for continuum absorption in the ion due to highly excited vibronic levels associated with a lower energy electronic state, as previously proposed.

The above description was proposed in order to describe fragmentation spectra observed in the red spectral region, which had been studied extensively. Two red photons must be absorbed in order to reach the lowest energy fragmentation channel of the methylnaphthalenes. Andrews solidstate spectra suggested the presence of ultraviolet absorption bands for the ions. One ultraviolet photon is sufficient to induce fragmentation. This process should be less susceptible to power broadening. Our observed ultraviolet fragmentation spectrum for 2MN appears in Figure 6. It was recorded as the ratio of the fragment ion $(M-1)^+$ to parent ion (M^+) , thus compensating for the wavelength dependent production of parent ions. The ion absorption is represented by the broad feature centered near 308.7 nm. The sharp peaks at 308.4 and 308.6 nm in Figure 6 are generated at wavelengths where the W2 alone generates strong ionization through resonances in the S1 state. This ultraviolet fragmentation spectrum was not strongly affected by saturation effects. The absorption wavelength and linewidth are similar to those previously observed in solidstate media. Additional vibronic structure was not observed at higher energies, which provides evidence that geometry and electronic structure change little between the S1 state and the ion. Similar ultraviolet absorption bands were resolved in the fragmentation spectra for naphthalene, and additional transitions were studied

by ionizing different vibronic intermediate states in S1 naphthalene. In the case of naphthalene, two ultraviolet photons must be absorbed by the ion to reach the fragmentation threshold. Even in this case, power broadening was not observed under our experimental conditions. We concluded that the observed linewidths represent homogeneous broadening inherent to intramolecular dynamics of the molecules. It arises from resonance vibronic interaction between the state excited and highly excited vibrational combination levels associated with lower lying electronic states. This suggests that the sharpest ion spectra will be observed for transitions to the lowest energy excited states. For the naphthalenes, the transitions should occur in the 1.3-1.4 μm region.

Preliminary studies show that dimer fragmentation spectra can be recorded by monitoring mass peaks corresponding to dimer and higher species as a function of wavelength of the fragmenting laser. By this method, we recorded relatively continuous fragmentation spectra in the red region for the naphthalene dimer cation. The trimer and tetramer species provided highly structured spectra of great interest. We are currently attempting to understand the origin of these spectra and to optimize conditions for cluster ion spectroscopy. The preliminary observation is that these spectra are easily recorded and that the cluster abundance can be made substantial by proper adjustment of beam conditions.

PROPOSAL FOR THE SECOND YEAR

This year we discovered new autoionizing upward ion dip transitions to Rydberg states of the naphthalene molecule. Autoionizing transitions are excitations to discrete states above the lowest ionization potential (IP), which interact weakly with the underlying ionization continuum. This allows ionization of the molecule through discrete transitions. These transitions have important potential detection applications because they can have large cross sections (on the order of 10^{-14} cm^2 in a cold beam), whereas direct transitions to continuum states are characterized by relatively small cross sections (of order 10^{-17} cm^2). We propose to continue the studies, investigating analogous transitions in other polyatomic molecules. At present, we are not able to detect these transitions near or below the ionization limit. Investigations next year will seek to resolve these lower energy transitions, with the goal of discovering sharp, zero background, spectroscopic features below the ionization limit that improve selectivity.

Direct Multiphoton Fragmentation

We intend to pursue studies of ion spectra, measured in two different ways, by fragmentation processes. The first of these is to excite directly the lowest energy electronic transition of the ion. This lowest excited state is not expected to be subject to strong coupling to the ground state. It is expected to be observed in the near infrared (at about $1.3 \mu\text{m}$ for naphthalene). This transition is formally symmetry allowed for the methylnaphthalenes, but symmetry forbidden for the naphthalene ion. (Even in the case of naphthalene, this is not expected to be

a problem, because vibronic coupling induced by u symmetry vibrations will intensify vibronic transitions to u symmetry levels. Typically, the dipole cross sections for these transitions will be a factor of 10 to 100 smaller than those for a fully allowed transition. Methylanthalene transitions will be an order of magnitude larger.) For sharp transitions, we expect resultant cross sections to range from 10^{-15} cm² to 10^{-16} cm². Given these cross sections, population transfer will be efficient at easily accessible pump intensities (10^6 W/cm²). Absorption of a second, higher energy photon, is then required in order to induce fragmentation through the hydrogen loss channel, for alkyl species (whereas, three more red photons will be required for naphthalene fragmentation). The PAH species have convenient strong red transitions, that will provide nearly continuous absorption, once electronic excitation from the first near infrared photon has undergone internal conversion to the ground electronic state. A simple experimental scheme facilitates this experiment. It is based on Raman shifting the output of a red laser source into the 1.3 μ m region in order to pump the first electronic transition, and then using the time delayed red pulse to increase the ion energy above the fragmentation threshold. The relative intensities of the beams will be adjusted to the ratio required for optimum pumping of the two transitions. The Raman shifted beam will be scanned by varying the wavelength of the red pump beam. Therefore the broad spectral dependence of the second transition will modulate the observed fragmentation spectrum. The red beam will be separated from, and delayed relative to the Raman shifted beam, using standard dichroic beam splitters. A hydrogen Raman cell will be used to shift the dye laser output by 4155 cm⁻¹, which is appropriate for spectroscopy of the first

electronic state of ions.

