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**Photoionization Mass Spectrometric Studies
of Selected Compounds in a Molecular Beam**

University of California

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Photoionization Mass Spectrometric Studies of Selected Compounds in a Molecular Beam

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PHOTOIONIZATION MASS SPECTROMETRIC STUDIES
OF SELECTED COMPOUNDS IN A MOLECULAR BEAM

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The University of New Mexico, 1978

Photoionization efficiency curves have been measured at moderate to high resolution for several species produced in supersonic molecular beams of acetone, acetone- d_6 and CS_2 . The molecular beam photoionization mass spectrometer which has been assembled for this work is described. The performance of this instrument has been characterized by a number of experiments and calculations.

As a result of adiabatic cooling during the nozzle expansion, photoion yield curves have been obtained for $CH_3COCH_3^+$ and $CD_3COCD_3^+$ at an effective resolution of approximately 12 meV. Partial condensation was observed in the acetone beam to the extent that sufficient concentrations of $(CH_3COCH_3)_2$, $(CD_3COCD_3)_2$, $(CH_3COCH_3)_3$ and $(CH_3COCH_3)_4$ were formed to permit the study of their photoionization efficiency behavior as well. Appearance potential curves have been determined for CH_3CO^+ , CD_3CO^+ and $(CH_3COCH_3) \cdot CH_3CO^+$ fragments. The measured ionization potentials of acetone and acetone- d_6 monomers are

9.694 ± 0.006 eV and 9.695 ± 0.006 eV respectively. Transitions to higher vibrational levels in $\text{CH}_3\text{COCH}_3^+$ are seen at 320, 695 and 930-1370 cm^{-1} above threshold. The effect of perdeutero substitution is to reduce these frequencies to 260 and 660-1100 cm^{-1} . Appearance potentials of CH_3CO^+ and CD_3CO^+ fragments are observed at 10.52 ± 0.02 eV and 10.56 ± 0.02 eV respectively. This study reports the first observation of a simple functional dependence of ionization potential with cluster size. The measured ionization energies for $(\text{CH}_3\text{COCH}_3)_n$, $n=1-4$, are found to decrease linearly as a function of $1/n$. This $1/n$ functional dependence compares favorably to that which would be expected on the basis of a straightforward perturbation model for the cluster ion system. Ionization thresholds for $(\text{CH}_3\text{COCH}_3)_2$, $(\text{CH}_3\text{COCH}_3)_3$ and $(\text{CH}_3\text{COCH}_3)_4$ are seen at 9.26 ± 0.03 eV, 9.10 ± 0.03 eV and 9.02 ± 0.03 eV respectively. Within experimental resolution, the ionization potentials of $(\text{CH}_3\text{COCH}_3)_2$ and $(\text{CD}_3\text{COCD}_3)_2$ are identical. The appearance potential of the process $(\text{CH}_3\text{COCH}_3)_2 \rightarrow (\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+ + \text{CH}_3 + e^-$ is found to be 10.08 ± 0.05 eV. By consideration of appropriate thermodynamic cycles, a lower bound for the acetone dimer ion binding energy is calculated to be 0.538 eV (12.4 kcal/mole) and the desolvation energy of

$(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$ is estimated to be 0.544 eV (12.5 kcal/mole).

The photoion yield curve of CS_2^+ has been measured between 1200-1240 Å at an optical resolution of about 30 meV. The $(\text{CS}_2)_2^+$ curve has also been determined in the wavelength range 1000-1290 Å. The observed ionization potentials for the monomer and dimer species are 10.056 ± 0.015 eV and approximately 9.63 eV respectively. These values in conjunction with an estimate of the dimer binding energy from second virial coefficient data are used to calculate a lower bound for the $(\text{CS}_2)_2^+$ binding energy of 11.0 kcal/mole.

Photoionization
Molecular Beams
Clusters
Acetone
Carbon Disulfide

I. INTRODUCTION: General Methods in the Study of Ionization and Dissociation Processes

The interaction of gaseous neutral molecules and various ionizing agents is a fundamental subject of chemical physics. Of particular interest are those quantities pertaining to the energetics and kinetics of positive ion formation. In order to obtain accurate information concerning these properties, a substantial number of experimental methods and data interpretation techniques have been developed. These data measurement and interpretation processes have been discussed and contrasted in considerable detail.¹⁻⁷ Examination of recent positive ion literature⁸ would seem to indicate that four general techniques have been most useful: ultraviolet absorption spectroscopy, electron impact methods, electron spectroscopy and photoionization.

For many molecules, ultraviolet absorption spectroscopy provides the most accurate ionization potential data. This experimental technique involves the measurement of total absorption cross section as a function of photon energy. At appropriate energies, excitation of ground state electrons into molecular orbitals of higher quantum number may occur, producing

corresponding absorption lines. Where it is possible to identify a Rydberg absorption band system, the band position ν_n of the members of the series can generally be fit to the modified Rydberg equation:

$$\nu_n = \nu_\infty - \frac{R}{(n-\delta)^2} \quad (1)$$

where ν_∞ is the ionization limit to which the series converges, R is the Rydberg constant ($109,737.312 \text{ cm}^{-1}$), n is the principal quantum number of the Rydberg orbital of wave number ν_n , and δ is the so-called quantum defect. Depending on the complexity of the absorption spectra, one or more Rydberg series may be found which converge to various vibrational levels in the ground and higher electronic states of the ion. Due to the high resolution at which atomic and molecular absorption lines can be measured (often better than $\pm 0.1 \text{ \AA}$), it is frequently possible to obtain very accurate values for the first adiabatic ionization potential. A considerable body of experimental data has resulted from utilization of this technique.⁹

Although extremely accurate information pertaining to various ionization limits is often accessible through ultraviolet absorption spectroscopy, this experimental method is somewhat limited in scope. Especially for polyatomic molecules, interpretation of the spectra is frequently rendered difficult or impossible as a result of absorption

line broadening due to predissociation or as a result of pseudo-continuous spectra arising from various competing Rydberg transitions. The saturated hydrocarbons appear to be particularly intractable in this regard, inasmuch as no Rydberg absorption band systems have been found for this class of molecules.¹⁰ The vacuum ultraviolet spectrum of acetone provides another interesting case of difficult interpretation. On the basis of intensity, three absorption bands were assigned by Duncan to a Rydberg series converging to an ionization potential of 10.26 eV.¹¹ A subsequent photoionization experiment by Watanabe¹² indicated a much lower ionization potential of 9.69 eV. Using the photoionization value as a reference, Watanabe was able to reanalyze the spectrum and identify another series converging to 9.705 eV. Finally, in addition to difficulties in spectrum interpretation, it is important that comparatively little information concerning dissociation processes is obtainable using ultraviolet absorption spectroscopy. Thus, it is obvious that complementary experimental techniques are needed to provide a more complete understanding of positive ion energetics and kinetics.

The various electron impact techniques are widely used methods for studying ionization and dissociation mechanisms. When a beam of electrons of sufficient energy is passed through a gas, a number of competitive and consecutive processes may occur. Major processes resulting in positive

ion formation are as follows:

(1)	$AB + e^- \rightarrow AB^+ + 2e^- + KE$	Direct Ionization
(2)	$AB + e^- \rightarrow AB^{++} + 3e^- + KE$	Multiple Ionization
	$\vdots$	
(3)	$AB + e^- \rightarrow AB^+ + 2e^-$	Parent Ion
	$\quad \quad \quad \rightarrow A^+ + B + 2e^-$	Fragmentation
(4)	$AB + e^- \rightarrow AB^* + e^-$	Autoionization
	$\quad \quad \quad \rightarrow AB^+ + 2e^- + KE$	
(5)	$AB + e^- \rightarrow AB^* + e^-$	
	$\quad \quad \quad \rightarrow A^+ + B^- + e^- + KE$	Ion Pair Production

Using electron impact as an ionization source, ionization potentials and appearance potentials are generally determined directly by plotting the ion current (usually mass selected) as a function of electron energy. From a number of theoretical approaches,¹³⁻¹⁸ it has been suggested that the electron bombardment ionization cross section should be, to a first approximation, a first order function of electron energy above threshold, with zero probability at onset. While there are exceptions, this prediction has been largely verified experimentally¹⁹ insofar as one generally observes, for simple ionization, a more or less asymptotic threshold followed by a roughly linear increase in ionization probability with excess energy. Careful interpretation of the ionization efficiency curve for each specie of interest may then be expected to yield a correct ionization or appearance potential.

Principally due to the relative ease by which an intense beam of electrons may be produced over a wide energy range, electron impact techniques have enjoyed considerable popularity as a means of measuring ionization and dissociation energetics. There are however serious problems which tend to limit the accuracy of these techniques. In particular, difficulties in obtaining a monoenergetic electron beam are well known.^{1,5,19} Problems involving interpretation of threshold behavior,^{2,5} variable energy transfer during impact,^{20,21} and pyrolysis effects²² are also significant. Considerable attention has been given to establishment of dependable ionization and appearance potential values by attempting to circumvent the various instrumental factors and by careful data interpretation.²³ Nevertheless, with more accurate low-energy experimental methods becoming increasingly available, it would appear that electron bombardment techniques are likely to be most viably applied to ionization and fragmentation studies above 25-30 eV (where the only competitive ionization source is synchrotron radiation), to experiments involving the generation of negative ions by resonance attachment, and to cases where electrons are capable of producing optically forbidden transitions.^{3,24,25}

Electron spectroscopy, a third general method for studying ionization and dissociation processes, chiefly

comprises three experimental techniques: photoelectron spectroscopy, Auger electron spectroscopy and Penning ionization. These techniques involve the measurement of the kinetic energy distribution of electrons ejected from molecules which have been excited by UV photons, X-ray photons, or metastable atoms respectively.

Photoelectron spectroscopy in particular has been widely employed in the study of molecular electronic structures. To briefly summarize the method, the kinetic energy analysis of the ejected photoelectrons takes advantage of the law of conservation of momentum in the process $AB + h\nu \rightarrow AB^+ + e^- + KE$ wherein the electron carries away the preponderance of the photon excess energy. To a very good approximation, the following relation then holds:

$$E_{\text{electron}} = h\nu - E_{\text{ion}}^{i,v,j} \quad (2)$$

where E_{electron} is the kinetic energy of the electron, $h\nu$ is the photon excitation energy, and $E_{\text{ion}}^{i,v,j}$ is the energy needed to produce an ion in electronic state i with vibrational and rotational states v and j respectively. Hence, for a given photon beam energy, the accessible ionization channels of the target molecule may be observed by analysis of the kinetic energy distribution of the ejected photoelectrons. An important alternative approach is the resonant photoionization or threshold photoelectron spectroscopy technique in which the photon energy is varied while tuning the detector so as to accept only those

electrons which have been ejected with near zero kinetic energy. Electronic states whose cross sections decrease rapidly as a function of excess energy are more readily observed in this way. The various experimental and analytical aspects of these methods have been reviewed in detail.^{3,26-34}

Electron and photon impact ionization efficiency curves often exhibit autoionization structure which dominates that due to simple ionization processes. A principal advantage of conventional photoelectron spectroscopy is that autoionization is observed only when the incident light energy matches an autoionizing state. For light sources above 17 eV, this happens rarely because of the low density of excited and ionic states in this energy region.²⁶ Similarly, threshold photoelectron experiments are affected by autoionization processes only when the energy of the ejected electrons lies within the bandpass of the detector. Thus, with recent energy analyzer designs attaining resolutions of better than 10-15 meV, photoelectron spectroscopy and resonant photoionization methods are frequently capable of providing accurate and relatively unambiguous measurements of direct ionization thresholds. However, the inability to discriminate between those photoelectrons formed in dissociative processes and those arising from simple ionization channels places a significant limitation on these techniques.

The use of ultraviolet light to bring about ionization in a direct threshold experiment forms the basis for the fourth general approach to the study of positive ion energetics and kinetics. The major observable processes resulting from the absorption of a short wavelength photon are analogous to those arising from electron impact:

- (1) $AB + h\nu \rightarrow AB^+ + e^- + KE$ Direct Ionization
- (2) $AB + h\nu \rightarrow AB^{++} + 2e^- + KE$ Multiple Ionization
- $\vdots$
- (3) $AB + h\nu \rightarrow AB^+ + e^-$ Parent Ion
- $\rightarrow A^+ + B + e^-$ Fragmentation
- (4) $AB + h\nu \rightarrow AB^*$
- $\rightarrow AB^+ + e^- + KE$ Autoionization
- (5) $AB + h\nu \rightarrow AB^*$
- $\rightarrow A^+ + B^- + KE$ Ion Pair Production

As with electron bombardment, the ionization efficiency curve (photoion current per photon current, plotted as a function of photon energy) generally provides straightforward ionization potential and appearance potential information. The use of ion mass analysis in conjunction with photoionization has virtually become standard practice insofar as it permits careful distinction between direct and dissociative ionization mechanisms and largely eliminates the possibility of error due to sample impurities.

The recent widespread application of photoionization mass spectrometry to the study of ionization and dissociation

processes seems to be principally due to the fact that many of the disadvantages of electron bombardment techniques are eliminated through the use of ultraviolet radiation as an ionizing medium. In contrast to the largely first order threshold behavior exhibited in electron impact ionization, it has been predicted theoretically^{14-16,18,35} and generally observed experimentally³⁶ that the cross section for a direct photoionization process approximates a zero order or step-like function of the excess ionizing energy. This property facilitates accurate measurements of first and higher ionization potentials and frequently allows the acquisition of information pertaining to ionic vibrational frequencies, Franck-Condon factors for ionization, etc. The excellent energy resolution available with current instrumental designs and the absence of effects due to variable energy transfer and pyrolysis are additional factors which make photon impact an attractive source for ionization and fragmentation experiments. The development and use of photoionization methods has been the subject of several reviews.³⁷⁻³⁹

Experimental factors which have restricted the potential of photoionization mass spectrometric techniques in the past include low ion currents due to the lack of sufficiently intense vacuum ultraviolet light sources coupled with small photoionization cross sections and

working resolution as a result of the internal thermal energy of the sample molecules. The former difficulty has been largely overcome by instrumental developments resulting in increased useable photon fluxes and by improvements in ion detection sensitivities through the use of pulse counting techniques. Improvements in ultimate resolution, on the other hand, have been achieved by cooling the sample gas directly or, very recently, by taking advantage of the adiabatic cooling properties of a supersonic nozzle expansion. The production of van der Waals molecules in sufficient concentrations to permit their investigation has proved to be an important additional benefit to molecular beam sampling methods.

It is clear that photoionization mass spectrometry represents a powerful experimental technique, especially when used in conjunction with a supersonic nozzle expansion. This thesis traces the historical development and reviews various experimental and analytical aspects of photoionization mass spectrometric methods. The characteristics which promote molecular beams as a particularly suitable sampling source are discussed. The photoionization efficiency curves for several species produced in supersonic molecular beams of acetone, acetone-d₆ and CS₂ are reported. Fine structure in the data is analyzed in terms of molecular and ionic electronic structures.

Thermochemical quantities which have been derived from these data are also discussed.

II. PHOTOIONIZATION MASS SPECTROMETRY

A. Historical Overview

The first experiments on photoionization of gases were performed shortly after the discovery of the surface photoelectric effect by Hertz in 1887. During the period 1900-1920, a number of studies were made on the effects of ultraviolet radiation on air and other compounds.⁴⁰ In general, it was found that ultraviolet light in the region 1250-1450 Å was effective in producing substantial ionization even though the ionization potentials of most of the constituents involved occur at wavelengths much lower than 1250 Å. Satisfactory explanations for these observations eluded the early investigators. Possible interpretations of these results include multistep ionization channels, ionization by accelerated photoelectrons or ionization of impurities such as mercury vapor.⁴¹

From 1923 to 1930, the photoionization of alkali metal vapors was extensively studied.⁴⁰ The relatively low ionization potentials of these compounds permitted the use of quartz optics and energy measurements were made with monochromatic light sources. In 1929, mass analysis was introduced to detect photoions from irradiated atomic potassium vapor.⁴² Terenin and Popov performed the first

study of molecular photoionization processes using mass selection in 1932.⁴³ In this investigation, a simple magnetic mass analyzer unambiguously established the ion pair production processes in the photoionization of thallium halides.

The use of photoionization as a general technique for the study of positive ion energetics was frustrated by the lack of a method to produce well-characterized monochromatic photon energies in the range necessary for ionization of most compounds. In 1950, however, the feasibility of energy measurements of dispersed radiation in the vacuum ultraviolet region was shown.⁴⁴ During the period 1953-1959, Watanabe and co-workers determined the ionization potentials of some 300 molecules utilizing 7-15 eV photons produced by a hydrogen D.C. capillary discharge and dispersed by a 1-meter vacuum monochromator.^{41,45} For ionization potential measurements up to approximately 11.5 eV, LiF windows were used on the photoionization chambers. At higher energies, windowless chambers were employed. Because mass analysis was not utilized, the possibility of error due to sample impurities was present. In addition, there was no way to distinguish between ionization of the parent molecules and processes such as fragmentation and ionization of dimers,⁴⁶ etc. Nevertheless, the threshold value

obtained were generally found to be in much better agreement with available spectroscopic ionization potentials than those onsets measured by electron bombardment. It must be noted that these studies still provide the best photoionization literature values for many compounds.

Meanwhile, the use of mass selection in photoionization methods did not appear again until 1956-57.^{47,48} In these experiments, undispersed ultraviolet radiation was transmitted through LiF windows into the mass spectrometer ionization chambers. Mass spectra were determined for photoionization products of several compounds and were observed to be considerably less complex than those obtained with electron impact.

Experiments combining the advantages of mass spectrometry with improved techniques in the production of monochromatic vacuum ultraviolet radiation were first performed by Hurzeler et.al.^{49,50} These investigators used a hydrogen D.C. capillary discharge photon source isolated from the body of a 1-meter Seya-Namioka vacuum monochromator by a LiF window. Dispersed light in the energy range 7.5 - 11.8 eV was passed through the ion source of a 60°-sector mass spectrometer. This design permitted the measurement of photoionization efficiency curves for parent and fragment ions of several compounds at an approximate resolution of 0.05 eV.

The obvious benefits of obtaining monochromatic photon energies above 11.8 eV in mass spectrometric studies encouraged the construction of windowless light source-vacuum ultraviolet monochromator arrangements as early as 1959.⁵¹ Since that time, photoionization in conjunction with mass analysis has been profitably used by many groups.⁵²⁻⁶⁴ Nevertheless, the basic design of the photoionization mass spectrometer has remained the same. As mentioned in Section I, instrumental improvements have primarily involved the application of technological advances in ion detection capability and the production of vacuum ultraviolet radiation. Higher ionizing photon fluxes have become available as a result of the development of more intense light sources and high resolution vacuum monochromators with increased light throughput. Ion detection sensitivity has been substantially enhanced by the use of pulse counting techniques. Consequently, photoionization mass spectrometric studies may now be made at optical resolutions typical of many vacuum ultraviolet absorption experiments. Dehmer and Chupka have employed resolutions as high as $0.016 \text{ \AA}$ or 0.0004 eV at the wavelengths studied.⁶⁵ The various aspects of current instrumental design in photoionization mass spectrometry will be discussed in a later section.

With the very high optical resolutions now

available, considerable attention has recently been given to methods for improving the working resolution of photoionization experiments. It has been aptly demonstrated⁶⁶⁻⁶⁹ that true spectroscopic accuracy and precision in the measurement and interpretation of photoion yield curves is possible only if thermal vibrational and rotational energy effects are largely eliminated or properly taken into account. In room temperature experiments on polyatomic molecules, these effects limit the ultimate resolution to approximately $3/2 kT$ or 0.039 eV. As mentioned previously, some success has been achieved in reducing the vibrational and rotational energy spread by a straightforward cooling of the sample gas.^{65,70-78} In the case of hydrogen, for example, an effective resolution of at least 0.006 eV can be attained by cooling the gas to liquid nitrogen temperature. Unfortunately, this method is not applicable to easily condensable compounds.

An alternative sampling technique which significantly lessens the detrimental effects of internal thermal energy is the use of supersonic nozzle expansions wherein one takes advantage of the substantial conversion of vibrational, rotational and random translational energy into directed mass motion. The benefits of combining contemporary photoionization mass spectrometric methods with molecular beam sampling were first demonstrated by

Parr and Taylor in 1973-74.⁷⁹⁻⁸¹ These investigators made high resolution studies of CO_2 and C_2H_2 using synchrotron radiation as a vacuum ultraviolet light source. Rotational temperatures of the target gas were estimated to be 40K for CO_2 and 118K for acetylene. In addition to producing effective thermal relaxation of the parent molecules, nozzle beams provide unique opportunities to study van der Waals clusters and hydrogen-bonded clusters inasmuch as these species can be formed in relatively large amounts under suitable expansion conditions. As a result, high resolution molecular beam-photoionization mass spectrometric methods are now finding considerable application to studies of various condensable gases and cluster molecules.⁸²⁻⁹²

B. General Considerations

As indicated in previous sections, photoionization mass spectrometry is an established technique for observing and characterizing the various photon absorption channels which result in ionization. Processes such as direct single and multiple ionization and parent ion fragmentation are easily distinguished through the use of mass analysis. Under favorable circumstances, electronic excitations to different ionic spin states as well as

excitations to optically allowed ionic vibrational levels may be identified in the experimental photoionization efficiency curves. Data pertaining to indirect autoionization and predissociation processes are also frequently accessible. For even the simplest polyatomic molecules, however, it is obvious that the number of possible transitions increases quickly as a function of excess photon energy above the first ionization threshold. In order to maximize the amount of useful information in a photoionization mass spectrometric study, it is therefore expedient to perform the experiment at high working resolution and to carefully interpret the results by drawing heavily on current understanding of molecular electronic structures and electronic spectra.