Dimer and Cluster Fragmentation

Our recent ion fragmentation experiments suggest an entirely different approach for ultrasensitive detection of ion fragmentation. In this method, supersonic beam expansion conditions are adjusted to favor formation of molecular dimers, vander Waals dimer species, or formation of larger molecular clusters. Ions of these species are then prepared by resonance enhanced photoionization under conditions that yield cold ions. Spectra of the dimer ions or cluster ions should resemble those of the monomer ions, analogous to the resemblance between absorption spectra of neutral monomers, dimers and larger clusters. Our studies indicate that the cold dimer and larger ions can be formed abundantly in the supersonic beam. They have relatively low dissociation thresholds. Therefore we will monitor fragmentation of the dimer ions induced by absorption of red laser photons. The available data indicate that for the cluster species, absorbed electronic energy is efficiently converted into internal vibrational energy, which then breaks intermolecular bonds. The rate of this process is unknown for PAH cluster ions. However, for simple neutral vander Waals species, such as benzene--He, Ne, Ar, etc. [10], this process occurs on a picosecond time scale, with resultant lifetime broadening typically 1 to 10 cm^{-1} . If cluster ions are characterized by similar fragmentation kinetics, this will be a highly useful detection technique. Obviously, it will be necessary to select molecular beam conditions appropriate to formation of the desired species. There is considerable freedom in choice of buffer species in the expansion mixtures, the temperature can be varied over a wide range, and preexpansion

pressure, nozzle diameter and nozzle length, can be varied so as to control cluster size distribution. We observed conditions where dimers and larger cluster ions appear to dominate over monomer species for the methylnaphthalenes. Spectroscopy of the cluster ions is of intrinsic interest, and can elucidate the relationship between matrix spectra and free jet spectra for ionic species.

In Figure 7a we show the mass spectrum of the dimer ion generated using UV excitation only in a supersonic beam. The mass spectrum obtained upon introduction of an additional 620 nm fragmenting beam is shown in Figure 7b. The dimer ion is efficiently dissociated at moderately low red intensities, producing additional parent ion, parent ion minus one hydrogen atom ($P - 1$)⁺, and parent ion minus C₂H_n. These latter species are observed in much greater abundance for dimer ion fragmentation than is observed for fragmentation of the parent ion under equivalent conditions. Recently we succeeded in recording the UV induced naphthalene ion cluster spectra for the dimer, trimer, and tetramer ions, shown in Figures 8. The spectra are interesting and unexpectedly different. Based on these observations, ion cluster fragmentation spectroscopy will be a highly productive area of research, requiring extensive investigation over the next few years.

CONCLUSION

Substantial progress has been made in each of the three areas originally proposed for research. Upward ion dip spectroscopy has been particularly productive and has clear, widespread applications. Future research in our laboratory will address the

generality of autoionizing Rydberg states for polyatomic species. Fragmentation processes in the naphthalenes are now moderately well understood, and the conclusions derived for them are expected to apply to larger aromatic species. Detailed results from the study of autoionizing Rydberg states and from ion fragmentation spectroscopy are included in the appendix to this report. The preliminary results for ion cluster fragmentation spectroscopy demonstrate that this will be a readily accessible spectroscopic technique.

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FIGURES

1. Energy level diagram showing the methods of resonant multiphoton ionization spectroscopy discussed in this report: (a) downward ion dip spectroscopy, (b) upward ion dip spectroscopy, and (c) autoionization Rydberg spectroscopy.
2. Energy level diagram showing the method of multiphoton ionization-fragmentation spectroscopy. M^+ denotes the parent ion and $M - 1^+$ denotes the fragment ion formed by loss of one hydrogen atom.
3. Spectrum of an autoionizing Rydberg series of naphthalene converging on the ionization limit associated with the ion excited to the vibrational combination level denoted $(8^1 7^1)$ with 1537 cm^{-1} vibrational energy.
4. Model for the multiphoton ion fragmentation process in the red spectral region for methylnaphthalenes.
5. Two-photon induced fragmentation spectrum for 2-methylnaphthalene in the red region, recorded at low and high laser intensities.
6. One-photon ultraviolet induced fragmentation spectrum of 2-methylnaphthalene.
7. Mass spectra recorded for 2-methylnaphthalene under dimer forming conditions with (a) UV excitation only and (b) with UV and red excitation.
8. One-wavelength 2-photon ionization spectra recorded for naphthalene (a) dimer, (b) trimer, and (c) tetramer species.

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