1. Photoionization Processes

a. Direct Ionization and the Franck-Condon Principle

The direct photoionization processes which are most commonly investigated by mass spectrometric methods involve the formation of a singly charged molecular ion AB^+ (i', v', j') in electronic state i' , vibrational state v' and rotational state j' as a result of the absorption of a photon by the neutral molecule AB (i'', v'', j'') in its electronic, vibrational and rotational states i'' , v'' and j'' respectively. The vast

majority of these transitions require incident radiation corresponding to the vacuum ultraviolet region (200-2000 Å). Consequently, the wavelength of the ionizing medium is typically much larger than the linear dimensions of the molecular wave functions. This fact implies that most electronic transitions resulting in the single ionization of a neutral molecule AB may, to a good approximation, be considered to be electric dipole transitions. The probability, P, of a transition between AB (i'', v'', j'') and AB^+ (i', v', j') can then be written in terms of the transition moment integral⁹³ $\vec{M}$ as follows:

$$P \propto \vec{M}^2 = |\langle \Psi'' | \sum \vec{p} | \Psi' \rangle|^2 \quad (3)$$

where Ψ'' and Ψ' are the initial and final state eigenfunctions and $\vec{p}$ is the dipole moment operator summed over all electrons and nuclei.

By introducing the Born-Oppenheimer approximation, the eigenfunctions $\Psi(q, Q)$ may be written as a single product of electronic and nuclear functions

$$\Psi(q, Q) = \Psi_e(q, Q) \Psi_n(Q) \quad (4)$$

where q and Q represent the electronic and nuclear coordinates respectively. Similarly, the dipole moment operator can be written as a sum of electronic and nuclear dependent terms

$$\sum \vec{p} = \sum \vec{p}_e + \sum \vec{p}_n. \quad (5)$$

The transition moment integral is then

$$\vec{M} = \langle \psi_e''(q, Q) \psi_n''(Q) | \Sigma \vec{p}_e + \Sigma \vec{p}_n | \psi_e'(q, Q) \psi_n'(Q) \rangle. \quad (6)$$

Separating this expression according to the electronic and nuclear parts of $\Sigma \vec{p}$ gives

$$\begin{aligned} \vec{M} = & \langle \psi_n''(Q) | \psi_n'(Q) \rangle \langle \psi_e''(q, Q) | \Sigma \vec{p}_e | \psi_e'(q, Q) \rangle \\ & + \langle \psi_n''(Q) | \Sigma \vec{p}_n | \psi_n'(Q) \rangle \langle \psi_e''(q, Q) | \psi_e'(q, Q) \rangle. \end{aligned} \quad (7)$$

Now $\langle \psi_e''(q, Q) | \psi_e'(q, Q) \rangle = 0$ since the electronic eigenfunctions are mutually orthogonal for an instantaneous nuclear configuration Q .⁹³ Therefore, the transition moment integral becomes

$$\vec{M} = \langle \psi_n''(Q) | \psi_n'(Q) \rangle \langle \psi_e''(q, Q) | \Sigma \vec{p}_e | \psi_e'(q, Q) \rangle. \quad (8)$$

If vibrational and rotational interactions are neglected, $\psi_n(Q)$ can be separated into a product of vibrational and rotational wavefunctions $\psi_v(Q)$ and $\psi_r(Q)$ respectively.

The above equation (8) may then be written²⁶ as

$$\begin{aligned} \vec{M} = & \langle (\frac{1}{Q}) \psi_v''(Q) \psi_r''(Q) | (\frac{1}{Q}) \psi_v'(Q) \psi_r'(Q) \rangle \\ & \times \langle \psi_e''(q, Q) | \Sigma \vec{p}_e | \psi_e'(q, Q) \rangle. \end{aligned} \quad (9)$$

This expression may be rigorously treated by integrating over rotational coordinates. In practice, however, rotational fine structure is unresolved in the photoionization efficiency curves of most molecules. Neglecting the rotational motion, the transition moment integral is simplified to

$$\vec{M} \propto \langle \psi_v''(Q) | \psi_v'(Q) \rangle \langle \psi_e''(q, Q) | \Sigma \vec{p}_e | \psi_e'(q, Q) \rangle. \quad (10)$$

The first term in Equation (10) is not automatically zero since vibrational functions belonging to different electronic states are often not mutually orthogonal. In general, the second term in Equation (10) does not vary significantly as a function of Q . To a good approximation, this integral may be written as $\langle \Psi_e''(q, Q_0) | \Sigma \vec{p}_e | \Psi_e'(q, Q_0) \rangle$ where Q_0 corresponds to a position of the nuclei which results in a maximum in the product $\Psi_v'' \Psi_v'$. Thus, the photoionization transition probability can be separated into factors which depend solely on the electronic motion and nuclear vibrational motion respectively:

$$P \propto |\langle \Psi_e''(q, Q_0) | \Sigma \vec{p}_e | \Psi_e'(q, Q_0) \rangle|^2 |\langle \Psi_v''(Q) | \Psi_v'(Q) \rangle|^2. \quad (11)$$

A major result of the foregoing wave mechanical derivation is the well-known Franck-Condon principle. Given the Born-Oppenheimer product separation of electronic and nuclear wavefunctions, neglect of rotational motion and the assumption of a constant nonzero electronic transition moment, the relative probabilities of an allowed set of transitions $AB(i'', v_n'') \rightarrow AB^+(i', v_m')$ are determined by the squares of the respective vibrational overlap integrals:

$$P_{i'', v_n'' \rightarrow i', v_m'} \propto \left[\int \Psi_{v_n}^{*''} \Psi_{v_m}' dQ \right]^2. \quad (12)$$

The ionizing transition characterized by the largest square of the vibrational overlap integral (or Franck-Condon factor) for $v'' = 0$ is of particular interest

to photoionization studies. The energy at which this transition occurs is generally called the "vertical ionization potential." For a given ionic electronic state, this quantity may or may not correspond to the "adiabatic ionization potential" which is defined as the energy at which occurs the transition

Strictly speaking, the term "vertical ionization potential" is in some degree a misnomer. For high vibrational quantum numbers, the correspondence principle indicates that those transitions in which the nuclear configurations are the same in the initial and final states are most probable.⁹⁴ For low vibrational quantum numbers, however, a large vibrational overlap does not always require the relative positions of the nuclei to be the same in the initial and final states.⁹⁵

b. Selection Rules

The proper identification and interpretation of observed features in experimental photoionization efficiency curves is facilitated by application of selection rules that indicate whether a given transition may be expected to be allowed or forbidden. From the discussion in the previous section (II.B.1.a.), it is evident that a photoionization transition is allowed if both integrals of Equation (11) are non-zero. Clearly, the value of each

integral is dependent upon the approximations used to define the wavefunctions and operators. Concerning the operators, most photoionization processes within several eV of threshold are well described as one-electron transitions. Therefore, appropriate selection rules may generally be determined by using a one-electron operator in the electronic transition moment term of Equation (11).

Electronic Selection Rules

Replacing $\Sigma \vec{p}_e$ with a dipole moment vector $\vec{p}_e$, electronic transitions in the process $AB \rightarrow AB^+$ are then subject to the general dipole selection rule. That is, an electronic transition between initial and final states belonging to the same point group is allowed if the product $\Gamma(\Psi_e^{*'}) \times \Gamma(\vec{p}_e) \times \Gamma(\Psi_e')$ is totally symmetric for at least one component of $\vec{p}_e$.⁹³ If a change of symmetry occurs between the molecule and ion, the above condition is applied using only those symmetry elements which are common to the two point groups. However, it may be shown that these symmetry requirements do not restrict the number of allowed electronic transitions in photoionization since the final state includes a free electron as well as the molecular ion.³ The final state wavefunction Ψ_e' is properly represented by a positive ion electronic component wavefunction $\Psi_e'^+$ and a one-electron continuum wavefunction ϕ_e .²⁶ Because the continuum wave ϕ_e may be characterized by a

mixture of s, p, d or f waves, the electron can always satisfy the angular momentum requirements necessary to make the electronic transition moment non-zero. This fact gives rise to the rule that all one-electron electronic transitions in photoionization are allowed. This rule remains true even if a degeneracy exists in one or both states involved in the transition since linear combinations of wavefunctions and dipole components can be found such that $\Gamma(\psi_e^{*'}) \times \Gamma(\vec{p}_e) \times \Gamma(\psi_e')$ is totally symmetric with respect to all common symmetry elements.

Spin Selection Rules

For systems characterized by small spin-orbit interaction, the electronic wavefunctions including spin are commonly separated⁹³ into the product of orbital and spin functions:

$$\psi_e = \psi_{\text{orb}} \psi_s. \quad (14)$$

The one-electron electronic transition moment becomes

$$\langle \psi_e^{*'} | \vec{p}_e | \psi_e' \rangle = \langle \psi_{\text{orb}}^{*'} | \vec{p}_e | \psi_{\text{orb}}' \rangle \langle \psi_s^{*'} | \psi_s' \rangle. \quad (15)$$

The dipole moment vector $\vec{p}_e$ does not appear in the spin term since it does not operate on spin coordinates. Now, $\langle \psi_s^{*'} | \psi_s' \rangle = 0$ for states of different spin due to orthogonality of spin functions corresponding to different spin values. Therefore, a transition is allowed only if total spin, S, is conserved between the initial and final states.

Since the final state in single photoionization involves the removal of an electron with spin $m_s = \pm 1/2$, the change in multiplicity between neutral molecule and ion must be

$$\Delta S = \pm 1. \quad (16)$$

This rule indicates, for example, that an ionizing transition from the singlet molecular ground state of a closed-shell molecule produces a doublet ionic state.

Vibrational Selection Rules

The electronic and spin selection rules outlined above describe the allowed one-electron electronic transitions in photoionization. In practice, however, these rules offer little information for interpreting the experimental photoion yield curves. In contrast, application of dipole vibrational selection rules can result in a considerable simplification of interpretation for molecules containing symmetry. In an electronically allowed transition, $\langle \Psi_e'' | \vec{p}_e | \Psi_e' \rangle$ is always non-zero. Hence, the vibrational overlap integral $\langle \Psi_{v_n}'' | \Psi_{v_m}' \rangle$ determines whether or not a transition $AB (i'', v_n'') \rightarrow AB^+ (i', v_m')$ is allowed. If the molecule and ion belong to the same molecular point group, $\langle \Psi_{v_n}'' | \Psi_{v_m}' \rangle$ is non-zero when the product $\Gamma(\Psi_{v_n}'')^* \times \Gamma(\Psi_{v_m}')$ is totally symmetric with respect to all point group symmetry operations. This condition requires that the vibrational levels in the

initial and final state have identical symmetry. This result contains significant implications for the analysis of photoionization spectra. Especially when supersonic molecular beam sampling is employed, the preponderance of target molecules in a photoionization experiment exist in the totally symmetric zero-point vibrational level of the ground state. Consequently, only transitions to totally symmetric vibrational levels of the ionic state are allowed. That is, restrictions exist on the number of possible transitions $AB(X, v_n'') \rightarrow AB^+(i', v_m')$.

In ionization from the $v'' = 0$ level of the ground state, three types of possible progressions may be distinguished. These types correspond to excitation of totally symmetric ionic vibrational modes, antisymmetric ionic vibrational modes and degenerate ionic vibrational modes respectively. Since the higher vibrational levels of a totally symmetric mode are necessarily also fully symmetric, excitation of a totally symmetric vibration occurs in a progression in single quanta. Several such progressions may be observed in a polyatomic molecule, depending on the number of fully symmetric modes. In contrast, the vibrational wavefunctions for antisymmetric modes are totally symmetric for even and antisymmetric for odd vibrational quantum numbers. As a result, transitions to the $v'=2,4,6,\dots$ levels of these modes are allowed

while transitions to the $v'=1,3,5\dots$ levels are forbidden. The vibrational selection rules pertaining to excitation of degenerate ionic vibrational modes are somewhat more complicated.^{26,93} However, it is sufficient to point out that weak transitions to the $v'=2,4,6\dots$ levels of degenerate modes may occur and transitions to $v'=3,5\dots$ levels may occasionally be very weakly allowed. Transitions to the $v'=1$ level of these modes are always strictly forbidden because the first level of a degenerate vibration is never fully symmetric.

The preceding considerations demonstrate that symmetry requirements may result in a substantial simplification of photoionization vibrational spectra. Thus far the discussion has been restricted to vibrational selection rules pertaining to molecules which have the same symmetry in both the ground and ionic state. In addition, it has been implicitly assumed that both electronic states involved in the transition are non-degenerate. Conditions at variance with the above lead to important complications which deserve brief mention. If ionization results in a final state in which the equilibrium conformation belongs to a different point group than that for the ground state molecule, only the common symmetry elements are considered. That is, a transition is allowed when the product $\Gamma(\Psi_{v_n}^* \leftarrow) \times \Gamma(\Psi_{v_m} \leftarrow)$ is totally symmetric with respect to all

common symmetry operations. Under these circumstances, fewer restrictions exist on the number of symmetry allowed processes. This relaxation of symmetry constraints contains diagnostic possibilities in terms of molecular structures. Consider, for example, a transition which would normally be forbidden for $v'=1$ on the basis of no change in equilibrium symmetry between molecule and ion. If the photoionization vibrational spectrum includes this mode in a progression in single quanta, a change in molecular point group may be inferred. This behavior is observed in the formation of a non-linear ion from a linear symmetric triatomic molecule. Much more difficult complications can arise if one or both of the molecular and ionic electronic states are degenerate. Those species which possess orbitally degenerate electronic states contain degenerate vibrational modes also. If the coupling between electronic and vibrational motion is negligibly small, vibrational selection rules apply as above. On the other hand, if vibronic interactions become significantly large, the product separation represented by Equation (4) is no longer valid. Complications which arise in photoionization spectra due to vibronic splittings are manifestations of the well known Jahn-Teller⁹⁶ and Renner-Teller⁹⁷⁻⁹⁸ effects.

Rotational Selection Rules

Each vibrational feature in a photoionization efficiency curve contains fine structure which is due to rotational transitions. In practice, this fine structure is rarely resolved. For those few cases in which some resolution has been achieved, rotational selection rules become important. While a detailed examination of these rules is superfluous to the present discussion, excellent investigations of this topic are available elsewhere.^{26,93}

Since the vast majority of photoionization processes are adequately described in terms of a single step one-electron transition, the selection rules presented above are sufficient for the analysis of most photoion yield curves. Features corresponding to multi-electron transitions are possible through configuration interaction and have been observed in certain photoelectron spectra.^{3,26} However, features of this type generally occur at excitation energies in excess of 20 eV and therefore are not likely to interfere with normal one-electron photoionization continua near threshold.

c. Autoionization

In addition to direct ionization processes, there exist several indirect two-step photon absorption mechanisms which are extremely important in photoionization

studies. These mechanisms involve the production of an intermediate molecular excited state lying above the first ionization limit followed by decay into one of four possible channels:

The transition probabilities for the various decay channels vary considerably from one molecular system to another. In general, autoionizing states possess relatively short lifetimes (about 10^{-14} sec.) with the result that this mechanism is often highly favored. Hence, nearly all photoionization efficiency curves are observed to contain some structure due to this phenomenon. Since the first excitation step represents a resonance process, autoionization manifests itself as peak-like structure on the experimental photoion yield curves such as would be expected from transitions involving discrete states. In accordance with the Heisenberg uncertainty principle, the peak widths increase proportionately as the autoionizing state lifetime decreases. Fluorescence emission, on the other hand, tends to be a relatively improbable decay channel for the intermediate excited state since this mechanism typically requires 10^{-8} seconds or more. Ion-pair formation can occur quite readily

where circumstance provides a favorable configuration of potential surfaces; however, the indirect process which most often competes significantly with autoionization is predissociation into neutral fragments. As a rule, autoionization features dominate the spectra of small molecules while predissociation becomes increasingly favored for more complex species.

The selection rules for autoionization and predissociation processes are determined by the rules corresponding to each step. Since the initial transition typically involves a straightforward one-electron excitation due to photon absorption, normal optical selection rules establish the accessible states. The second step in each case represents a radiationless transition. Therefore, it observes the monopole selection rule

$$\Gamma(\Psi_d) = \Gamma(\Psi_c) \quad (17)$$

where Ψ_d and Ψ_c represent the wavefunctions of the discrete intermediate excited state and the continuous final state respectively. If the equilibrium conformations in the two states of the system have common symmetry, Ψ_d and Ψ_c must have the same symmetry species in order for the autoionization or predissociation step to have non-zero probability. If the two states possess equilibrium orientations belonging

to different point groups, elements of symmetry common to both point groups are considered. A discussion of the derivation of these rules from Wentzel's expression for radiationless transition probability^{99,100} as well as a detailed treatment of specific selection rules for predissociation may be found elsewhere.⁹³

It should be noted that a molecule can undergo a transition from the ground state to a bound state lying above the first ionization limit through excitation of more than one electron as well as through excitation of a single non-valence electron. As indicated in the discussion on direct ionization processes, multi-electron excitation usually requires high energy photon absorption. The formation of the $2s2p\ ^1P$ autoionizing state of helium from the $(1s)^2\ ^1S$ ground state is an example of a two-electron mechanism;¹⁰¹ however, a photon energy of 60.0 eV is needed for this transition. At energies appropriate to normal photoionization continua (about 8-20 eV), autoionizing states produced by excitation of non-valence electrons are encountered far more often.

The peak-like features which arise in experimental photoionization efficiency curves as a result of non-valence electron autoionizing transitions can frequently be classified in terms of smooth progressions along one or more empirically determined series. The prototype for these

progressions is the Rydberg series of lines which are observed in the absorption spectrum of the ground state hydrogen atom. These lines become more closely spaced with increasing quantum number and merge into the ionization continuum as defined by the Rydberg equation

$$h\nu_n = IP - \frac{R}{n^2} \quad (18)$$

where IP is the ionization potential of H atom, R is the Rydberg constant, n is the principal quantum number of the excited electron and $h\nu_n$ is the excitation energy of the nth Rydberg state. If a non-valence electron is removed sufficiently far from the ion core of a polyatomic molecule, it experiences very nearly the action of a unit charge central field. Such a system may legitimately be considered more or less hydrogen atom-like. Accordingly, there exists a Rydberg-like series of states which can be approximately fitted to the modified hydrogen atom formula given in Equation (1). In this formula, the quantum defect, δ , represents the deviation of the molecular Rydberg series from the H atom case. Each optically allowed quantum state above the zero-point level of the molecular ion ground state represents the ionization limit for an excited electron series of this type. Further, each series contains discrete states which lie above the threshold of the first ionization continuum. Each of these bound states may be considered

to consist of an excited Rydberg electron plus an excited ion core. Radiationless transitions from these states to the ionization continuum should result in a well-defined progression of peak-like autoionization features in the photoion yield curves. Thus, the analysis of resolvable autoionization structure in photoionization studies principally involves the empirical correlation of peak positions with one or more modified Rydberg formulas.

Radiationless autoionizing transitions from bound molecular Rydberg states occur by the transfer of energy from the excited ion core to the Rydberg electron. While varying amounts of ion core electronic, vibrational and rotational energy may be involved in this transfer,¹⁰¹ most observed autoionization processes may be interpreted in terms of the interaction of discrete and continuum electronic configurations. The theoretical aspects of this type of autoionization have been extensively investigated by Fano¹⁰²⁻¹⁰⁴ and Mies¹⁰⁵ using configuration interaction methods. Autoionization by configuration interaction entails the transition of the excited molecular core to a lower electronic state, with the excess energy carried away by the ejected photoelectron. Since the electron is not restricted to a specific kinetic energy, the resulting ion may be formed in any final state with a lower energy than that of the Rydberg state. According to the

theoretical treatments of Bardsley¹⁰⁶ and Smith,¹⁰⁷ the vibrational intensity distribution within a particular electronic state may often be directly correlated with the Franck-Condon factors connecting the excited autoionizing state with the final state.

When the excited bound state of a molecule consists of an electron in a high principal quantum number Rydberg orbital and an ion core with enough vibrational excitation such that the total energy of the system exceeds the ionization limit, vibrational autoionization may occur. The physical picture for this type of autoionization is that the excited molecular ion core undergoes vibrational relaxation whereupon the vibrational energy of the core is converted into enough electronic energy to eject the Rydberg electron. The vibronic coupling which gives rise to this process corresponds to a breakdown of the Born-Oppenheimer approximation. The energetics of the vibrational autoionization mechanism has been the subject of several theoretical discussions.¹⁰⁸⁻¹¹⁴ An important conclusion from the various models is that the rate of vibrationally induced autoionization is expected to lie between the slow process of fluorescence emission and the fast rate of autoionization by configuration interaction. This prediction has been verified by photoionization experiments on the H₂ molecule.^{78,115,116} A second con-

clusion from the theory is Berry's "propensity rule"¹¹⁰ which states that autoionization processes which involve a minimum change in vibrational quantum number are most probable. Experimentally, the aforementioned H₂ photoionization efficiency curves appear to support this selection rule. In contrast, a recent analysis¹¹⁷ of the photoion yield curve of NO indicates that $\Delta v < -1$ transitions are quite common.

In principle, autoionization by rotational-electronic interaction is also possible in a manner analogous to vibrationally induced processes. This mechanism has in fact been observed in the very high resolution H₂ photoionization measurements of Chupka and Berkowitz.^{78,116} However, this phenomenon is not expected to be resolved in photoionization efficiency curves taken under normal optical conditions.

2. Photoionization Efficiency Curves.

A photoion yield curve typically contains a record of many superimposed ionization features over a range of excess energy above the first ionization limit. Once the fundamental conditions for producing specific structure in photoionization efficiency curves are understood, it is possible to translate this record into molecular and ionic state energetic information. A logical method for

categorizing this information is to consider separately those quantities which can be obtained from (1) threshold data, (2) fine structure data and (3) appropriate thermodynamic cycles. In addition, there are numerous experimental aspects of data collection and analysis which deserve mention. The special problems pertaining to appearance potential measurements of dissociative processes will be discussed in a separate section.

a. Physical Conditions Leading to Coarse and Fine Structure

For a given chemical system, the fundamental properties of interest in a photoionization measurement are generally the first and higher ionization limits. As indicated previously, photoionization methods are particularly suited for threshold determinations of this type for two main reasons. First, the availability of high intensity light sources and sophisticated vacuum ultraviolet monochromators permits excellent photon energy resolution. Second, the photoionization cross sections for direct ionization channels commonly exhibit a step-like behavior as a function of excess photon energy near threshold. The so-called threshold laws which have been derived from theoretical quantum-mechanical treatments^{14-16,18,35} of the ionization process are generally used to interpret the observed cross-section energy dependences. These treat-

ments suggest that the functional form of the probability of ionization, $P(E)$, depends principally on the number of electrons, n , leaving the ionization site as given by the expression

$$P(E) \propto k(E-E_T)^{n-1}, E > E_T \quad (19)$$

where E is the ionizing energy, E_T is the threshold energy and k is a constant. For direct single photoionization, $n=1$ and Equation (19) becomes

$$P(E) \propto k(E-E_T)^0. \quad (20)$$

That is, the ionization efficiency is predicted to behave as a zero-order function of the excess energy, rising abruptly at the onset and remaining constant as E increases.

It is very important to avoid overextending the photoionization threshold law beyond its legitimate scope. As Rosenstock has indicated,¹ the validity of the law may be restricted to a very narrow energy range above threshold. Also, the range of validity may significantly depend on the system studied. In the absence of complicating factors, experimental evidence suggests that the cross section for a direct photoionization process tends to increase sharply at onset and fall off slowly at higher energies. This behavior is perhaps best illustrated by the simple photoionization efficiency curve for He^{118} as shown in Figure 1. Deviations from a cross-section energy

Figure 1. Photoionization Cross Section for Helium
(from Ref. 118).

dependence of this type are not uncommon, however. For example, the photoion yield curves of the alkali atoms exhibit fairly gradual thresholds and large variations at higher energies. In any case, photoionization threshold values are usually well enough defined that near spectroscopic accuracy in the determination of ionization potentials is commonly achieved.

For a polyatomic closed-shell molecule, a large number of superimposed step-like features corresponding to various electronic, spin, vibrational and rotational transitions might reasonably be expected in an idealized high resolution photoionization efficiency curve. Such steps would represent discrete increases in the photoionization cross section as a function of energy due to the availability of additional ionization channels. Structure of this type is indeed observed in the photoion yield curves of many molecules. However, for reasons to be discussed later, the appearance of direct ionization mechanisms as essentially discontinuous steps in photoionization spectra requires favorable conditions with respect to competing indirect processes.

According to the selection rules developed previously, all one-electron electronic transitions are allowed in photoionization. Therefore, the coarse structure

of an experimental photoionization efficiency curve should in principle contain thresholds corresponding to all energetically accessible excitations from the molecular ground state to the ground and higher electronic states of the ion. For many molecules, a photon energy scan in the range of about 10 eV above onset reveals one or more higher ionization limits. Transition probabilities for first and higher ionization thresholds typically vary only within a factor of two or three.

Because of resolution limitations, very fine rotational structure is rarely seen in experimental photoion yield curves. Splittings due to spin are also frequently undiscerned. Thus, the preponderance of observed direct ionization fine structure above threshold arises from transitions between the ground molecular state and available excited ionic vibrational states. Unraveling the complex vibrational structure in the spectra of a polyatomic ion is clearly a formidable task. As mentioned previously, this task is significantly simplified in the case of a molecule containing symmetry by the existence of vibrational selection rules in electronic transitions. For example, only eight of the twenty-four normal modes of acetone ion are A_1 fully symmetric (assuming acetone retains C_{2v} symmetry upon ionization). Therefore, progressions in

single quanta are allowed for these vibrations only. Transitions from $v''=0$ to the $v'=1$ state of the other 16 modes are strictly symmetry forbidden. As a result, the analysis of vibrational structure near the first ionization onset involves the consideration of relatively few excitations.

The relative probabilities of symmetry allowed transitions $AB(i'', v_n'') \rightarrow AB^+(i', v_m')$ typically give rise to a distinctive distribution of step heights in a given photoionization efficiency curve. To a good approximation, these probabilities correlate with corresponding squares of normalized vibrational overlap integrals (Franck-Condon factors). Two physical characteristics are important in determining the value of these integrals: (1) the difference in equilibrium geometry between the molecular and ionic state and (2) the difference in normal vibrational frequencies.⁹⁴ Computations using harmonic oscillator wavefunctions indicate that the former factor is generally the larger. The influence of equilibrium geometry change on the shape of photoion yield curves is well illustrated by Rosenstock's adaptation¹ of Krupenie's calculations,¹¹⁹ shown in Figure 2. For a small change in equilibrium conformation, a strong $v''=0 \rightarrow v'=0$ band is expected. In addition, the adiabatic transition is usually accompanied by short and weak

Figure 2. Calculated Franck-Condon Factors and Idealized Photoionization Efficiency Curves Corresponding to Various Changes in Bond Length for a Single Oscillator (from Ref. 1).

vibrational progressions. This behavior generally corresponds to the removal of a non-bonding electron in a system in which the initial and final state symmetries are identical. In contrast, the ejection of a bonding or antibonding electron will likely result in a significant change in equilibrium geometry. In such cases, long vibrational progressions may be seen and the maximum transition probability may occur for $v''=0 \rightarrow v' \neq 0$. The most active modes are typically those which involve a change in nuclear positions near the site where the ejected electron was primarily localized. For very large changes in potential energy surface, it is not certain that the adiabatic transition will be observed above background.

A change in symmetry between the molecular and ionic state may be expected to significantly affect the Franck-Condon envelope. For example, the photoion yield curve of NH_3 exhibits a weak adiabatic transition^{94,120} and a large number of vibrational steps, even though the first ionization limit corresponds to the removal of an essentially non-bonding electron. This distribution of relative transition probabilities apparently results from the change in geometry from pyramidal to planar upon ejection of the electron. Another example is the long vibrational progressions which occur in transi-

tions between bent and linear triatomic equilibrium configurations, such as for NO_2 .¹²¹

Two additional points concerning vibrational structure in photoionization efficiency curves deserve mention. First, the comparison of photoionization spectra for two or more isotopes of a given compound can facilitate the assignment of vibrational transitions. Particularly when ionization occurs by the removal of a non-bonding electron, isotopic variations in the ionic curves should roughly parallel those seen in the vibrational spectra of the neutral molecule. Second, if a variation in the spacing of a long progression of vibrational levels is found, it is possible in principle to obtain a measure of the anharmonicity of that particular mode. The vibration of a diatomic molecule provides the most straightforward example of this procedure. For a single oscillator with vibrational frequency ν , the energy levels E_v are given by the expression

$$E_v = h\nu\{(v+\frac{1}{2}) + x(v+\frac{1}{2})^2 + y(v+\frac{1}{2})^3 + \dots\} \quad (21)$$

where v is the vibrational quantum number and x and y represent first and second order anharmonicity constants respectively. If the linear and quadratic terms only are retained, the vibrational energy level spacing ΔE_v can be written

$$\Delta E_v = h\nu + 2h\nu x(v+1) \quad (22)$$

where v is the vibrational quantum number of the lower energy state of two adjacent levels. That is, ΔE_v should be a linear function of v with a slope of $2h\nu$. Hence, a plot of ΔE_v versus v should yield the first anharmonicity constant, x .

While direct vibrational excitations constitute a major source of fine structure in experimental photoion yield curves, indirect photon absorption mechanisms often compete significantly. For a given chemical system, the shape of the photoionization efficiency curve can be profoundly affected by the relative rates at which various autoionization and predissociation processes occur. Since configuration interaction induced autoionization usually occurs rapidly, broad peak-like features may be observed when this phenomenon is present. Features of this type occasionally dominate the structure arising from direct ionization continua, especially for small molecules. In contrast, the slower vibrational autoionization processes are manifested by very narrow peak widths, as required by the uncertainty principle. As described previously, peak positions corresponding to a given autoionization series are correlated when possible with modified Rydberg equations.

Predissociation mechanisms are not directly observed using photoionization mass spectrometric

techniques. Nevertheless, the competition between pre-dissociation and autoionization is crucial to the spectra obtained by these methods. From arguments relating the density of the oscillator strength for discrete excitations to the variation in absorption cross section,¹⁰⁴ it may be demonstrated theoretically that the average absorption cross section should vary smoothly and continuously through an ionization limit.¹⁰¹ Consequently, if the photoionization and photon absorption cross sections for a given molecule are nearly identical, step-like thresholds above the first ionization limit will not be seen in the photoion yield curve. This suggests that relatively fast non-ionizing absorption mechanisms are necessary in order to obtain step function fine structure due to direct ionization channels. In general, fluorescence emission is much too slow to achieve this effect. However, if pre-dissociation occurs at a sufficient rate to partially depopulate Rydberg states converging to the various thresholds, discontinuous onsets may be observed. This is frequently the case, especially for larger molecules.

The complex possibilities for fine structure in photoionization efficiency curves may be illustrated by a few examples. Figure 3 shows the photoionization cross section curve for Ar^+ .⁷³ Direct ionization occurs to

Figure 3. Photoionization Efficiency Curve for Argon (from Ref. 73).

the $^2P_{3/2}$ spin state of the ion. The splitting by spin-orbit interaction is large enough (about 0.178 eV) to be easily resolved and the spectrum above threshold is dominated by a well defined electronic autoionization series converging to the upper $^2P_{1/2}$ state. Individual peaks are fairly broad as expected for relatively fast configuration interaction induced processes. Perhaps the most interesting feature of the curve is the absence of a discontinuous threshold for the formation of the excited spin state. This behavior results from the fact that almost all photon absorption leads to ionization. In other words, fluorescence emission (the only possible non-ionizing photon absorption mechanism for this system) does not appreciably compete with autoionization.

As shown in Figure 4, the photoionization efficiency curve of NO^{89} exhibits substantial fine structure above the first ionization limit. Excitation of successive vibrational levels in the $^1\Sigma^+$ ionic ground state results in a regular staircase structure. Although the initial onset undoubtedly corresponds to the $v''=0 \rightarrow v'=0$ transition, a small difference in the equilibrium configurations of the molecule and ion is indicated by the distribution of transition probabilities. Predissociation appears to be the dominant indirect absorption process inasmuch as the threshold of each vibrational level is extremely sharp;

Figure 4. Photoionization Efficiency Curve
for NO (from Ref. 89).

however, weak vibrationally induced autoionization channels produce a definite structure superimposed on the direct ionization continua. This structure has very recently been reassigned¹¹⁷ to a combination of np and nd δ Rydberg levels. Given this assignment, the individual peaks are quite narrow. A relatively slow rate of vibrational autoionization produces this phenomenon.

The photoion yield curve of CS₂¹²² shown in Figure 5 provides an interesting contrast to the NO data. In this curve, the preponderance of observed autoionization is presumably due to configuration interaction. These autoionization features are so intense that they obscure the direct photoionization structure throughout most of the spectrum. In fact, the interference is so great that the only transition to an electronically excited state which is clearly seen is the threshold of the $^2\Sigma_u^+$ state at about 14.5 eV. By comparison, photoelectron spectroscopy studies^{123,124} resolve several electronic states of CS₂⁺ with ionization potentials in the energy range 12-20 eV. A significant change in the shape of the potential energy surface between the molecule and ion is suggested by the very weak initial onset.

b. Molecular and Ionic State Energetic
Information

The primary emphasis of the preceding dis-

Figure 5. Photoionization Efficiency Curve for CS_2^{122} (from Ref. 3).

cussion has been to consider how various features in a photoionization efficiency curve can arise from specific sets of conditions relating the molecular and ionic electronic structures. At this point, it is appropriate to briefly summarize the numerous properties pertaining to molecule and ion energetics which can be derived from an analysis of these features.

From coarse threshold structure, ionization potentials of ground and higher electronic states of an ion can be determined. The near step function behavior of most onsets in photoionization generally allows considerable accuracy in these measurements. On occasion, intense autoionization peaks may dominate the direct ionization continua to such an extent that one or more electronic state thresholds are lost. Under these circumstances, the relatively autoionization-free photoelectron spectroscopy techniques can provide essential complementary data.

In a photoion yield curve with suitably resolved fine structure, the energy differences between the zero-point level and higher spin, vibrational and rotational levels of a given electronic state may in principle be determined by measuring the separations of appropriate thresholds. For many compounds, ionic vibrational frequencies and splittings due to spin-orbit

interaction can be directly obtained in this manner; however, rotational structure is rarely resolved. In contrast to typical infrared spectra for neutral molecules, the best resolution generally occurs for the low frequency vibrations. Information pertaining to the change in the molecular potential energy surface upon ionization is contained in the Franck-Condon envelope for each vibrational mode. In cases where a long progression of a given ionic vibration is observed, examination of the variation in the spacing between successive levels may lead to a measure of the anharmonicity of that mode.

Indirect photon absorption processes both influence the direct ionization structure and provide additional information concerning molecular and ionic states. For systems in which predissociation is the predominant indirect mechanism, observed fine structure onsets due to direct ionization will typically be sharp. If autoionization channels are negligible, the heights of the various vibrational steps can be clearly related to corresponding Franck-Condon factors. On the other hand, if the photoion yield curve contains substantial contribution from autoionization, a correct measure of step height may be difficult. Autoionization structure which can be correlated with one or more modified Rydberg series

can often be useful in that the limits of these series may identify threshold values which might otherwise be obscure. Furthermore, the quantum defects used to generate these series are interesting insofar as they provide a measure of the deviation of the excited molecular electronic structure from the case of an ideal central field.

In addition to properties which may be obtained directly from the experimental photoionization efficiency curves, a substantial amount of molecular and ionic thermochemical data can be generated by using measured threshold values in appropriate thermodynamic cycles. This procedure may be illustrated by a few examples. For direct molecular photoionization, the following relation holds:

$$\text{IP}(\text{AB}^+) = \Delta H_f(\text{AB}^+) - \Delta H_f(\text{AB}) \quad (23)$$

where $\text{IP}(\text{AB}^+)$ represents the ionization potential of AB and where $\Delta H_f(\text{AB}^+)$ and $\Delta H_f(\text{AB})$ refer to the heats of formation of AB^+ and AB respectively. If $\Delta H_f(\text{AB})$ is known, the determination of $\text{IP}(\text{AB}^+)$ permits the calculation of $\Delta H_f(\text{AB}^+)$. Another example is the cycle

where IP_1 and IP_2 represent the ionization potentials of AB and $(AB)_2$ respectively and D_2 and D_2^+ refer to the dissociation energies of the dimer and dimer ion. Since AB^+ may be formed by either of the two pathways shown, the following relation holds:

$$IP_1 = -D_2 + IP_2 + D_2^+. \quad (25)$$

In a suitable photoionization mass spectrometric study, IP_1 and IP_2 can be directly measured. Therefore, if D_2 is known or can be estimated, the dimer ion dissociation energy, D_2^+ , may be calculated. Threshold values for ionic fragmentation processes can also be used in appropriate cycles to derive such quantities as proton affinities, free radical heats of formation, etc. Examples will be given in a later section.

c. Instrumental and Thermal Effects

An ideal measure of photoionization cross section would necessarily involve an infinitely fine resolution determination of the photoion yield for neutral molecules in their lowest state of internal energy. These conditions could be met only if it were possible to study the sample at OK using an infinitely small photon energy bandwidth. Consequently, the observed data of an actual photoionization experiment may be expected to contain effects due to practical instrumental and thermal limitations. It is important to minimize these effects in order

to improve the data collection. Properly taking the remaining limitations into account is essential for careful data analysis.

Instrumental factors which may influence the shape of experimental photoionization efficiency curves include the transmission efficiency of the ion optics, the collection efficiency of the ion detector, the monochromator entrance and exit slit widths, the output characteristics of the light source, and optical deficiencies resulting in non-homogeneous light and photoelectron production. The variation of ion transmission probability with excess photon energy above threshold is generally negligible over the energy range corresponding to individual photoion yield curve features. In addition, for experimental designs incorporating large ion accelerating voltages, the ion detector collection efficiency is virtually constant as a function of excess energy. Therefore, these factors are usually unimportant⁶⁷ and are not considered further.

A major systematic instrumental limitation in photoionization experiments is the unavoidable energy spread of dispersed radiation from continuum light sources. This spread introduces an uncertainty in the measurement of photoionization thresholds which can be minimized but not entirely eliminated. This effect generally occurs in the following manner. The range of the energy band which

a given lamp-monochromator system passes is principally determined by the slit widths employed on the monochromator entrance and exit arms. The variation in photon intensity over such a band, $E_0 \pm \delta$, typically approximates a triangular or trapezoidal function centered on the nominal photon energy E_0 . The convolution of a slit function of this type with a nearly step-like direct ionization threshold may be expected to produce a sigmoidal feature with the inflection point theoretically corresponding to the ionization onset.⁶⁷ The exact location of the threshold naturally becomes less certain as the s-shaped structure becomes broader. To the extent that photon intensity can be sacrificed, narrower slits can be used to establish more precise onsets. However, this procedure is finally limited by the ultimate resolution of the monochromator optics.

Given the highly refined current technology for producing intense, nearly monochromatic photon beams, uncertainties in the measurement of photoionization onsets can be made very small. A far more serious problem is spurious photoion yield curve features which can arise from various sources. For example, Nicholson has shown¹²⁵ that false structure in photoionization spectra can result from the use of a discrete-line light source. These features were seen in the vicinity of the very strong Lyman α

(1215.7 Å) and Lyman δ (1025.7 Å) lines in experiments using the many-line pseudo-continuum produced by a hydrogen discharge lamp. Now, phenomena of this type should occur independently of the system studied. Therefore, it is possible to identify such artifacts by comparing the photoionization efficiency curves for several species.

Other sources of spurious structure are ionizing photoelectrons and non-homogeneous light originating from defects in instrumental design. Large numbers of photoelectrons can be released from a metal surface which intersects the ultraviolet photon beam. If these particles are accelerated by a sufficient potential inside the apparatus, unwanted ionization may occur. This effect can be minimized by designing the instrument so as to prevent as much as possible the dispersed light from hitting metal surfaces near the ionization region. Collectors can be installed to attract most of the stray particles which are formed. Photoelectrons which experience substantial acceleration into the sampling area should produce ionization even if the photon energy lies well below the first ionization limit of the system. Moreover, since cross sections for electron impact ionization are generally much larger than those for photoionization, artifacts arising from a process of this type are likely to be large. Consequently, the absence of

photoion signal below the true initial onset is a good indication that the contribution to a photoionization efficiency curve from photoelectron bombardment is small. In contrast, the deleterious effects of non-homogeneous light are likely to be fairly subtle. Dispersed radiation far removed from the nominal monochromatic photon energy can be transmitted to the ionization region as a result of ghosts, stray light and higher order reflections from the diffraction grating. Spurious reflections inside the monochromator body are also possible. The last effect is typically eliminated by removing unnecessary reflecting surfaces and by painting the inside of the monochromator flat black. Higher order grating reflections, on the other hand, can be dealt with by using a light source with negligibly low photon intensity at integral multiples of the desired energy E_0 . If suitable filters exist, these can also be employed. Ghosts and stray light arise from imperfections in the grating which are periodic and non-periodic respectively.¹²⁶ It is quite difficult to determine precisely the extent to which a "monochromatic" photon beam may contain impurity light due to these imperfections; however, intense artificial lines or severe levels of scattered light should be obvious upon comparison with standard spectra. Needless to say, it is wise to utilize the highest quality grating possible.

In previous sections, brief mention has been made of the importance of the average internal thermal energy of the sample in limiting the working resolution of a photoionization experiment. Specifically, if a significant number of neutral target molecules exist in excited vibrational and rotational states, the photoion yield curve exhibits "hot bands," threshold tailing and loss of fine structure definition. In the present context, "hot bands" refer to those features in a photoionization efficiency curve which arise from allowed transitions from excited vibrational levels of the molecular ground state. These features will occur at lower photon energies than those corresponding to direct ionization onsets from $v''=0$. Structure of this type is particularly troublesome for systems in which the $v''=0 \rightarrow v'=0$ transition is weak. In such cases, the true adiabatic ionization potential may correspond to a poorly defined step well above the first appearance of photoions. Dibeler and co-workers have clearly demonstrated⁷⁵ the extent to which hot bands affect ionization thresholds for diatomic halogen molecules at room temperature. Since the energy separation of rotational states is often smaller than typical optical resolutions, individual rotational "hot bands" are not commonly observed. Instead, the rotational energy of the sample approximates a Boltzmann distribution with an average energy of $3/2 kT$

(about 0.039 eV at 298K) for polyatomic species. This rotational envelope causes tailing of the initial onset and an overall loss of ultimate resolution.

It is clearly advantageous to maximize the effective resolution of photoionization spectra by sampling molecules with low internal temperatures. As mentioned previously, the two established techniques for doing this are (1) straightforward cooling of non-condensable gases and (2) supersonic nozzle beam sampling. The latter method will be considered in detail in Section II.C.

3. Appearance Potential Measurements of Fragmentation Processes

At sufficiently high photon energies, the photoionization mass spectrum of a polyatomic molecule typically includes several fragmentation products in addition to the parent ion. These fragments can arise from such processes as direct dissociation to an ion pair or decomposition of the parent ion. The latter mechanism is observed most often. Experimental detection of this mechanism depends on the rate at which dissociation occurs. Fragment ion signals are seen directly only if decomposition takes place in the ionizer. On the other hand, fragment ions which are produced after mass analysis contribute to

the parent ion peak while dissociation products which are formed in the acceleration and magnetic field regions are not observed at all. Those ions which decompose prior to mass analysis but after acceleration give rise to so-called "metastable ion" signals. A fragment ion from a metastable decomposition is detected at an apparent mass position of m^* as given by the expression

$$m^* = \frac{(m_f)^2}{m_p} \quad (26)$$

where m_f and m_p are the masses of the fragment ion and parent ion respectively. Since metastable ion peaks generally occur at non-integral mass values and are usually much broader than normal mass spectral features, transitions of this type are easily identified.

The fragmentation processes of very small polyatomic ions can be successfully described quantitatively in terms of theoretically and experimentally determined details of potential surfaces. This approach becomes impractical for larger ions, however. For complex systems, statistical theories provide a more accessible means of treating dissociation mechanisms. The most widely applied method in this regard is the quasi-equilibrium theory developed by Rosenstock and co-workers.¹²⁷⁻¹³⁰ This theory is based upon a number of important assumptions. First, the time required for decomposition of the parent

ion is considered to be long with respect to the ionization and initial internal excitation step. Second, dissociation is judged to be slow enough that the excitation energy in the reactant ion has time to be redistributed over all degrees of freedom. Finally, fragmentation is assumed to occur along competitive and sometimes consecutive unimolecular reaction paths where each decomposition process may be described in terms of a separate reaction coordinate with an appropriate activation energy and activated complex. The first two assumptions are generally consistent with experimental observations¹³¹ and allow the ionic dissociation mechanisms to be considered independently of the initial excitation. In view of the low operating sample pressures typically employed in mass spectrometers, few ions experience collisions with other molecules or ions before extraction from the ionizer. Thus, in effect, ionic fragmentation takes place in an isolated system at internal equilibrium. The final assumption represents a model which is essentially common to the absolute rate theory of Eyring, et. al.¹³² as well as RRKM theory.^{133,134} Given the above assumptions, the microcanonical quasi-equilibrium theory rate expression may be written as given by Wahrhaftig¹³⁰

$$k_1(E) = \frac{\sigma}{h} \frac{W_1^\ddagger(E - \epsilon_1)}{\rho(E)} \quad (27)$$

where $k_1(E)$ is the reaction rate along reaction path 1 with activation energy ϵ_1 as a function of the reactant ion internal energy E , σ is the symmetry factor representing the number of identical paths for the decomposition, h is Planck's constant, $W_1^\ddagger(E - \epsilon_1)$ is the number of states of the activated complex lying between ϵ_1 and E , and $\rho(E)$ is the density of states for the parent ion. It must be briefly noted that other approaches to unimolecular ionic fragmentation theory have been proposed as well.^{130,135,136}

The quantities which are of primary interest in a photoionization mass spectrometric study of dissociative processes are the observed onsets of ionic fragmentation, commonly called appearance potentials. In particular, it is useful to obtain a measure of these thresholds for molecules in minimum internal energy states. The utility of direct ionization potentials in suitable thermodynamic cycles has been demonstrated previously. In a similar manner, appearance potentials can be used to deduce substantial amounts of thermochemical data. For instance, the reaction

may be characterized by the following thermochemical relations

$$AP(A^+) = \Delta H_f(A^+) + \Delta H_f(B) - \Delta H_f(AB) \quad (29)$$

$$AP(A^+) = IP(A) - D(AB) \quad (30)$$

where $AP(A^+)$ is the appearance potential of the A^+ fragment, $IP(A)$ represents the ionization potential of the free radical A , $D(AB)$ is the bond dissociation energy of $A-B$ and $\Delta H_f(A^+)$, $\Delta H_f(B)$ and $\Delta H_f(AB)$ represent the heats of formation of A^+ , B and AB respectively. Frequently, properties such as $D(AB)$ and $\Delta H_f(AB)$ are known from other work. Thus, experimentally determined appearance potentials may permit the calculation of such relatively inaccessible thermodynamic values as $\Delta H_f(B)$ or $IP(A)$.

Another example is provided by the cycle

where AP_1 and AP_2 are the appearance potentials of A^+ and ABA^+ respectively and D_2 and D_2' represent the bond dissociation energies of $(AB-AB)$ and $(AB-A^+)$. The two mechanisms giving rise to the formation of A^+ suggest the following relation:

$$AP_1 = -D_2 + AP_2 + D_2' \quad (32)$$

This relation is very similar to Equation (25). If D_2 is known or can be estimated, the direct measurement of AP_1 and AP_2 allows the calculation of the $(AB-A^+)$ dissociation energy. Moreover, subtraction of Equation (32) from

Equation (25) gives the interesting expression:

$$(IP_1 - IP_2) - (AP_1 - AP_2) = D_2^+ - D_2'. \quad (33)$$

This equation provides some measure of the influence of the B substituent on the dimer ion bond. In favorable chemical systems, incorporation of appearance potential determinations into other suitable thermodynamic cycles can lead to calculations of solvation energies, proton affinities, electron affinities, etc.

In addition to their direct importance in thermochemical calculations, appearance potentials may be used in determining ion-molecule reaction mechanisms and internal energies of reactive ions.¹³⁷ The effect of isotopic substitution on the relative cross sections for fragment ions is also interesting. In contrast to the typically very small differences observed in the ionization potentials of isotopic parent species, isotope effects in appearance potentials can be fairly large. If the appropriate force fields are known, these effects can be related to the zero-point energy differences of the various constituents in the ionization and fragmentation processes. A particularly instructive study in this regard is the photoionization mass spectrometric experiment on H_2CO , $HDCO$ and D_2CO performed by Guyon, Chupka and Berkowitz.¹³⁸

Using the threshold law for direct photoionization processes and the quasi-equilibrium theory

rate expression given in Equation (27), it is possible to derive a theoretical expression for the ionization efficiency of a primary fragment ion.¹³¹ For the purpose of this discussion, it is sufficient to point out that this expression predicts a fairly complicated relationship between the ionization efficiency and the energy of the ionizing medium. This prediction is generally borne out in actual appearance potential measurements. For the most part, fragment ion yield curves are observed to rise gradually from threshold and rarely exhibit well differentiated fine structure features.

The determination of meaningful appearance potential values from experimental curves is a non-trivial task. Aside from various difficulties associated with the instrumental sensitivities, at least five major factors have been identified¹³⁹ which can cause fragmentation thresholds to appear at higher photon energies than the proper thermochemical onsets. It is useful to restate these problems in some detail inasmuch as they illustrate many important physical aspects of decomposition processes.

(1) According to the quasi-equilibrium theory, the rate of ionic dissociation is a function of the largely randomized total internal energy content of the parent ion. It follows then that the thermochemical threshold for fragmentation corresponds to a given minimum

excitation energy. However, it may be possible that the transition probability for forming the reactant ion at the appropriate internal energy is very small. Under these circumstances, the onset of dissociation will be observed at the ionizing energy necessary to excite the next highest accessible state in the parent ion. Since the Franck-Condon envelope is often narrow in the electronic ground state of the ion, this would frequently be the case if direct $AB(X, v'', j'') \rightarrow AB^+(A, v'; j')$ channels were the only means of populating higher ionic states. Fortunately, autoionization and multi-electron excitation mechanisms as well as transitions to higher electronic states are generally effective in providing the necessary thermal energy range. The possible occurrence of this problem can typically be inferred from the photoionization efficiency curve or photoelectron spectrum of the parent species.

(2) In reactions where transitions from excited molecular or ionic electronic states are required in order for the ground state internal energy content of the ion to reach thermochemical fragmentation thresholds, selection rules may exist which nominally forbid the necessary transition. Because of the relatively long time periods available for observable dissociation (10^{-4} - 10^{-5} seconds), these rules rarely

restrict the possibilities for decomposition, however. In other words, intersystem crossings generally can occur.

(3) If all reaction coordinates for a particular fragmentation process contain potential barriers, E_1^* , the experimental appearance potential will be displaced from the thermochemical onset by the minimum barrier height, $E_{\min}^*$. In other words, Equation (29) becomes

$$AP(A^+) = \Delta H_f(A^+) - \Delta H_f(B) - \Delta H_f(AB) + E_{\min}^* \quad (34)$$

Experimental evidence indicates that $E_{\min}^*$ may range from zero to nearly one electron volt.^{1,140} While there are apparently no strict rules, $E_{\min}^*$ is often very small for decompositions involving single bond ruptures. On the other hand, large barrier heights are common for reactions involving rearrangement of bonds. Attempts have been made to develop a procedure whereby $E_{\min}^*$ may be deduced from the kinetic energy release in the fragmentation process. The various approaches which have been used are discussed by Rosenstock.¹

(4) From the quasi-equilibrium rate expression, Equation (27), the minimum rate for dissociation may be written as

$$k_{1,\min} = \frac{\sigma}{h\nu(\epsilon_1)} \quad (35)$$

where ϵ_1 represents the activation energy for the

reaction. In order for a decomposition process to be readily observed in a typical mass spectrometer, a rate constant in the range of 10^5 - 10^7 sec^{-1} is necessary. If $k_{i,\text{min}}$ falls well below this range, fragment ion signals may not be seen until a significant amount of additional internal energy is deposited in the reactant ion. This excess energy is commonly known as the kinetic shift.⁶⁹ In general, dissociation processes which exhibit this effect may be identified by the occurrence of strong metastable peaks. Since ions of this type arise from slower decompositions than those which take place in the ionizer, comparison of fragment ion and "metastable ion" appearance potentials may be expected to yield at least part of the kinetic shift. While no certain experimental method exists as yet for measuring the remaining part of this shift, a relationship between this quantity and the kinetic energy release in metastable decompositions has been suggested.^{141,142} Ion-trapping techniques represent a potentially useful means of determining very nearly the full kinetic shift. Gordon and Reid have employed this method¹⁴³ to investigate the excess energies required for a few reactions. These measurements are in fair agreement with Vestal's quasi-equilibrium theory calculations¹³¹ which estimate the kinetic shift for a

number of typical fragmentation mechanisms. Vestal's results indicate that the additional energy needed for a reaction rate of 10^5 - 10^6 sec^{-1} is often negligible. In contrast, kinetic shifts of up to 2 eV are predicted for such processes as the loss of H atom from benzene and toluene ions.

(5) For many systems, a large number of competitive and consecutive ionic decomposition processes may occur within a few eV of the first ionization limit. Under these circumstances, it is often difficult to see many of the higher energy channels at the appropriate thermochemical thresholds. If reaction competition is strong, a less favored mechanism generally requires substantial energy in excess of the activation energy in order to produce detectable fragmentation. That is, large kinetic shifts are observed for these dissociations. Moreover, the first decomposition in a consecutive process does not produce daughter ions and neutral fragments in specific energy states. Rather, these reaction products are typically formed with a wide distribution of excitation energy. As a result, appearance potential curves corresponding to successive fragmentation mechanisms exhibit poorly defined onsets, rising almost asymptotically from background.

In contrast to the various factors which displace appearance potentials to higher energies, the distribution of excess internal energy in the sample molecules prior to ionization serves to lower the observed onsets. Since the rate of dissociation may be considered to be largely independent of particular excitation mechanisms (according to quasi-equilibrium theory), virtually all of the initial thermal energy in a parent molecule should be effective in ionic decomposition processes. Experimental fragment ion curves may then be expected to contain a low energy "tail" below the proper (OK) thermochemical threshold. In practice, this effect often cancels some of the errors introduced by the five problems mentioned above. The influence of sample thermal energy on appearance potential measurements has been carefully investigated.⁶⁶⁻⁶⁹ One empirical method of correcting for internal energy effects requires data collection at two or more temperatures followed by comparison of threshold differences with changes in internally stored energy calculated from heat capacity data.¹⁴⁴ An alternative method is described by Chupka.⁶⁹ Once again, it should be noted that substantial decreases in the thermal energy of the molecules can be achieved by sampling from a supersonic nozzle expansion. This

technique will greatly diminish, but not entirely eliminate, the shift in onsets.

In summation, many processes pertaining to the dissociation of excited molecular ions may be studied using photoionization mass spectrometric methods. Appearance potentials, in particular, provide an important measure of the energetics of ionic decompositions. These values are perhaps most useful in determining various thermochemical properties of molecules, ions and free radicals. However, it is clear that a careful interpretation of experimental appearance potential data requires due consideration of numerous possible sources of error.

C. Supersonic Molecular Beam Sampling

The first recorded attempt to generate large numbers of molecules in straight line trajectories appears to be Dunoyer's sodium beam work in 1911.¹⁴⁵ Since that time, molecular beam techniques have been widely employed in experimental studies of the properties and behavior of atoms and molecules. Effusive or oven beam methods and supersonic nozzle beams are two particularly useful techniques which have been developed.

Beginning with Otto Stern's work in 1919, much of the attention of early investigators was given to the design and utilization of effusive beams. These

techniques have consistently been found to be appropriate to various applications and numerous detailed reviews of these methods and results are available.¹⁴⁶⁻¹⁵² Briefly stated, beam production systems of this type generally consist of a linear manifold of three chambers which communicate only through small apertures or slits. The oven or source chamber contains a gas at a temperature roughly defined by the temperature of the walls. If the pressure in this enclosure is maintained low enough that the mean free path of the gas particles exceeds the diameter or width of the opening, the molecules escape freely through the aperture into the second cavity. This chamber typically serves to collimate the effusive flow so that the third cavity receives a well defined beam for investigation or detection. In order to sustain the effusive beam, it is necessary to evacuate the second and third enclosures with suitable vacuum pumps. This assures that the mean free paths of the particles in the beam and in the background gas are longer than the dimensions of the apparatus. In effect, effusive beam methods establish a sampling regime which is characterized by a relatively collision-free unidirectional flow of molecules.

For all their advantages, oven beam techniques suffer from practical limitations in intensity and

energy. Intensity restrictions exist because of the mean free path considerations mentioned above. Thus, equivalent effusive beam pressures rarely exceed 10^{-6} - 10^{-5} torr under typical vacuum conditions. Beam energy limitations arise from the lack of gas box construction materials able to withstand temperatures in excess of 3000K. Since source gas temperatures above this quantity are not feasible, the maximum attainable average translational energy of molecules in a thermal oven beam corresponds to $2kT$ or about 0.5 eV. These intensity and energy problems substantially inhibit the applicability of effusive beam methods in experiments having inherently low signal-to-noise ratios and in studies of moderate energy collision processes.

The desire to increase beam intensities has encouraged the development of alternative beam sources. One moderately successful technique consists of replacing the single source chamber orifice with an array of parallel channels. This method was apparently first employed by Zacharias in 1953.¹⁴⁸ Significant enhancement of beam intensities can be achieved using multi-channel arrays, especially at lower net pumping speeds in the collimating chamber.¹⁵³ However, far more intense molecular beams can be produced by substantially

increasing the source chamber pressure so that the conventional effusive flow field is transformed into a supersonic jet. An additional beam defining aperture is typically placed in the jet in order to meet the increased pumping requirements. This instrumental approach represents the basis of nozzle beam technology.

Supersonic molecular beams developed quite slowly in comparison to oven beam methods. The earliest supersonic jet experiments appear to have been performed by Johnson^{154,155} in 1926-27. In these studies, a mercury atom beam was operated at source pressures such that the particle mean free path was much smaller than the narrowest dimension of the exit aperture. Cryogenic pumping was employed to handle the increased throughput. Consequently, an additional beam defining element and pumping chamber were not needed. Maximum intensities were observed to be in excess of 100 times larger than those expected for a conventional effusive beam. Another interesting early paper is Rodebush's review of "molecular rays" published in 1931.¹⁵⁶ In this article, a beam defining design is suggested which bears a striking resemblance to many sonic nozzle - conical skimmer arrangements used today.

It remained for Kantrowitz and Grey¹⁵⁷ to reassert the powerful possibilities of supersonic nozzle beam techniques. The instrumental scheme proposed by these authors in 1951 included a converging-diverging (or Laval) source chamber nozzle and a conical skimmer serving as the entrance orifice of the collimating cavity. A theoretical analysis anticipated several advantages to this design, including large increases in beam intensities. These predictions were partially verified in the experimental companion paper of Kistiakowsky and Slichter¹⁵⁸ and more fully confirmed by several later studies.¹⁵⁹⁻¹⁶³ In this regard, the work of Becker and Bier¹⁵⁹ is particularly noteworthy in that these authors found that a free jet from a converging nozzle was at least as effective in producing intense molecular beams as a tailored expansion from a nozzle with a diverging exit section. A sizeable body of literature pertaining to the design, quantitative characterization and application of supersonic nozzle beams presently exists. These developments are adequately described in various review articles.^{153,164-167}

Supersonic jets begin as a continuum flow of gas issuing from the source chamber. However, as the gas expands into a region of low pressure, the particle

density is rapidly reduced, resulting in a transition from continuum flow to nearly free molecular flow. Consequently, nozzle sources are akin to oven beams in that they may be used to produce a relatively collisionless unidirectional stream of sample molecules. In contrast to effusive sources, a nozzle expansion results in directed mass motion of the gas upstream of the first beam defining orifice. This aperture then serves to extract the high intensity central portion of the jet. This precollimation effect markedly increases the beam flux into the first collimation chamber. While actual beam performances generally fall well below predictions based on the formulas of Kantrowitz and Grey¹⁵⁷ and Parker et. al.,¹⁶⁸ equivalent beam pressures of 10^{-4} torr are commonly achieved.

In practice, the principal causes of nozzle beam intensity attenuation are background scattering phenomena and skimmer interactions. The extent to which each of these effects contributes to molecular beam destruction largely depends on the nozzle-skimmer distance. At large separations, beam intensities are reduced as a result of appreciable scattering of the free jet molecules by the background gas. As the nozzle-skimmer distance is shortened, background scattering diminishes in effect and intensities rise. Beam

performances are observed to pass through a maximum and then fall off as further reductions in the nozzle-skimmer distance are made. At still smaller separations, beam intensities typically pass through a minimum and eventually begin to rise again. This functional dependence arises from increased scattering of the jet molecules at the skimmer as well as scattering from the nozzle exhaust chamber walls. Finally, at very small nozzle-skimmer spacings, the skimmer operates in continuum flow, resulting in a large throughput and generally overwhelming pumping speed demands.

Because of their importance in limiting maximum attainable beam intensities, numerous experimental and theoretical investigations have been made with the intent of characterizing and finding ways to circumvent background scattering and skimmer interference phenomena.¹⁶⁹⁻¹⁷³ In general, it has been found that the deleterious effect of background scattering is best minimized by decreasing the expansion chamber pressure. On the other hand, skimmer interactions are somewhat more difficult to control. In this regard, considerable attention has been given to improving beam performance by optimizing the skimmer geometry.¹⁷⁴⁻¹⁷⁷ Unfortunately, intensity enhancements which result from changes in skimmer shape are

typically fairly small.¹⁶⁷ For molecular beams of condensable compounds, it is possible to virtually eliminate skimmer interference by cooling the nozzle exhaust chamber walls and skimmer cone to liquid nitrogen or liquid helium temperatures; however, a practical disadvantage of this method is the frequent plugging of the beam defining orifice which necessarily occurs. In the final analysis, complete removal of the skimmer is perhaps the most desirable and definitely the most straightforward solution, but this measure requires enormous pumping speeds in the test chambers. These considerations play a crucial role in the vacuum and hardware features of supersonic nozzle beam sources. Depending on the particular application, most current instrumental designs represent some type of compromise between high beam intensity and the two related factors of economy and practicality.

In addition to the relatively high sample intensities which may be achieved, nozzle beams possess several other well known characteristics:

(1) Since the sample molecules undergo collisions in a supersonic expansion, extensive energy transfer between various degrees of freedom can take place. These transfer processes lead to a conversion of the initial internal and random translational energies

of the molecules into directed mass motion. As a result, individual molecular velocities are closely grouped about a mean flow velocity which significantly exceeds that expected for an effusive beam.^{157,160-163}

(2) As the jet expands isentropically into a vacuum, the rate of molecular collisions decreases rapidly. Energy transfer becomes correspondingly less probable as the transition from continuum to nearly free molecular flow proceeds. At various points in the expansion, the probabilities of further relaxation of the vibrational, rotational and random translational degrees of freedom become prohibitively small. Consequently, the conversion of thermal energy into directed mass motion is typically substantial but not complete. The expected variation of internal and random translational temperatures as a function of distance along the expansion (as given by Anderson¹⁶⁷) is shown in Figure 6. Final temperatures are determined by the number of collisions required for the respective relaxation processes as well as by such expansion conditions as nozzle source pressure, expansion chamber pressure, etc. In general, the vibrational relaxation process is completed most quickly, followed by the rotational and then translational degrees of freedom.

1

Figure 6. Variation of Vibrational, Rotational and Translational (Parallel and Perpendicular to Expansion Axis) Temperatures in a Free Jet as a Function of Axial Distance, x , in Nozzle Diameters, D_N (from Ref. 167).

(3) Depending on various source conditions, supersonic expansions of gas mixtures can lead to preferential enhancement of the concentrations of one or more components along the beam axis. This mass separation effect was apparently anticipated by Dirac¹⁷⁸ and was first reported by Tahourdin¹⁷⁹ in 1946. Under most circumstances, gas mixture beams are observed to be enriched in heavier species along the centerline of the expansion. This phenomenon has come to be known as a "positive enrichment" or "positive separation." Mass separation effects of this type arise from interactions of the gas mixture jet with the sampling hardware¹⁸⁰ as well as from radial migration of the heavier molecules toward the beam axis due to a pressure diffusion mechanism in the free expansion.¹⁸¹⁻¹⁸⁴ However, preferential enhancement of lighter components or "negative separation" can also occur.^{185,186} The mechanism for this phenomenon appears to involve selective aspiration of light background molecules through the shock wave structure of an underexpanded free jet.^{178,187} Since the background gas chiefly consists of molecules skimmed from the expansion, favorable source conditions will result in the observation of higher concentrations of the lighter species of a gas mixture downstream of the skimmer. It is clear that

nozzle beams of mixed gases possess several advantageous features. It is obviously possible to produce intense beams of a given compound by suitably "seeding" the jet with another gas so that selective mass separation takes place. An important consequence of this behavior is that aerodynamic enrichment phenomena in flow regimes may be effectively utilized as a gas and isotope separation technique.¹⁸⁸ Finally, gas mixture jets provide a means to overcome the previously discussed energy limitations which exist for oven beams.^{153,166} This feature arises from the fact that heavy molecules are accelerated by lighter species in a nozzle expansion such that the final velocity of a gas mixture beam corresponds to that velocity which would be expected for a uniform gas having a molecular weight equivalent to the concentration-weighted average of the various components in the mixture. Hence, the mean jet velocity of a dilute mixture of one or more heavy species in a light carrier gas will be very nearly equal to that of the pure carrier gas. By taking advantage of positive mass separation effects in tandem with this aerodynamic acceleration, fairly intense high energy beams of heavy components in mixed gases can be achieved. This method has been used to obtain supersonic nozzle expansions in the 0-37 eV range.¹⁸⁹

(4) Under appropriate expansion conditions, the low molecular temperatures produced in supersonic jets can lead to partial condensation of the sample gas. As a result, weakly bound cluster molecules can be produced in relatively large amounts. Full condensation does not occur because the rate of necessary three-body molecular collisions decreases rapidly as the expansion proceeds. At present, there exists no rigorous theory to quantitatively determine the extent of cluster formation for a given system.¹⁹⁰ However, the degree of observable condensation has been observed to be a function of such experimental conditions as the initial composition of the test gas, source pressure, source temperature, nozzle orifice diameter, expansion chamber background pressure and skimmer interaction effects. Considerable effort has been expended to arrive at empirical correlations of cluster production with source parameters and various scaling laws for the kinetics of condensation in nozzle flows have been developed.¹⁹⁰⁻¹⁹⁸ Precise correlations of this type clearly require accurate measurements of the relative concentrations of cluster species in the expansion. Unfortunately, these measurements are a non-trivial task. In particular, the mass spectrometric detection methods most often used for this purpose contain sub-

stantial uncertainties due to the usual mass discrimination effects, as well as unknown variations in ionization cross sections with cluster size and the largely indeterminable contributions to a given cluster ion signal from fragmentation of higher clusters. Also, it is necessary to account for any significant pre-expansion equilibrium concentrations of weakly bound complexes. Nevertheless, several general trends are consistently observed in free jet studies. Definite cluster production increases often result from elevated source pressures, decreased source temperatures and larger nozzle openings. Important additional contributions from skimmer interaction effects¹⁹⁹ are illustrated in Figure 7. Therefore, within the limitations of a given instrumental design, a number of parameters may be adjusted to optimize the concentrations of individual cluster species; i.e., dimers, trimers, tetramers, mixed clusters, etc.

Several of the features mentioned in the foregoing paragraphs promote supersonic nozzle beams as a unique and useful sampling method for photoionization mass spectrometric investigations. Perhaps the most straightforward advantage of this technique is the facile control which can be exercised over the position and

Figure 7. Effect of Skimmer and End Wall Temperatures on Argon Monomer and Dimer Beam Intensity:
 A = 20K Skimmer and End Wall,
 B = 295K Skimmer and 20K End Wall, C = 20K Skimmer and 295K End Wall, D = 295K Skimmer and End Wall
 (from Ref. 199).

concentration of the target gas. The former parameter is fixed by the instrumental geometry. At the same time, sample concentration is primarily determined by the various expansion conditions. Consequently, this factor may be held constant for hours at a time by carefully monitoring source pressure, source temperature, etc. Another fundamental advantage of molecular beams is that they provide a sampling regime which may be conveniently and alternately quenched and fully restored through the use of a beam flag. Hence, experimental background corrections are easily made. Needless to say, the relatively high intensity of supersonic jets is also a valuable asset in photoionization work, especially in view of the fact that photon fluxes and photoionization cross sections are typically much smaller than corresponding values for electron impact methods. On the other hand, nozzle beams permit the realization of fairly large equivalent sample pressures (10^{-5} - 10^{-4} torr) without unduly increasing the background pressure in the ionization region. Hence, a suitable vacuum may easily be maintained in the monochromator, test chamber and mass spectrometer. Under these conditions, it is advantageous to extract the photoions in a direction perpendicular to the molecular beam flow.

By quickly drawing out the ions into a region of relatively low pressure, it is possible to substantially minimize the incidence of undesirable ion-molecule reactions.

The characteristic occurrence of extensive energy transfer in supersonic expansions represents a distinct asset in photoionization studies. The principal advantage in this regard is the high effective resolution accruing to photoion yield measurements from vibrational and rotational relaxation in free jets. This positive aspect of supersonic molecular beam sampling has been adequately discussed in previous sections. However, a related phenomenon which deserves additional consideration is the process of partial condensation. This by-product of low internal temperatures in nozzle beams is particularly useful in photoionization mass spectrometry in that it greatly facilitates the investigation of the energetics of interesting cluster molecules and their respective ions. To fully appreciate this contribution of supersonic molecular beam sampling, it is necessary to digress slightly by considering the characteristics and importance of weakly bound species.

A molecule may generally be regarded as weakly bound if it contains at least one bond which has a

strength of 0.4 eV or less. Most of these molecules may conveniently be classified as resulting from one of two categories of interactions: (1) van der Waals forces and (2) the hydrogen bond. The term "van der Waals forces" is a collective designation which refers to a weakly attractive total intermolecular interaction corresponding to the complex interplay of several attractive and repulsive elements.²⁰⁰ A principal type of attraction in this interplay is the so-called London, or dispersion, energy which may be thought of as arising from statistically present instantaneous dipoles in atoms or molecules. The London energy is present in any collection of particles and this effect, along with exchange (Pauli) repulsion, largely accounts for the existence and equilibrium configuration of many cluster molecules. Rare gas cluster species like Ar_2 , Kr_2 and Xe_2 are essentially bound as a result of London forces alone while other attractive terms (charge-transfer stabilization, induction interactions, etc.) contribute in varying amounts to the formation of such clusters as ArClF and $\text{C}_6\text{H}_6\text{-Cl}_2$.²⁰⁰ Hydrogen bonding, the second important class of weak intermolecular interactions, is a well known phenomenon which is crucial to many interesting and valuable properties of water,

ammonia and various organic compounds. This attraction principally occurs in molecules containing hydrogen and such electronegative constituents as nitrogen, oxygen or fluorine. A useful and fairly accurate qualitative picture of hydrogen bonding is that a H atom which is covalently bound to a strongly electronegative atom may experience a relatively small but significant electrostatic attraction toward another region of high electron density. This picture is consistent in a simple fashion with the characteristically asymmetric hydrogen bond geometry A-H---B, where the A-H covalent bond distance is much shorter than the separation between H and B. In reality, there are at least four possible contributions (positive and negative) to hydrogen bond formation: electrostatic interaction, London-type van der Waals forces, exchange interaction and bond delocalization.²⁰¹ In any case this category of fairly weak bonding may be expected to be important in such cluster species as $(H_2O)_2$, $(NH_3)_2$ and $(HF)_2$.

As indicated above, one or more types of weak attractive forces are operative in any aggregation of atoms or molecules. Consequently, weakly bound molecules may be expected to be present in almost all gases, at least in trace quantities. In spite of the low concentrations in which cluster molecules are usually found

in equilibrium systems, substantial evidence exists which suggests that these species are important in establishing many of the bulk properties of gases and are influential in various other aspects of physical chemistry, including chemical kinetics, nucleation and condensation phenomena, energy transfer processes and spin relaxation.²⁰⁰ For example, a crossed molecular beam study has convincingly demonstrated that van der Waals dimers participate strongly in the formation of certain interhalogens by exchange reactions.²⁰² In this investigation, the following six-center reactions

were observed to proceed easily at thermal collision energies (about 3 kcal/mole) while reaction products for the straightforward four-center $\text{Br}_2 + \text{Cl}_2$ mechanism were not observed at collision energies up to about 25 kcal/mole. Several other reactions involving weakly bound molecules are known as well.²⁰³⁻²⁰⁵ Another interesting example is the postulated formation of small van der Waals clusters as the products of the first few addition reactions in the homogeneous nucleation of argon.¹⁹⁷ The following consecutive steps are suggested:

Weakly bound clusters are likely to play an equally significant role in the kinetics of other nucleation processes.²⁰⁰ Because of the importance of van der Waals and hydrogen-bonded molecules, numerous theoretical and experimental methods have been employed in order to determine the structure and properties of these species. These methods and results have been extensively reviewed.^{200,206-208}

Photoionization mass spectrometry in conjunction with molecular beam sampling is a powerful technique for studying weakly bound molecular and ionic complexes. The information which is provided by the measurement of cluster photoionization efficiency curves is much the same as in monomer studies. For instance, first and higher ionization potentials of cluster molecules may be obtained from the various thresholds of the appropriate photoion yield curves. If well resolved autoionization structure is present, energy separations of excited molecular Rydberg states may be determined. Other types of information include ionic vibrational frequencies, Franck-Condon factors for direct ionization and fragment ion appearance potentials. As indicated in

Sections II.B.2 and II.B.3, important thermochemical data can be derived by introducing measured cluster ionization and appearance potentials into appropriate thermodynamic cycles.

D. Experimental Design

The experimental techniques employed in photoionization mass spectrometric studies very much depend on the specific applications. However, a common denominator in virtually all of these applications is the need to overcome difficulties imposed by the relatively low monochromatic photon fluxes (e.g., compared to electron bombardment sources) currently obtainable. In particular, it is desirable to maximize the light throughput of the monochromator, the ion transmission and collection efficiencies of the mass spectrometer and the sensitivity of ion detection. This discussion will emphasize those instrumental features which have been successfully employed in the measurement of photoionization efficiency curves. It is convenient to consider separately experimental techniques pertaining to (1) the light source-monochromator system, (2) the sampling source and ionizer, (3) the mass analyzer and (4) the ion detection system.

Light Source - Monochromator

The ionization potentials of the vast majority

of fairly simple molecules fall in the energy range of 8-20 eV. As a consequence, vacuum ultraviolet light is required for most photoionization work. For this purpose, a wide variety of line emission and continuum light sources have been developed.²⁰⁹ However, a literature survey of contemporary photoionization studies would seem to indicate that there are at present three practical light sources for the determination of photoion yield curves. The rare gas continua excited in a capillary discharge²¹⁰ collectively represent the most widely employed type of non-discrete source. With helium as a lamp gas, useful intensities in the range 580-1100 Å may be obtained. With argon, krypton and xenon, the spectral distributions cover the wavelengths 1050-1550 Å, 1250-1800 Å and 1480-2000 Å respectively. Available intensities are generally fairly reasonable, except in the region of 950-1100 Å. For most efficient results, the continua are excited in a repetitive discharge. Either pulse-amplifying circuits or thyatron-triggered circuits may be used. With a pulsed discharge lamp, it has been estimated that about 10^{10} photons/sec-Å may be obtained at 800 Å using the He Hopfield continuum.⁹⁰ A second very useful source of vacuum ultraviolet light is the molecular hydrogen spectrum produced in a D. C. capillary discharge. Although the

hydrogen spectrum below $1670 \text{ \AA}$ does not qualify as a true continuum, this light source contains a series of densely packed lines which are quasi-continuous in the wavelength region $850\text{--}1670 \text{ \AA}$. This spectrum has been very carefully characterized by Samson, as shown in Figure 8.²⁰⁹ As indicated in this figure, available photon intensities at typical resolutions range from about 5×10^8 photons/sec to 2×10^{10} photons/sec at the Lyman α atomic line. Finally, synchrotron radiation is an excellent, but largely unavailable, continuous vacuum ultraviolet light source. This radiation arises from high energy electrons (or possibly other charged particles) undergoing centripetal acceleration in a magnetic field. At relativistic electron energies, the instantaneous distribution of emitted light is confined to a narrow cone in the plane of the particle trajectory. The axis of this cone points in the direction of the electron's motion. As a result, it is quite feasible to extract much of this light into a spectrograph or monochromator. In principle, synchrotron radiation is an ideal light source inasmuch as it has a smooth wavelength dependence extending from the soft x-ray region to the infrared. General discussions of this radiation source are available.^{209,211-213} From photoionization experiments

Figure 8. H₂ Spectrum Between 850 and 1750 Å.
 Lamp Pressure, 250μ; Discharge
 Current, 400mA. Pt-Coated Grating,
 1200 lines/mm. (from Ref. 209).

performed at the University of Wisconsin,^{79-81,91} it would appear that current synchrotron facilities are capable of providing vacuum ultraviolet photon intensities that are somewhat higher than or at least equivalent to those obtainable with conventional discharge lamps. More ambitious electron storage ring projects, such as the one under development at Brookhaven National Laboratory, should result in even higher intensities.

A meaningful comparative analysis of the rare gas continua, the hydrogen many-line pseudo-continuum and synchrotron radiation necessarily entails numerous practical considerations. For instance, the advantages of the undeniably superior spectral characteristics of synchrotron radiation are substantially offset by the general unavailability of this photon source. In addition, careful precautions in instrumental design must be taken to avoid contamination of the high vacuum (about 10^{-10} torr) required for this light source.²¹² Because high photon intensities are produced over a very large energy range, undesired contributions from higher order reflections from the grating must also be taken into account. In contrast, the many-line spectrum obtained from a molecular hydrogen D.C. capillary discharge is in principle clearly inferior for high

resolution photoion yield curve applications. As mentioned in Section II.B.2., the possible experimental artifacts arising from the use of a source containing semi-discrete lines must be considered. Furthermore, photoionization studies must be restricted to the wavelength region of 900-1650 Å. However, the hydrogen spectrum offers the advantage of being by far the most conveniently obtained. Capillary discharge lamps and appropriate regulated D.C. power supplies are both commercially available and fairly simple to operate. Since no suitable materials exist for light transmission below 1040 Å, it is best to be able to operate a monochromator without windows. Inasmuch as the H₂ quasi-continuum can be intensely excited at lamp pressures as low as a few hundred microns, a hydrogen source may be easily coupled into a system of this type. In other words, a good vacuum may be maintained in the monochromator with a relatively modest differential pumping design. Moreover, a properly operated lamp will work for many hours with very little sputtering. The spectral quality associated with rare gas continua lies in between the smooth continuum of synchrotron radiation and the many-line hydrogen emission. In a similar manner, the experimental techniques for producing repetitive rare gas discharges are more accessible

than electron storage ring facilities, but somewhat more difficult than H_2 D.C. discharge methods. Although they are fairly expensive, the necessary power supplies and pulsing equipment are commercially available. More important, high lamp pressures (about 40-100 torr) are required for intensely excited continua. For krypton and xenon, sealed lamps with windows are typically employed. A helium lamp, on the other hand, must be operated windowless. Consequently, the monochromator differential pumping requirements are quite severe. The use of high purity gases is advisable in these discharges as is the incorporation of a back-pumping port at the lamp cathode. This latter procedure prevents the narrow monochromator entrance slit from being clogged by significant amounts of sputtering deposits.

From a practical instrumental standpoint, it is clearly advantageous to perform photoionization studies with a vacuum ultraviolet monochromator in which selected and variable light dispersion is accomplished without movement of the entrance and exit slit assemblies. Two commonly employed monochromator classes are the Seya-Namioka type,²¹⁴⁻²¹⁶ in which the wavelength scan is provided by simple rotation of a concave diffraction grating about a vertical axis through the grating center and the near-normal inci-

dence type,²¹⁷ in which the wavelength is varied by rotation and translation of the grating along the bisector of the angle subtended by the slits at the center of the grating. With regard to photoion yield curve experiments, the principal asset of the Seya-Namioka mounting is the wide angle (about 70°) between the entrance and exit arms. In comparison with the near-normal incidence type, this configuration permits considerably more freedom in apparatus design. Unfortunately, conventional Seya-Namioka monochromators are by no means equal to near-normal incidence mountings in terms of ultimate resolution and maximum dispersed light throughput. Losses in these categories arise primarily because of characteristically large astigmatism effects. Substantial improvement in the performance of the Seya-Namioka design can be achieved through the use of curved slits.²¹⁸

For a given monochromator, the physical properties of the grating which most affect the throughput of the instrument are the blaze angle, the surface coating and the density of grooves. The first property is determined in the manufacturing process²⁰⁹ and does not require further discussion here. With regard to surface films, an appropriate coating should be chosen for the region of interest since the reflec-

tances of the most commonly used materials vary considerably over the vacuum ultraviolet wavelength range.¹²⁶ For work in the region of 1150-1500 Å, an aluminum-coated grating with a thin MgF₂ overcoating appears to be the best choice. These materials provide reflectances as high as 80% between 1200-1500 Å. The reflectance properties of LiF are quite good (55-60%) in the range of 1000-1200 Å, but an overcoating of this substance is hygroscopic and must be protected from moisture. At wavelengths shorter than 900 Å, the use of gratings containing surface films of gold or platinum is advisable. At the same time, the groove density of a grating affects the throughput of a monochromator in that the resolution obtained with given entrance and exit slit widths is directly proportional to the number of rulings. That is, a grating with twice as many grooves permits approximately the same resolution at twice the slit size. On the other hand, if the lamp spectrum is constant as a function of wavelength, the intensity of the dispersed light leaving the exit arm is proportional to the square of the slit widths. Consequently, increasing the groove density by a factor of two can result in as much as a fourfold enhancement in monochromatic photon intensity. It should be noted that practical limitations on the spacings in classically

ruled diffraction gratings exist because of the tendency for ghosts and stray light levels to increase with groove density. This is apparently not the case for holographically recorded gratings¹²⁶ and the production of very finely spaced optical components is possible through this technique.

Dispersed light from the grating is focused at the monochromator exit slit and then diverges. In order to effectively apply this monochromatic radiation to photoionization, it is necessary either to place the exit arm of the instrument as near the ionization region as possible or to refocus the diverging beam into the ionizer by means of an appropriate mirror. Each of these methods has certain disadvantages. For example, special insulating precautions to prevent arcing must be taken if the former technique is used in conjunction with an ion box maintained at high voltage. Also, physically incorporating the monochromator into the mass spectrometer test chamber makes a variable slit assembly somewhat inaccessible. From the standpoint of practical design, it is much easier to position the monochromator outside the ionization region. Now, the use of a refocusing mirror clearly introduces an additional reflecting surface and therefore intensity losses. However, these losses can be minimized by utilizing a grazing

incidence optical configuration. This technique has been employed in the present study (see Section III.B.).

The final aspect of a monochromatic photon production system is the process of light detection. This measurement is generally accomplished by using one of two established methods. In the first monitoring technique, the transmitted light is allowed to impinge on a window covered with a thin layer of fluorescent material. A photomultiplier is then used to determine the fluorescent intensity. Because of its relatively constant quantum efficiency at wavelengths below $1300 \text{ \AA}$, the most commonly employed phosphor is sodium salicylate. Several other substances may also be used, including diphenylstilbene, tetraphenyl butadiene and terphenyl. An excellent discussion of the characteristics of various fluorescent materials is found in Samson.²⁰⁹ The second monitoring method consists of a simple photoelectric detector having a nickel photocathode. The success of this technique rests on the fact that the photoelectric yield of a heat treated nickel cathode is nearly constant in the wavelength range of $473 \text{ \AA}$ to $1000 \text{ \AA}$.²¹⁹

Sampling System and Ionizer

Sample introduction in ordinary mass spectrometry usually involves some type of gas-handling

system and a leak arrangement to the ionizer. For photoionization efficiency curve measurements, it is particularly important to maintain a constant source pressure over substantial lengths of time. The need to minimize ion-molecule reactions and collisional removal of ions from the mass analyzer typically places an upper limit on the practical sample pressures which can be employed. Details of conventional sampling techniques may be found in any of numerous books on mass spectrometry.^{220,221} The many advantages of supersonic molecular beam sampling methods in photoionization mass spectrometry have been examined previously. Variations in nozzle beam production systems are generally fairly minor and the sampling system described in Section III.A. closely follows standard instrumental design features for this technique.

The most distinctive structural characteristics of an ion source used in photoionization are the entrance and exit holes which provide for necessary passage of the monochromatic light through the ionization region to the photon monitor. With molecular beam sampling, a similar passageway (along the beam axis) must be included to avoid concentration build-up of the target gas. Otherwise, there is considerable instrumental and electrical design freedom due to the many satisfying aspects of a

photon beam as an ionizing medium. In contrast to electron impact methods, large ion draw-out fields can be utilized without affecting the photon energy. Space charge effects are confined to the very small amount arising from the photoionization processes. Furthermore, the ability to perform ionization without the use of a hot filament allows the ion box to be maintained at any reasonable desired temperature during the whole course of an experiment. For efficient ion collection, it is advisable to cross the light beam with the sample gas as near the ion exit port as possible. Also, it is desirable to include at least a crude electron gun to facilitate initial tuning of the mass spectrometer, especially for those minor constituents giving rise to small photoion signals. Finally, it is important to guard against ionization from high energy photoelectrons originating outside the ion source. As mentioned previously, this problem can usually be eliminated by an appropriate set of collectors.

Mass Analyzer

In view of the low photoion signals typically encountered in photoionization efficiency curve determinations, a crucial feature of any mass spectrometer employed for this purpose is high ion transmission.

On the other hand, mass resolution requirements are generally fairly modest (e.g., about 1 amu in 100-400). Two mass analyzer types which have found wide application are quadrupole mass spectrometers and magnetic deflection instruments. The former type of analyzer has developed from the initial demonstration that a quadrupole electric field can act as a variable band-pass mass filter.²²² Design criteria and equations of ion motion in this type of field are well characterized.²²³ Excellent medium resolution quadrupole mass spectrometers are commercially available. These instruments are fairly compact and generally have very good transmission properties, including a wide acceptance angle for ion trajectories.²²⁴ Adequate ion transmission can also be achieved with otherwise conventional magnetic spectrometers equipped with special ion optical features.^{54,225,226} A particularly useful and elegantly simple device in this regard is the electrostatic quadrupole lens system designed by Giese.^{227,228} Ion transmission efficiencies approaching unity have been claimed^{55,140} for a normal-entry homogeneous magnetic-sector instrument using these focusing lenses.

Ion Detection

In early photoionization experiments, ion

detection was usually accomplished by directly measuring the anode current of a multi-stage electron multiplier (e.g., with a vibrating reed electrometer). While this technique is perfectly adequate for conventional photoionization studies of major constituents in a sample gas, more sensitive detection methods are required for photoion yield curve measurements of species which are present in low concentration. The development of pulse counting techniques represents a vitally important instrumental advance which has markedly increased the sensitivity of ion detection. In one technique, ions are allowed to impact the electron multiplier directly. Voltage pulses produced at the anode of the multiplier are typically amplified, shaped and analyzed for height. The pulse height analysis (discriminator) step serves to selectively pass signal pulses, eliminating many of the weaker dark current pulses which have passed through fewer multiplier stages. Finally, those pulses which are accepted in the discriminator stage are counted. Random fluctuations in the data may be reduced by employing longer counting times. The use of low photon energies in conjunction with the low monochromatic photon intensities generally obtainable frequently results in extremely small background count rates. Consequently, under favorable conditions, signals as low as

0.03-0.1 count/sec can be detected and reproduced. A second very sensitive counting method involves the use of the Daly scintillation detector.²²⁹ Ions entering this detector are accelerated through some 30-40 keV and impinge on an aluminum-coated target which ejects several secondary electrons per ion. The number of electrons produced at each impact depends on the mass of the incoming ions. The secondary electrons are then accelerated by the same electric field and strike an organic plastic scintillator covered with a very thin vacuum-deposited reflecting and conducting layer of aluminum. Electrons pass through the Al film to the plastic phosphor with negligible energy loss. The presence of the film allows the face of the scintillator to be grounded and provides for increased light collection efficiency. The light generated by the phosphor is detected by a photomultiplier which may be conveniently positioned outside the vacuum system. Voltage pulses are then analyzed and counted as before.

III. APPARATUS

The apparatus used in this study consists of a moderate resolution mass spectrometer which has been modified to include a supersonic molecular beam sampling system and a photon ionization source. The various instrumental design elements will be considered first, followed by a description of the data collection process in a typical experiment.

A. Nozzle Beam Source and Ionizer

The nozzle beam system and ionization region are shown in Figure 9. A supersonic molecular beam is obtained by expanding a gas through a 0.004" diameter nozzle orifice at stagnation pressures of up to 2000 torr. The nozzle exhaust chamber is pumped by two 4" Stokes Model 150-1 ring jet booster pumps which maintain a vacuum of about 10^{-3} torr. Forepumping is accomplished by two Welch 1397B mechanical pumps. The nozzle was machined from nickel and mounted in a boron nitride support. The nozzle is also equipped with a bevel gear arrangement to permit translation of the orifice along the beam axis. This translation can be controlled from outside the vacuum system. The boron nitride is laced with small heating wires so that the assembly can be operated above room temperature. The nozzle gas inlet

Figure 9. Nozzle Beam Sampling and Ion Source: (1) Ion Box at +10 kV (see text), (2) 12 x 10 MΩ to Provide Uniform Acceleration of Ions over 10 kV, (3) Tuning Fork Chopper, (4) Secondary Skimmer, (5) Electromagnetic Beam Flag, (6) Primary Skimmer and Skimmer Support, (7) Nozzle, (8) Nozzle Support and Bevel Gears for Nozzle Advance, (9) Nozzle Exhaust Chamber, (10) Second Differential Pumping Chamber: (P₁) 575 liters/sec (see text), (P₂) 700 liters/sec¹(see text), (P₃) 1400 liters/sec 6" Diffusion Pump.

tube is connected to the external gas handling arrangement by flexible tubing coupled to a feedthrough in the expansion chamber wall. A simple three-way gas manifold allows the introduction of more than one compound if desired. For pure gases or gas mixtures, sample pressure is governed by metering valves in addition to the two-stage regulators on the gas bottles. A fixed vapor pressure of liquid samples is maintained by carefully controlling the source temperature. Stagnation pressures are monitored by a Texas Instruments precision pressure gauge.

The high intensity central portion of the free jet expansion is extracted with a 0.018" diameter conical skimmer into a second differential pumping region. This chamber is pumped by a 4" NRC Model VHS-4 diffusion pump to a pressure of less than 10^{-5} torr. The skimmer was machined from stainless steel to a length of 7/16" with external and internal semi-apex angles of 40° and 30° , respectively. The expansion is further collimated by a 0.040" conical skimmer before entering the main chamber. An electromagnetic plunger, situated between the primary and secondary skimmers, serves as an effective beam flag. Also fabricated from stainless steel, the secondary collimator is 5/8" long and contains external and interior angles of 60° and 45° , respectively. Downstream of this

skimmer, the molecular beam passes through a small box where ions may be produced either by electron bombardment or by photon absorption. A liquid nitrogen-cooled surface is used to trap those molecules which escape ionization. A liquid nitrogen-trapped 6" CVC Model PMC-6B diffusion pump maintains the main chamber pressure at less than 3×10^{-7} torr when the beam is running. A Welch 1397B mechanical pump (17.7 cfm) is used to back the diffusion pumps in both the ionization chamber and the second differential pumping region.

The small ion box is gold-plated and contains entrance and exit ports for dispersed ultraviolet light, a tungsten filament arrangement to provide electron bombardment capability, and an inner surface to which a small ion repelling voltage (+0-20V) may be applied. Electron bombardment is controlled by a Model ER-1 emission regulator (LASL PN#200426). In addition to regulating the emission current of 10-200eV electrons, this unit provides biasing voltages to the electron collector, filament shield and ion repeller and also monitors the trap (collector) current. A bar magnet (not shown in Figure 9) is positioned directly in back of the ion box to focus the electrons into the path of the molecular beam. When photoionization is used, the light beam and molecular beam cross at right angles. In this

mode, the emission regulator operates on a dummy load (a 5Y3GT full-wave vacuum rectifier) and mainly serves as a source of repeller voltage. In either case, the ion box and emission regulator are designed to "float" at +10kV. Positive ions extracted from the box are uniformly accelerated (see Figure 9) by the 10kV potential into a pair of quadrupole lenses^{227,228} which focus the ions into a line image at the mass spectrometer entrance slit. Lens parameters have been calculated from the formulas of Lu and Carr.²²⁸ Variable voltages in the appropriate ranges (about $\pm 283V$ and $\pm 204V$) are provided by a quadrupole lens bias power supply (LASL PN#205346).

In order to maximize the beam number density in the ionization region, it is necessary to align the nozzle orifice, the primary and secondary skimmers and the ion box molecular beam entrance and exit slits such that all of the openings lie along the same axis. It proved to be convenient to use a portable He-Ne laser for this purpose. As a first step, the laser was mounted on a flange directly over the ion source. A level was used to approximately orient the laser beam along a vertical axis passing through the center of the ion box exit slit. In this configuration, the laser beam was observed to pass very nearly through the center of the narrower entrance slit also. It was possible to obtain a sufficiently good

alignment by slightly widening the entrance slit with a file. Now, the chamber separator containing the secondary skimmer was designed with fairly wide slots in place of clearance holes for the mounting screws. Consequently, it was possible to significantly adjust the position of the skimmer hole. This adjustment capability enabled the laser beam to be directed through the collimating orifice. Fine adjustment was made by visually maximizing the observed laser beam reflection. At the same time, the nozzle, boron nitride block and primary skimmer were designed to be mounted together in a stainless steel support. A satisfactory alignment of the nozzle and skimmer orifices was confirmed by using another He-Ne laser. The assembly containing the nozzle and skimmer was placed in the apparatus as aligned above and positioned such that a laser beam reflection could be seen on the nozzle tip. That is, it was possible to shine a laser through all five relevant openings. Final adjustment was made in accordance with the visual maximum of the spot on the nozzle tip.

B. Monochromatic Vacuum Ultraviolet Source

The salient experimental design features of the light source-monochromator system used in this study are illustrated in Figure 10. The many-line spectrum of H_2

Figure 10. Schematic Diagram of Photoionization Mass Spectrometer: (A) Light Source-Monochromator System, (B) Ionization Chamber, (C) Mass Analyzer and Detector; (1) McPherson Model 630 D.C. Capillary Discharge Lamp, (2) Monochromator Entrance Slit, (3) First Differential Pumping Chamber, (4) Second Differential Pumping Chamber, (5) 1/2-Meter Seya-Namioka Vacuum Ultraviolet Monochromator, (6) Grating, (7) Monochromator Exit Slit, (8) Grazing Incidence Alignment Mirror, (9) Micrometer for Mirror Adjustment, (10) Molecular Beam Crosses Photon Beam at Right Angles, (11) Ion Box, (12) Photomultiplier Tube, (13) Sodium Salicylate Coated Window, (14) Uniform Acceleration Region, (15) Electrostatic Quadrupole, (16) Mass Spectrometer Entrance Slit, (17) Drift Tube, (18) 60° -Sector Electromagnet, (19) Mass Spectrometer Exit Slit, (20) Electron Multiplier; (P₁) 47 liters/sec Roots Blower, (P₂) 700 liters/sec 4" Diffusion Pump, (P₃) 700 liters/sec 4" Diffusion Pump, (P₄) 1400 liters/sec 6" Diffusion Pump, (P₅) 700 liters/sec 4" Diffusion Pump.

produced by a McPherson Model 630 D.C. capillary discharge lamp is used as a photon source. In view of the performance results of Cann,²³⁰ the standard 6-mm discharge capillary is replaced by one with a 3-mm bore. Excitation is provided by a McPherson Model 730 D.C. power supply. In order to extend the obtainable photon wavelength range below $1040 \text{ \AA}$ (the transmission limit for lithium fluoride), the light source-monochromator system is required to operate without windows. Consequently, the entrance arm of a Jarrell-Ash Model 78-650 1/2-meter Seya-Namioka vacuum ultraviolet monochromator has been modified to include two stages of differential pumping. These stages consist of chambers which are separated by slits just wide enough to pass all of the available light. In addition, the lamp is equipped with a plunger which is designed to seal against the entrance slit jaws of McPherson monochromators, limiting the H_2 gas leak to an area of the slit width x 5 mm. It was necessary to fabricate a special plunger in order to properly mate the McPherson lamp with the Jarrell-Ash instrument. The first differential pumping region (monochromator entrance slit cavity) is evacuated by a small Leybold-Heraeus R-152 Roots blower backed by a Welch 1397B mechanical pump. The pump-out lead is wrapped with cooling coils and loosely packed with copper

strips to inhibit warm oil vapor from rising into the monochromator. The entrance slit cavity communicates with the second differential pumping region through a 2-mm wide opening. The vacuum in the second cavity is maintained by a 4" CVC Model PMC-4B diffusion pump equipped with a water-cooled baffle. Forepumping is again provided by a Welch 1397B pump. Finally, a 6-7mm wide slit passes the light into the main monochromator chamber. This region is pumped by a liquid nitrogen-trapped 4" CVC Model PMC-4B diffusion pump. The mechanical pump employed for the ionization chamber (see Section III.A.) is used for this region also. Thus, H_2 is allowed to flow through the lamp and is pumped out through the entrance slit by the system described above. With the lamp operated at 1 torr H_2 and with the entrance slit at 200 μ , the normal operating pressure in the monochromator is 2.5×10^{-5} torr.

The actual performance of the monochromator differential pumping system described above is very close to that predicted by simple pumping speed calculations. The necessary equations for these calculations may be found in Samson.²⁰⁹ From the kinetic theory of gases, the molecular mean free path L is given by

$$L = \frac{1}{n\pi d^2 \sqrt{2}} \quad (41)$$

where d is the molecular diameter in centimeters and n is the number of molecules per cm^3 . For hydrogen, d is about $2.4 \times 10^{-8} \text{ cm}$. A useful expression for n is $(P\mu/T) \cdot (9.7 \times 10^{15})$ where $P\mu$ is the pressure in microns and T is the temperature in K. Therefore, the mean free path of H_2 upstream of the monochromator entrance slit (1 torr lamp pressure) is approximately

$$\begin{aligned} L &= \left\{ \sqrt{2} \cdot \pi \left(\frac{1000\mu}{300\text{K}} \right) (9.7 \times 10^{15}) (5.76 \times 10^{-16} \text{ cm}^2) \right\}^{-1} \\ &= 0.012 \text{ cm} \\ &= 120\mu. \end{aligned} \tag{42}$$

That is, L is very nearly as large as a typical entrance slit width, w . Moreover, in each differential pumping region, L may be expected to be larger than the width of the appropriate slits. Now, for $L > w$, the gas flow may be considered to be free molecular. Consequently, the pressure in each cavity of the vacuum system may be roughly estimated using the following molecular flow expression for the conductance, C :

$$C = 3.6 A_s \sqrt{T/M} \text{ liters/second} \tag{43}$$

where A_s is the slit area in cm^2 and M is the molecular weight. If a 200μ entrance slit is used, the conductance C_1 of the first slit is

$$\begin{aligned} C_1 &= 3.6 (0.02 \times 0.5) \sqrt{300/2.02} \\ &= 0.439 \text{ liters/second.} \end{aligned} \tag{44}$$

The area of the second slit is 0.2cm (width) x 1.27cm (height) = 0.254cm². The conductance C₂ is

$$\begin{aligned} C_2 &= 3.6 (0.254) \sqrt{300/2.02} \\ &= 11.14 \text{ liters/second.} \end{aligned} \quad (45)$$

Finally, the area of the third slit is 0.7cm (width) x 1.27cm (height) = 0.889cm². The corresponding conductance C₃ is then

$$\begin{aligned} C_3 &= 3.6 (0.889) \sqrt{300/2.02} \\ &= 39 \text{ liters/second.} \end{aligned} \quad (46)$$

The pressure in the first differential chamber, P₁, is given by

$$P_1 = \frac{P_0 C_1}{C_1 + S_1} \quad (47)$$

where P₀ is the lamp pressure and S₁ is the effective pumping speed in the chamber. The remaining pressures may also be calculated from analogous equations. Since each vacuum pump is equipped with some type of cooled baffle, the effective pumping speeds S₁, S₂ and S₃ are significantly lower than the nominal maximum speeds. Reasonable estimates for these quantities are 35 l/sec, 350 l/sec and 350 l/sec respectively. Hence, at 1 torr H₂ in the lamp,

$$\begin{aligned} P_1 &= (1 \text{ torr}) \frac{0.439}{0.439 + 35} \\ &= 1.2 \times 10^{-2} \text{ torr.} \end{aligned} \quad (48)$$

Further,

$$\begin{aligned} P_2 &= (1.2 \times 10^{-2} \text{ torr}) \frac{11.14}{11.14 + 350} \\ &= 3.7 \times 10^{-4} \text{ torr.} \end{aligned} \quad (49)$$

Lastly, the pressure in the main chamber of the monochromator should be

$$\begin{aligned} P_3 &= (3.7 \times 10^{-4} \text{ torr}) \frac{39}{39 + 350} \\ &= 3.7 \times 10^{-5} \text{ torr.} \end{aligned} \quad (50)$$

Given the various assumptions, this calculated value is in excellent agreement with the monochromator operating pressures observed in practice.

The principal optical component is a MgF_2 -coated, 2400 lines/mm Jobin-Yvon holographic grating blazed at $1200 \text{ \AA}$. A large groove density is employed in order to increase the throughput of dispersed light as mentioned in Section II.D. For the most part, grating alignment was performed in accordance with the Jarrell-Ash monochromator instruction manual. Light dispersed from the grating is focused on the monochromator exit slit and refocused into the center of the ionizer by a platinum-coated 80° angle of incidence alignment mirror. A metal plate containing an aperture for transmitting the light is placed between the alignment mirror and ionizer and floated at +30-50V in order to collect photoelectrons arising from the mirror surface. The mirror design is based on calculations by Berlyn Brixner

of Group M-5 at LASL. This optical component has a radius of curvature of about 1000 mm and is about 110 mm long, 35 mm high and 10 mm wide. An adjustable mirror mounting was fabricated so that a suitable focus could be achieved in the ionizer. Final alignment was accomplished by establishing the molecular beam axis with a He-Ne laser in the manner described in Section III.A. and adjusting the focusing mirror until a sharp line image could be superimposed on the laser beam as observed on a piece of frosted glass. The astigmatism of this optical configuration is severe enough that some of the dispersed light impinges on the outside of the ion box. However, it is estimated that at least 60-80% of the photon beam is directed into the ion source.

After passing through the ionizer, the dispersed light strikes a sodium salicylate coated window. Because of the low density (about 10^{-4} torr) of the sample and the characteristically small cross sections for photon absorption, the photon beam is essentially unattenuated by the molecular beam. The transmitted photon intensity is determined by using an RCA 6199 photomultiplier to monitor the resulting sodium salicylate fluorescence. The quantum efficiency of a fresh coating of $\text{NaC}_7\text{H}_5\text{O}_3$ is known to exhibit the following

consistent behavior: a constant yield from 400-1250 Å and a gradual monotonic increase of about 20% from 1250 Å to 1500 Å.²³¹ A picoammeter is used to measure the current output from the photomultiplier. Signals are typically one to two orders of magnitude higher than the photomultiplier dark current.

The lamp output is observed to vary significantly with H₂ pressure. At very low pressures (<300μ), the discharge appears quite pale and measured intensities are uniformly low. Upon raising the pressure from 300μ to about 700-1200μ, a bright pink discharge is obtained and substantial increases in the molecular hydrogen peak intensities result. Above 1.2 torr, the discharge turns much more red and the atomic lines (Lyman α, Lyman β, etc.) are seen to be enhanced while the molecular hydrogen spectrum diminishes in intensity. In the H₂ pressure range of 7-10 torr, the lamp changes to bright pink once again with an attendant gain in the molecular hydrogen lines being observed. Further pressure increases produce striations in the discharge capillary and instability occurs. The most satisfactory operating regime in terms of the H₂ load on the rest of the vacuum system as well as overall spectral intensity has been found to be 600-1000μ. A

part of the H_2 spectrum obtainable with the present apparatus is shown in Figure 11. With 200 μ entrance and exit slits, the resolution is approximately 1.5 $\text{\AA}$ or 12 meV at 1200 $\text{\AA}$. A comparison of this spectrum with Samson's results²⁰⁹ in Figure 8 shows an excellent peak-to-peak correspondence in the 1160-1280 $\text{\AA}$ range.

An estimate of the absolute photon intensity at a given wavelength may be calculated from the response characteristics of the type of photomultiplier used and from measured values of the absolute quantum efficiency of sodium salicylate. With 200 μ slits, the current output from the photomultiplier at Lyman α is approximately 10^{-5} ampere at 600V. The typical sensitivity of RCA 6199 photomultipliers at 600V is 0.7 ampere/lumen for 4400 $\text{\AA}$ light.²³² This quantity is suitable for the above photomultiplier signal since 4400 $\text{\AA}$ corresponds closely to the fluorescent emission maximum of $\text{NaC}_7\text{H}_5\text{O}_3$ at 4200 $\text{\AA}$.²⁰⁹ Now,

$$(0.7 \text{ ampere/lumen}) \cdot (804 \text{ lumen/watt}) = 563 \frac{\text{amperes}}{\text{watt}}. \quad (51)$$

Therefore,

$$(10^{-5} \text{ ampere}) \cdot \left(\frac{1}{563} \frac{\text{watt}}{\text{ampere}} \right) = 1.78 \times 10^{-8} \text{ watt}. \quad (52)$$

For 4400 $\text{\AA}$ photons,

$$\begin{aligned} E = h\nu &= (6.626 \times 10^{-34} \text{ joule} \cdot \text{sec}) \cdot \left(\frac{3 \times 10^{10} \text{ cm/sec}}{4.4 \times 10^{-5} \text{ cm}} \right) \\ &= 4.52 \times 10^{-19} \text{ joule/photon}. \end{aligned} \quad (53)$$

Figure 11. H₂ Spectrum Between 1160 and 1280 Å.
 Lamp Pressure, 1000μ; Discharge
 Current, 300 mA. MgF₂ - Coated
 Grating, 2400 lines/mm; 200μ
 Entrance and Exit Slits.

Hence, the estimated photon intensity, I_f , from the sodium salicylate fluorescence may be calculated as follows:

$$\begin{aligned} I_f &= \frac{1.78 \times 10^{-8} \text{ joule/sec}}{4.52 \times 10^{-19} \text{ joule/photon}} \\ &= 3.9 \times 10^{10} \text{ photons/sec.} \end{aligned} \quad (54)$$

The absolute quantum efficiency of $\text{NaC}_7\text{H}_5\text{O}_3$ appears to be about 65 percent.²⁰⁹ As a result, the above value indicates that the Lyman α photon intensity, I_α , striking the detector window is

$$\begin{aligned} I_\alpha &= (3.9 \times 10^{10} \text{ photons/sec}) \cdot \frac{1}{(.65)} \\ &= 6.1 \times 10^{10} \text{ photons/sec.} \end{aligned} \quad (55)$$

A reasonable range for the Lyman α photon intensity may be established by repeating the above calculations with the reported values for minimum and maximum sensitivity for RCA 6199 phototubes. At 600V, these numbers are 0.16 ampere/lumen and 4.5 amperes/lumen respectively.²³² The corresponding estimates of maximum, $I_{\alpha,\text{max}}$, and minimum, $I_{\alpha,\text{min}}$, Lyman α intensities are

$$I_{\alpha,\text{max}} = 2.7 \times 10^{11} \text{ photons/sec.} \quad (56)$$

$$I_{\alpha,\text{min}} = 9.4 \times 10^9 \text{ photons/sec.} \quad (57)$$

From Figure 11, it is evident that the photomultiplier current output for much of the H_2 spectrum lies within a factor of two of 4×10^{-7} ampere or about $\times 25$ below that at Lyman α . Using the value for typical sensitivity of

an RCA 6199 photomultiplier, a similar calculation to those above indicates that typical photon intensities are approximately 2.5×10^9 photons/sec. Thus, it is apparent that the overall spectral intensity obtained with the present apparatus is roughly equal to that reported by Samson (see Figure 8).²⁰⁹

C. Mass Analysis and Ion Detection

The basic configuration of the mass spectrometer and detector is shown in Figure 10. Mass analysis is accomplished by a 60° -sector electromagnet (LASL PN#149614) with a 17.750" radius of curvature. This instrument was developed by Silvio Balestrini at Los Alamos for bomb cloud sample analysis and was initially designed for moderate to high resolution (1 amu in 1000). In the present experimental arrangement, the drift tube entrance and exit slits are opened wide enough to maximize ion transmission while maintaining sufficient resolution to cleanly separate 1 amu in 200. The magnet current is delivered by a KEPCO Model JQE 100-5 power supply which has been set up for constant current operation by the addition of an external sensing resistor and an external current control resistor. The current output of the power supply is determined and regulated by a magnet scan unit (Model SCU-2, LASL PN#205435). Initial alignment of the instrument was

achieved by various optical and mechanical methods. Final alignment was obtained by ionizing a beam of Kr atoms and tuning the magnet to the $^{84}\text{Kr}^+$ signal. This peak could be unambiguously identified from the relative natural abundances of the isotopes of krypton. The magnet was shifted to adjust the radius of curvature, r , of $^{84}\text{Kr}^+$ until the mass spectrometer equation for this ion was satisfied. For this instrument, the mass spectrometer equation of motion is

$$m/e = 9.8067 \times 10^{-2} \frac{H^2}{V} \quad (58)$$

where m is the ion mass in atomic mass units, e is the number of electronic charges per ion, H is the magnetic field strength in gauss and V is the potential drop in volts that each ion experiences (very nearly the applied ion accelerating voltage plus the repeller voltage). This relation may be derived from the fundamental expression

$$\frac{mv^2}{r} = Hev \quad (59)$$

which equates the centrifugal force of the ion ($\frac{mv^2}{r}$) with the deflecting force (Hev) which acts on an ion in a magnetic field. In this expression, m is the mass in grams, H is in esu, e is in esu, v is the ion velocity in centimeters per second and r is in centimeters. By rearrangement, Equation (59) becomes

$$v = \frac{Her}{m} \quad (60)$$

During acceleration through a potential of V (in esu), an ion gains kinetic energy eV . Provided that this energy is large compared to the initial energy of the ion,

$$eV = \frac{mv^2}{r} = \frac{H^2 e^2 r^2}{2m} \quad (61)$$

or

$$m/e = \frac{H^2 r^2}{2V}. \quad (62)$$

In order to obtain H in gauss, it is necessary to divide by c^2 , where c is the velocity of light in centimeters per second. V in practical volts may be used if this expression is multiplied by 299.793. To convert from grams to amu, Avogadro's number must be included in the numerator and e in electronic charges may be obtained by dividing the expression by 2.082×10^9 . Hence

$$\frac{m}{e} = \frac{H^2 r^2}{2V} \cdot \frac{(6.023 \times 10^{23})(2.99793 \times 10^2)}{(2.082 \times 10^9)(2.998 \times 10^{10})^2}. \quad (63)$$

That is,

$$\frac{m}{e} = 4.825 \times 10^{-5} r^2 \frac{H^2}{V}. \quad (64)$$

The corresponding relation for r in inches is

$$\frac{m}{e} = 3.113 \times 10^{-4} r^2 \frac{H^2}{V}. \quad (65)$$

Substituting the value for the radius of curvature of the present instrument gives Equation (58).

In the alignment procedure, the applied ion accelerating voltage was measured by using a voltage

divider and a digital multimeter. At the same time, H was determined by a Harvey-Wells Model FC-502 NMR field control unit and a Hewlett-Packard Model 5300A measuring system coupled with a Model 5302A frequency counter. H in gauss may be calculated from the straight line relationship between the magnetic field strength and the frequency of proton resonance (4257.76 Hz/gauss). This instrumentation was retained for mass identification purposes during the whole course of the present investigation.

With electron bombardment, sufficient numbers of mass selected ions are transmitted to permit detection by means of a Faraday cup arrangement or a multi-stage electron multiplier. The current output from these devices is passed to a Keithley Model 417 picoammeter. The gain of the EMI 9642/2B 18-stage photomultiplier used in the present study has been measured as a function of negative potential at the cathode and is given in Table I. A mu metal magnetic shield is kept around the multiplier at all times. In the photoionization mode, pulse counting is performed using a PAR Model 1120 amplifier-discriminator and a PAR Model 1112 photon counter. It has proved to be necessary to employ a 20 db attenuator between the output of the electron multiplier and the amplifier-discriminator in order to eliminate a

Table I. Gain of EMI 9642/2B Electron Multiplier
as a Function of Cathode Potential

<u>Voltage Applied</u>	<u>Gain</u>	<u>Voltage Applied</u>	<u>Gain</u>
-600	.200	-2300	7.47×10^5
-700	.986	-2400	1.13×10^6
-800	4.26	-2500	1.75×10^6
-900	1.73×10^1	-2600	2.65×10^6
-1000	5.33×10^1	-2700	3.97×10^6
-1100	1.66×10^2	-2800	5.77×10^6
-1200	4.26×10^2	-2900	8.42×10^6
-1300	1.08×10^3	-3000	1.23×10^7
-1400	2.66×10^3	-3100	1.68×10^7
-1500	5.87×10^3	-3200	2.34×10^7
-1600	1.23×10^4	-3300	3.14×10^7
-1700	2.41×10^4	-3400	4.14×10^7
-1800	4.68×10^4	-3500	5.28×10^7
-1900	8.70×10^4	-3600	6.71×10^7
-2000	1.61×10^5	-3700	8.28×10^7
-2100	2.74×10^5	-3800	1.03×10^8
-2200	4.54×10^5	-3900	1.23×10^8

troublesome background count rate (80-200 counts/sec) arising from electronic noise. With this technique, extremely low background signals result at the expense of some 60% of the genuine signal.

It need hardly be stated that it is extremely important to operate the mass spectrometer and detector under high vacuum conditions. A drift tube and detection chamber pressure of less than 2×10^{-7} torr is maintained by a 4" CVC Model PMC-4 diffusion pump equipped with a Freon-cooled trap. Forepumping is accomplished by a Welch 1405 mechanical pump.

D. Apparatus Performance Calculations

The performance of the molecular beam photoionization mass spectrometer described in the previous sections has been characterized by a number of experiments and calculations. Included in these results are estimates of beam number density (equivalent sample pressure), ionization and collection efficiencies for electron impact and ionization and collection efficiencies for photoionization.

A molecular beam of krypton was used to calculate a typical equivalent sample pressure for the present system. As a first step, the ionization chamber diffusion pump was throttled to permit the ion current measurement for quasi-static sample. Prior to sample

introduction, the main chamber pressure was observed to be 3.4×10^{-7} torr. With a nozzle source pressure of 38 torr Kr and the beam flag in, the pressure in this cavity rose to 1.0×10^{-6} torr. In other words, approximately 6.6×10^{-7} torr Kr was added to the system as measured by a standard ion gauge. Near static conditions were confirmed by the fact that opening and closing the beam flag had only a minor effect on the ionization chamber pressure. With the flag closed, the current output of the electron multiplier at 1500V due to $^{84}\text{Kr}^+$ was 1.56×10^{-9} amperes. Now, the natural abundance of ^{84}Kr is 56.9% and the concentrations of Kr_n may be expected to be negligible under these sample conditions. Thus, the pressure rise due to ^{84}Kr was $(6.6 \times 10^{-7} \text{ torr}) \cdot (.569)$ or 3.76×10^{-7} torr. This number must be multiplied by .538 to account for ion gauge calibration.²³³ Consequently, the true pressure rise due to ^{84}Kr was $(3.76 \times 10^{-7} \text{ torr}) \cdot (.538)$ or 2.02×10^{-7} torr. The corresponding concentration of ^{84}Kr in molecules per cm^3 may be estimated from Loschmidt's number, n_0 . That is,

$$n_0 = 2.687 \times 10^{19} \text{ molecules/cm}^3 \text{ at } 760 \text{ mm Hg.} \quad (66)$$

Hence, the background concentration of ^{84}Kr , $[^{84}\text{Kr}]_b$,

from this experiment is given by

$$\begin{aligned} [^{84}\text{Kr}]_b &= (2.687 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3}) \cdot \frac{2.02 \times 10^{-7} \text{ mm Hg}}{.760 \times 10^3 \text{ mm Hg}} \\ &= 7.14 \times 10^9 \text{ molecules/cm}^3. \end{aligned} \quad (67)$$

Assuming that the mass spectrometer collection efficiency is the same for both free jet and quasi-static samples, it is possible to derive the Kr nozzle beam number density by measuring the appropriate electron multiplier signal for $^{84}\text{Kr}^+$. With identical electron gun conditions, the maximum $^{84}\text{Kr}^+$ picoammeter current reading as a function of nozzle source pressure was 7.5×10^{-11} ampere using the Faraday cup or 4.4×10^{-7} ampere from the electron multiplier at 1500V. This reading was observed at a stagnation pressure of 108 torr Kr. The ^{84}Kr molecular beam number density, $[^{84}\text{Kr}]_m$, may then be calculated from the relation

$$\begin{aligned} [^{84}\text{Kr}]_m &= [^{84}\text{Kr}]_b \cdot \frac{4.4 \times 10^{-7} \text{ ampere}}{1.56 \times 10^{-9} \text{ ampere}} \\ &= 2.01 \times 10^{12} \text{ molecules/cm}^3. \end{aligned} \quad (68)$$

The corresponding equivalent sample pressure for ^{84}Kr , $P_{^{84}\text{Kr}}$, is given by

$$\begin{aligned} P_{^{84}\text{Kr}} &= (2.01 \times 10^{12} \frac{\text{molecules}}{\text{cm}^3}) \cdot \frac{760 \text{ mm Hg}}{2.687 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3}} \\ &= 5.69 \times 10^{-5} \text{ torr}. \end{aligned} \quad (69)$$

The total monomer equivalent sample pressure, P_{Kr} , is

$$\begin{aligned} P_{Kr} &= \frac{5.69 \times 10^{-5} \text{ torr}}{0.569} \\ &= 1.0 \times 10^{-4} \text{ torr.} \end{aligned} \quad (70)$$

Under similar source conditions, ion signals for other compounds do not vary greatly from those mentioned above. Therefore, sample pressures of about 10^{-4} torr may be considered typical for the present experimental design.

Using the ^{84}Kr beam number density in conjunction with the measured electron trap current and various other constants for the ionization process, the electron bombardment ionization efficiency, I.E. (EB), and mass spectrometer collection efficiency, C.E. (EB), may be estimated. A reasonable value for the Kr monomer beam velocity is 5×10^4 cm/sec.²³⁴ Hence, the ^{84}Kr beam flux $\phi_{^{84}\text{Kr}}$, may be calculated as follows:

$$\begin{aligned} \phi_{^{84}\text{Kr}} &= (2.01 \times 10^{12} \frac{\text{molecules}}{\text{cm}^3}) (5 \times 10^4 \text{ cm/sec}) \\ &= 1.0 \times 10^{17} \frac{\text{molecules}}{\text{cm}^2 \cdot \text{sec}} . \end{aligned} \quad (71)$$

The current output of the ionizer electron collector in the above determinations was 1 mA or $6.24 \times 10^{15} \frac{\text{electrons}}{\text{sec}}$. The latter quantity is taken to be the number of electrons available for ionization per second, I_e . An estimate of the ionization cross section, σ_e , for Kr by 50 eV electron

impact may be derived from the data of Beran and Kevan.²³⁵
 By linear interpolation, σ_e is approximately $4.6 \times 10^{-16} \text{ cm}^2$.
 Assuming that the beam area, A , facing the electron flow
 is 0.1 cm^2 and also that the electrons are effective for
 ionization over a path length, d , of 1 cm , the number of
 ions produced per second, $N_{84\text{Kr}}^+$, may be calculated as
 follows:

$$\begin{aligned} N_{84\text{Kr}}^+ &= I_e [^{84}\text{Kr}]_m \sigma_e d \\ &= (6.24 \times 10^{15} \text{ sec}^{-1}) \cdot (2.01 \times 10^{12} \text{ cm}^{-3}) \cdot (4.6 \times 10^{-16} \text{ cm}^2) \cdot (1 \text{ cm}) \\ &= 5.77 \times 10^{12} \text{ sec}^{-1}. \end{aligned} \quad (72)$$

As mentioned previously, the observed $^{84}\text{Kr}^+$ ion current
 was 7.5×10^{-11} amperes. Thus, the $^{84}\text{Kr}^+$ detection rate,
 $D_{84\text{Kr}}^+$, is equal to $4.68 \times 10^8 \text{ sec}^{-1}$. From these quantities,
 the net efficiency, N.E. (EB), as well as I.E. (EB) and
 C.E. (EB) may be computed:

$$\begin{aligned} \text{N.E. (EB)} &= \frac{D_{84\text{Kr}}^+}{A \cdot \Phi_{84\text{Kr}}} = \frac{4.68 \times 10^8 \text{ sec}^{-1}}{(0.1 \text{ cm}^2)(10^{17} \text{ cm}^{-2} \text{ sec}^{-1})} \\ &= 4.68 \times 10^{-8} \end{aligned} \quad (73)$$

$$\begin{aligned} \text{I.E. (EB)} &= \frac{N_{84\text{Kr}}^+}{A \cdot \Phi_{84\text{Kr}}} = \frac{5.77 \times 10^{12} \text{ sec}^{-1}}{(0.1 \text{ cm}^2)(10^{17} \text{ cm}^{-2} \text{ sec}^{-1})} \\ &= 5.77 \times 10^{-4} \end{aligned} \quad (74)$$

$$\begin{aligned} \text{C.E. (EB)} &= \frac{\text{N.E. (EB)}}{\text{I.E. (EB)}} = \frac{D_{84\text{Kr}}^+}{N_{84\text{Kr}}^+} \\ &= 8.11 \times 10^{-5}. \end{aligned} \quad (75)$$

Because of the many assumptions involved in these calculations, the true values for N.E. (EB), I.E. (EB) and C.E. (EB) may differ substantially from the numbers above. In fact, it seems almost certain that the mass spectrometer collection efficiency is higher than 8×10^{-5} since the observed mass peaks are quite sharp when the instrument is operated at high resolution. Moreover, further opening of the drift tube slits produces only a very small enhancement of the signal intensity (i.e., there are probably negligible losses at the slits).

It is interesting to compare the foregoing electron impact results for ^{84}Kr with similar calculations for the photoionization of acetone at Lyman α . For these computations, it is necessary to make several preliminary assumptions and estimates. Since the beam velocity of CH_3COCH_3 was not measured in the present study, a value of 5×10^4 cm/sec will be employed once again. Also, a specific measurement of acetone equivalent sample pressure was not performed; however, a comparison of electron bombardment ion signals for $\text{CH}_3\text{COCH}_3^+$ and $^{84}\text{Kr}^+$ indicates that this parameter likely falls in the range of 10^{-5} - 10^{-4} torr. The beam volume which interacts with the ionizing medium is taken to be the same as before (0.1 cm^3). The $1215.7 \text{ \AA}$ photon

intensity, I_α , has been calculated previously (see Equation (55) in Section III.B.). Finally, it is necessary to establish a reasonable value for the photoionization cross section of acetone, σ_{Ac} , at Lyman α . Beran et. al. have determined that σ_{Ac} is 3.13 times larger than the cross section for NO at 11.6-11.8 eV.²³⁶ Now, the photoionization cross section for NO in this energy range is apparently about $3 \times 10^{-18} \text{ cm}^2$.¹² Consequently, σ_{Ac} at 11.6-11.8 eV is approximately $9.4 \times 10^{-18} \text{ cm}^2$. In view of the fact that the photoion yield curve of acetone rises slightly in going from this region to Lyman α ,²³⁷ 10^{-17} cm^2 is an acceptable σ_{Ac} for these calculations.

Assuming an equivalent acetone sample pressure, P_{Ac} , of 10^{-4} torr, the CH_3COCH_3 beam number density, $[Ac]$, may be calculated as follows:

$$\begin{aligned}
 [Ac] &= P_{Ac} \cdot \frac{2.687 \times 10^{19} \text{ molecules/cm}^3}{.760 \times 10^3 \text{ mm Hg}} \\
 &= 3.5 \times 10^{12} \text{ molecules/cm}^3.
 \end{aligned}
 \tag{76}$$

The acetone beam flux, Φ_{Ac} , is then estimated by the relation

$$\begin{aligned}
 \Phi_{Ac} &= (3.5 \times 10^{12} \frac{\text{molecules}}{\text{cm}^3}) \cdot (5 \times 10^4 \frac{\text{cm}}{\text{sec}}) \\
 &= 1.75 \times 10^{17} \frac{\text{molecules}}{\text{cm}^2 \text{ sec}}.
 \end{aligned}
 \tag{77}$$

The number of acetone ions produced per second, N_{Ac}^+ , may be computed from the following expression:

$$\begin{aligned} N_{Ac}^+ &= I_{\alpha} [Ac] \sigma_{Ac} d \\ &= (6.1 \times 10^{10} \text{ sec}^{-1}) \cdot (3.5 \times 10^{12} \text{ cm}^{-3}) \cdot (10^{-17} \text{ cm}^2) \cdot (1 \text{ cm}) \\ &= 2.1 \times 10^6 \text{ sec}^{-1}. \end{aligned} \quad (78)$$

The $\text{CH}_3\text{COCH}_3^+$ signal for the present apparatus is typically 400 counts/second at Lyman α . However, only 40% of the genuine ion count is detected when the 20db attenuator is employed in the data collection electronics. Hence, the appropriate acetone ion detection rate, D_{Ac}^+ , is 1000 sec^{-1} . The net photoionization efficiency N.E. (hv), and the ionization and collection efficiencies, I.E. (hv) and C.E. (hv), may be calculated as before:

$$\begin{aligned} \text{N.E. (hv)} &= \frac{D_{Ac}^+}{A \cdot \Phi_{Ac}} = \frac{10^3 \text{ sec}^{-1}}{(0.1 \text{ cm}^2) \cdot (1.75 \times 10^{17} \text{ cm}^{-2} \text{ sec}^{-1})} \\ &= 5.7 \times 10^{-14} \end{aligned} \quad (79)$$

$$\begin{aligned} \text{I.E. (hv)} &= \frac{N_{Ac}^+}{A \cdot \Phi_{Ac}} = \frac{2.1 \times 10^6 \text{ sec}^{-1}}{(0.1 \text{ cm}^2) \cdot (1.75 \times 10^{17} \text{ cm}^{-2} \text{ sec}^{-1})} \\ &= 1.2 \times 10^{-10} \end{aligned} \quad (80)$$

$$\begin{aligned} \text{C.E. (hv)} &= \frac{\text{N.E. (hv)}}{\text{I.E. (hv)}} = \frac{D_{Ac}^+}{N_{Ac}^+} \\ &= 4.8 \times 10^{-4}. \end{aligned} \quad (81)$$

If P_{Ac} is taken to be 10^{-5} torr, C.E. (hv) is equal to 4.8×10^{-3} . In any case, the estimated mass spectrometer collection efficiency for photoionization is considerably

higher than the ^{84}Kr electron bombardment result. Nevertheless, this value is still far below the ion transmission efficiencies claimed by Chupka and Berkowitz^{55,140} for a similar instrument. The reason for this discrepancy is not readily apparent.

E. Data Collection Procedures

The vacuum pumps on the nozzle exhaust chamber and second differential molecular beam pumping chamber are not equipped with liquid nitrogen traps and are operated only during the course of an experimental run. Consequently, the first step in preparing the apparatus for a photoionization efficiency curve measurement is to activate these pumps. Once the system achieves a suitable vacuum, the sample compound may be introduced into the gas manifold and expanded through the nozzle aperture. This gas flow is regulated according to the approximate stagnation pressure required and at least 15-30 minutes are provided for the expansion to stabilize. Also, a flow of H_2 lamp gas is initiated such that a discharge capillary pressure of 600-1000 μ is obtained. Improved lamp stability has been found to result from operating the discharge for as much as one hour before beginning the experiment. Typical power supply conditions are 1500V and 450mA. At the same time, the remaining electronic instruments are turned on and allowed to warm up. A

schematic representation of much of the operating and data collection instrumentation is given in Figure 12. The magnet is roughly tuned to the desired m/e position using the NMR field control unit and frequency counter arrangement described in Section III.C. Electron bombardment or photoionization at an intense spectral line (e.g., Lyman α , 1160 Å, etc.) is used to identify and maximize the mass peak corresponding to the specie of interest. Ion transmission is optimized by adjusting the repeller voltage (controlled by the Model ER-1 emission regulator) as well as the voltages applied to the pair of quadrupole lenses. When fine tuning of the ion signal is accomplished, the resonance pattern displayed by the NMR field control unit is centered on the oscilloscope scale. This pattern is carefully monitored in order to detect and prevent a mass drift.

The photoionization efficiency is determined by the ratio of ion signal to photon signal as a function of wavelength (or photon energy). At each point, mass resolved ion counts are accumulated for a specified period of time and the total count is recorded. The photo-multiplier current reading, which is proportional to the monochromatic light intensity, is also recorded. Voltages of about -3500V and -600V are typically applied to the

Figure 12. Schematic Representation of Major Operating and Data Collection Electronics for the Photoionization Mass Spectrometer. Not Shown are the Electronics for Delivering and Monitoring the Magnet Current (see text).

electron multiplier and RCA 6199 photomultiplier tube, respectively. The lamp intensity has been found to remain stable to $\pm 2\%$ at each wavelength. The H_2 spectrum is scanned by manually advancing the monochromator. In the present study, data has generally been taken at 1-2.5 $\text{\AA}$ intervals. Inasmuch as a 2400 lines/mm grating is used in conjunction with a grating drive mechanism designed for 1180 lines/mm, it is necessary to establish wavelength calibration with the known hydrogen atom and molecule emission lines.^{209,238}

It is important to make background corrections in both the photoion and photon signals. Fortunately, these effects are quite small. A particularly low ion counting background rate can be achieved if all ion gauge filaments are turned off. Under these conditions, the ion count with the molecular beam flagged is typically about 0.02-0.1 count/sec. Thus, reproducible ion signals of 0.03-0.05 count/sec are detectable. Background counts are accumulated after every five or six data points in order to carefully monitor this factor. In addition, a reference data point is occasionally repeated to check for small changes in beam intensity, collection efficiency, etc. Since a holographically recorded diffraction grating is used, stray light levels are expected to be substan-

tially reduced.¹²⁶ Consequently, the photon signal correction should very nearly be the photomultiplier dark current. As mentioned previously, it is possible to reproduce in substantial detail the H₂ spectrum given by Samson.²⁰⁹

IV. RESULTS AND DISCUSSION

A. Preliminary Observations with Electron Impact

Prior to the full assembly and optimization of the monochromatic vacuum ultraviolet photon source, a considerable number of parent, cluster and fragment ions were seen using electron bombardment on various compounds in molecular beams. As indicated in Section III.D., measurements on rare gas species were made in order to test and characterize the sampling system and mass spectrometer. In this regard, the observed similarity of the nozzle stagnation pressure dependence of rare gas monomer and dimer ion signal intensities in the present study as compared to the room temperature skimmer and endwall results of Bailey *et. al.*¹⁹⁹ (see Figure 7) is of particular interest. A number of other compounds were studied with the object of determining the feasibility of their investigation by photoionization. A summary of the ions detected and additional relevant comments are given in Table II.

B. Photoionization of Acetone and Acetone-d₆

The application of high resolution molecular beam-photoionization mass spectrometry to complex organic molecules remains a largely unexplored possibility.

Table II. Summary of Electron Bombardment Results
for Various Compounds in Molecular Beams

<u>Molecular Beam Constituents</u>	<u>Ions Observed</u>	<u>Comments</u>
Argon, Krypton, Xenon	Kr^+ , Kr_2^+ , Xe^+ , Xe_2^+ , Ar^+ , Ar_2^+ , KrAr^+ , XeAr^+	Source pressure dependence of monomer and dimer signal intensity similar to warm skimmer results of reference 199.
Ammonia	NH_3^+ , NH_4^+ , NH_2^+ $(\text{NH}_3)_2^+$, $(\text{NH}_3)_3^+$, $(\text{NH}_3)_n \text{H}^+$, $n=2-15$	Extensive fragmentation: $(\text{NH}_3)_{n-1}\text{H}^+$ signal intensities $\times 25-50$ larger than those for $(\text{NH}_3)_n$ with 100-140 eV electron impact.
Carbon Dioxide	CO_2^+ , $(\text{CO}_2)_n^+$, $n=2-7$	
Acetone	$\text{CH}_3\text{COCH}_3^+$, CH_3CO^+ $(\text{CH}_3\text{COCH}_3)_n^+$, $n=1-6$ $(\text{CH}_3\text{COCH}_3)_n \text{H}^+$, $n=1-6$	See Section IV.B.
Propionaldehyde	$\text{CH}_3\text{CH}_2\text{CHO}^+$ and fragments	Extensive fragmentation; no dimer ions seen.
Cyclopentane	$\text{C}_5\text{H}_{10}^+$ and fragments.	Substantial fragmentation; no dimer ions seen.
Oxygen	O_2^+ , $(\text{O}_2)_2^+$	
Water	H_2O^+ , OH^+ , $(\text{H}_2\text{O})_n^+$, $n=2-5$ $(\text{H}_2\text{O})_n \text{H}^+$, $n=2-5$	Particularly large signal corresponding to $(\text{H}_2\text{O})_3\text{H}^+$ observed.
Nitric Oxide and Carbon Dioxide	NO^+ , CO_2^+ , $(\text{NO})_2^+$, $\text{NO}^+\cdot\text{CO}_2$, $(\text{CO}_2)_2^+$, $(\text{CO}_2)_3^+$	Mixed dimer signal small.
Carbon Dioxide and Water	H_2O^+ , H_3O^+ , $(\text{H}_2\text{O})_2^+$, $(\text{H}_2\text{O})_2\text{H}^+$, CO_2^+ , $(\text{H}_2\text{O})_3^+$, $(\text{H}_2\text{O})_3\text{H}^+$, $\text{CO}_2 \cdot \text{H}_2\text{O}^+$, $\text{CO}_2 \cdot \text{H}_3\text{O}^+$, $(\text{CO}_2)_2^+$	Mixed dimer signals small.

Except for monomer and cluster studies of ethylene⁸² and smaller alcohols,^{91,92} this method has generally been confined to experiments involving parent molecules with five atoms or less.^{79-81,83-90} Departing from this trend, the present study is in part concerned with the photoionization of several species produced in supersonic nozzle expansions of acetone and acetone-d₆ vapor. As the simplest aliphatic ketone, the ionization and dissociative properties of acetone are of significant interest as being representative of a sizeable homologous class of substances. Consequently, this compound has been extensively studied by various methods including electron impact,²³⁹⁻²⁵⁴ photoionization,^{12,36,45,50,58,237,255-257} photoelectron spectroscopy,²⁵⁸⁻²⁷¹ photoelectron-photoion coincidence spectroscopy,^{272,273} vacuum ultraviolet absorption spectroscopy,¹¹ Penning ionization,^{274,275} charge transfer spectra²⁷⁶ and electron energy loss spectroscopy.²⁷⁷ The more recent of these experiments have produced fairly consistent first and higher ionization potential values for the parent species and appearance potential values for the acetyl fragment ion. Little additional ionic state information has been determined, however.

Using nozzle beam sampling techniques, the photoionization efficiency curves for $\text{CH}_3\text{COCH}_3^+$ and CH_3CO^+ have been measured more precisely in order to obtain such data as low energy ionic vibrational frequencies, Franck-Condon factors for direct ionization and effects of thermal relaxation on threshold values. Photoion yield curves have been determined for $\text{CD}_3\text{COCD}_3^+$ and CD_3CO^+ as well. In addition, photoionization mass spectrometric measurements of $(\text{CD}_3\text{COCD}_3)_2^+$, $(\text{CH}_3\text{COCH}_3)_n^+$, $n=2-4$ and $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$ are reported.

1. Experimental

For the photoionization study of acetone, an intense supersonic expansion was produced by seeding CH_3COCH_3 vapor at 20-25°C in H_2 . Total stagnation pressures were varied between 350-750 torr in order to maximize the concentration of given components in separate experiments. Inasmuch as some enhancement of cluster ion intensities relative to the parent could be achieved by increasing the beam stagnation pressure, the ratio of H_2 to acetone used was generally higher for the polymer studies. However, the functional dependence of cluster ion signal and H_2 source pressure was not found to be particularly strong. Considerable care was taken to maintain a constant acetone source

temperature and total stagnation pressure throughout each run. Because mass analysis was employed during the whole course of the present study, Mallinckrodt Spectrar grade acetone (99.5% minimum purity) was used without further purification; 99.5 atom % D acetone-d₆, obtained from Aldrich Chemical Co., Inc., was used directly for the isotope work.

Two different monochromator entrance and exit slit widths were used, depending upon the intensity of the specie investigated. Operating conditions for the discharge lamp were typically 0.8 torr H₂ pressure and 450 mA discharge current. The acetone and acetone-d₆ monomer studies were performed at an estimated resolution of 1.5 Å corresponding to the use of 200μ slits. Counts were collected for 500-600 seconds per data point at approximately 1 Å intervals. Counting rates in the region 1240-1280 Å varied from about 15 counts/second to approximately 0.5 count/second at threshold (at Lyman α, counting rates could be varied from 200 counts/second to 650 counts/second, depending upon lamp pressure and nozzle expansion conditions). For cluster and fragment ion studies, 500μ monochromator entrance and exit slits were used, resulting in a resolution of approximately 3.75 Å or 30 meV at 1200 Å. Readings were taken at 1.5-2.5 Å intervals for 600-900 seconds per data point.

Typical counting rates ranged from 0.03 count/second to 5 counts/second. In each run, a reference point was repeated periodically to account for any drift in the mass peak, collection efficiency, etc.

2. Results

A partial mass spectrum for an acetone- H_2 molecular beam (600 torr total stagnation pressure) was obtained using 100 eV electron bombardment. Signals corresponding to acetone monomer and cluster ions were observed at m/e 58, 116, 174, 232, 290, and 348. Fragment ions at m/e 43 and 101 were seen in concentrations $\times 3$ - $\times 4$ those of the monomer and dimer ion, respectively. In addition, small peaks corresponding to ions of the form $(CH_3COCH_3)_nH^+$, $n = 1-6$, were observed at m/e 59, 117, 175, 233, 291, and 349. These ions presumably originate from high energy fragmentation of cluster species or ion-molecule reactions involving some of the numerous parent, cluster, and fragment ions formed; i.e., $(CH_3COCH_3)_n^+$, $(CH_3COCH_3)_n \cdot CH_3CO^+$, CH_3^+ , H_2^+ , H^+ , etc. Protonated acetone and acetone cluster ions have been previously reported in field ionization²⁷⁸ and ion-molecule reaction²⁷⁹⁻²⁸⁵ studies.

In contrast, the photoionization mass spectrum for the acetone- H_2 beam was markedly less complex in the

region 1100-1300 Å. At 500 torr total stagnation pressure, ions of the form $(\text{CH}_3\text{COCH}_3)_n^+$, $n = 1-4$, were observed at Lyman α in the approximate ratio 100:40:5:3. Signals at m/e 59, 117, 175, etc. were seen only in those concentrations which would be expected on the basis of natural isotopic abundances of ^{13}C and D. At 1160 Å, the CH_3CO^+ and $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$ ions (m/e 43 and 101) could be seen in very low concentrations. The relative simplicity of the photoionization spectra was taken as strong evidence that only simple ionization and fragmentation processes occur.²⁸⁴

Photoion yield curves obtained in the present work are shown in Figures 13-20. With the exception of the acetone tetramer and acetone- d_6 dimer, each ion was investigated at least twice. The spectra were found to be reproducible in substantial detail. The measured ionization potentials (IP) and appearance potentials (AP) of the various species are given in Table III, along with ionic vibrational structure information which has been derived from the experimental curves.

3. Discussion

a. Acetone and acetone- d_6 monomer ions

The photoionization efficiency curves for acetone and acetone- d_6 parent ions are characterized

Figure 13. Photoion Yield Curve for $(\text{CH}_3\text{COCH}_3)^+$
 from 1240 to 1285 $\text{\AA}$.

Figure 14. Photoion Yield Curve for $(\text{CD}_3\text{COCD}_3)^+$ from 1248 to 1282 $\text{\AA}$.

Figure 15. Appearance Potential Curves for CH_3CO^+ and CD_3CO^+ from 1148 to 1183 $\text{\AA}$.

Figure 16. Photoion Yield Curve for $(\text{CH}_3\text{COCH}_3)_2^+$
 from 1239 to 1351 Å.

Figure 17. Photoion Yield Curve for $(\text{CD}_3\text{COCD}_3)_2^+$ from 1270 to 1349 $\text{\AA}$.

Figure 18. Photoion Yield Curve for $(\text{CH}_3\text{COCH}_3)_3^+$ from 1334 to 1369 Å.

Figure 19. Photoion Yield Curve for $(\text{CH}_3\text{COCH}_3)_4^+$ from 1324 to 1379 Å.

Figure 20. Appearance Potential Curve for
 $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$ from 1190 to
 1241 Å.

Table III. Summary of Energetic Information for
Acetone and Acetone-d₆ Parent,
Fragment and Cluster Ions

<u>Ionization or Appearance Potential (eV)</u>					
Ion	m/e	This Work	PI Literature ^a	PES Literature ^b	Ionic Vibrational Structure
CH ₃ COCH ₃ ⁺	58	9.694±0.006	9.71±0.01 ²³⁷	9.709±0.005 ²⁵⁸	320±50 cm ⁻¹
			9.69±0.01 ⁴⁵	9.70±0.01 ²⁶¹	695±50 cm ⁻¹
				9.72±0.01 ²⁶⁶	930-1370 cm ⁻¹
CD ₃ COCd ₃ ⁺	64	9.695±0.006			260±50 cm ⁻¹ 660-1100 cm ⁻¹
CH ₃ CO ⁺	43	10.52±0.02	10.33 ²⁵⁵		
			10.37 ²⁵⁶ (298K)		
			10.45 ^{255,256} (OK) ^c		
			10.42 ²³⁷ (298K)		
CD ₃ CO ⁺	46	10.56±0.02			
(CH ₃ COCH ₃) ₂ ⁺	116	9.26±0.03			
(CD ₃ COCd ₃) ₂ ⁺	128	9.25±0.03			
(CH ₃ COCH ₃) ₃ ⁺	174	9.10±0.03			
(CH ₃ COCH ₃) ₄ ⁺	232	9.02±0.03			
(CH ₃ COCH ₃)·CH ₃ CO ⁺	101	10.08±0.05			

a. Selected photoionization literature values.

b. Selected photoelectron spectroscopy literature values.

c. This value determined by adding the calculated internal energy of acetone at room temperature to the measured 298K acetyl ion appearance potential.

by sharp thresholds and distinct steplike structure at higher energies. The well-resolved fine structure and the apparent absence of hot band effects are direct results of the efficient thermal relaxation achieved by sampling from a supersonic nozzle expansion. Within the estimated resolution of $1.5 \text{ \AA}$, the observed first ionization onsets are very nearly step functions. This result would indicate that the rotational envelope for acetone has been narrowed to approximately a width of 12 meV or less through supersonic gas expansion; i.e., the rotational temperature of the sample is $\approx 100\text{K}$. Rotational temperatures of $\leq 118\text{K}$ have been achieved in previous nozzle beam photoionization studies.^{79,90} Similarly, vibrational temperatures are apparently lowered to the extent that significant population of states occurs only within a narrow energy band above the ground state. The measured ionization potential of CH_3COCH_3 is in good agreement with previous photoionization and photoelectron spectroscopy results (see Table III). Ionization probably occurs at a 2p lone-pair electron site on the oxygen atom,²⁸⁶ resulting in a large $v''=0$ to $v'=0$ onset.³⁶ In addition, the observed photoion yield curve exhibits several fine structure features within 0.2 eV of threshold, including two abrupt steps at 320 cm^{-1} and 695 cm^{-1} and a broad rise from

about 930-1370 cm^{-1} . The estimated uncertainty of these values is $\pm 50 \text{ cm}^{-1}$. Inasmuch as identical structure was not seen at the appropriate energies in a crude photo-ionization efficiency curve determination of diethyl ether (IP=9.55-9.60 eV), it may be concluded that these steps are not experimental artifacts arising from stray light or the type of photon source used. Rather, these features presumably occur because sufficient excess energy is available to excite higher vibrational levels of the ion. Removal of a nonbonding electron should have a minimal effect on many low energy vibrational frequencies of the molecule since these frequently correspond to structural deformations. Consequently, it should be possible to correlate the observed ionic transitions with known low energy vibrations in acetone.^{287,288}

Steps corresponding to measured methyl group torsional frequencies in neutral acetone $\nu_{12} = 105.3 \text{ cm}^{-1}$ and $\nu_{24} = 108.4 \text{ cm}^{-1}$ are not seen in this work. Since the ionic torsional modes are not totally symmetric (assuming CH_3COCH_3 retains C_{2v} symmetry upon ionization), vibrational selection rules indicate that transitions to these levels from the neutral acetone ground state are symmetry forbidden.^{26,93} Also, it is quite likely that the target molecules do not experience sufficient vibrational relaxation during the expansion

to permit observation of these very low energy transitions. Indeed, these frequencies lie nearly at the limit of the experimental optical resolution. The onset of 320 cm^{-1} appears to correspond with the A_1 symmetric C-C-C deformation mode (ν_8), to which is assigned the 385 cm^{-1} band in the vibrational spectra of the neutral molecule. This ionic transition was tentatively identified in a previous photoelectron spectroscopy study.²⁶⁶ Several normal modes could conceivably give rise to the observed feature at 695 cm^{-1} , including the symmetric C-C stretch (ν_7) and two out-of-plane skeletal fundamentals (ν_{19} , ν_{23}). In neutral acetone, these modes occur at 777 cm^{-1} , 530 cm^{-1} and 484 cm^{-1} , respectively. Since the out-of-plane vibrations involve the carbonyl group directly, these frequencies could be substantially altered upon ionization. To a lesser extent, a shift is expected for the C-C stretch as well. Within the estimated resolution limits, a possible contribution from $2\nu_8$ must also be considered. A specific assignment for this transition is not attempted; however, the vibrational selection rules favor the A_1 symmetric modes (ν_7 , $2\nu_8$). In previous studies, an ionic vibrational feature has been observed at 1200 cm^{-1} which has been assigned to either the C-O stretch²³⁷ or the methyl group symmetric deformation mode.²⁶⁶ In the present work, this feature

appears significantly broader than the lower energy transitions. It seems likely that the manifold at 930-1370 cm^{-1} arises from several unresolved vibrational excitations, possibly including the CH_3 asymmetric and symmetric deformation modes (ν_4 , ν_5 , ν_{15} , ν_{16} , ν_{21}), the CH_3 rocking modes (ν_6 , ν_{11} , ν_{18} , ν_{22}) and the asymmetric C-C stretch (ν_{17}). A broad peak centered at about 1300 cm^{-1} in the acetone electron energy loss spectrum has been interpreted in a similar fashion.²⁷⁷ Again, the A_1 symmetric modes (ν_4 , ν_5 , ν_6) are favored by the selection rules. At energies above 1400 cm^{-1} from threshold, the photoion yield curve becomes very complex. This is due principally to the increasing superposition of ionization continua and the onset of dissociative processes. The occurrence of autoionization at 0.1-0.2 eV above threshold has also been suggested.²⁵⁹

Within stated error limits, the measured ionization potential of CD_3COCD_3 is identical to that for the acetone parent (see Table III). Fine structure in the acetone- d_6 photoionization curve consists of a transition at 260 cm^{-1} and a broad rise from about 660-1100 cm^{-1} . In the vibrational spectra of the neutral molecule, perdeutero substitution has the effect of reducing ν_8 by about 65 cm^{-1} and lowering the

CH_3 rocking and deformation modes by $160\text{--}400\text{ cm}^{-1}$.²⁸⁸
A reduction in ν_7 and ν_{17} by about 100 cm^{-1} and 200 cm^{-1} respectively is also observed. These results favor the assignment of the 260 cm^{-1} mode to ν_8 and the higher energy manifold to a composite of C-C stretches (ν_7 , ν_{17}) and methyl group excitations. Vibrational selection rules apply as in the case of CH_3COCH_3 .

In view of the aforementioned wavelength dependence of sodium salicylate fluorescence quantum efficiency between $1250\text{--}1500\text{ \AA}$ (see Section III.B.), care must be exercised in interpreting the parent ion efficiency curves over a wide energy range; however, this effect is undoubtedly small ($<0.5\%$) for individual features occurring in less than 30 meV . Consequently, it should be possible to derive fairly accurate relative Franck-Condon factors from the step heights of the observed structure near threshold. For $\text{CH}_3\text{COCH}_3^+$, the measured relative transition probabilities for the first three onsets are $1.00:0.35:0.12$. The relative values for the first two steps in the $\text{CD}_3\text{COCD}_3^+$ curve are about $1.00:0.25$. It must be emphasized that the initial thresholds may include some contribution by unresolved transitions to (and from) the low energy methyl group torsional modes.

b. CH_3CO^+ and CD_3CO^+ fragment ions

Appearance potential curves for acetyl fragment ions from acetone and acetone- d_6 are shown in Figure 15. The measured threshold value of 10.52 ± 0.02 eV for CH_3CO^+ is 0.1-0.2 eV higher than previous room temperature determinations (see Table III) and is, in fact, 0.07 eV higher than the calculated OK value of Murad and Inghram.²⁵⁵ The relatively high appearance potential and the near absence of curvature at onset provide evidence of substantial thermal relaxation of the acetone parent molecules in the present work. In view of the apparent uncertainty in the earlier measurements,^{237,255,256} the present determination strongly suggests that the OK appearance potential is likely 10.54 eV or higher.

Murad and Inghram have used their extrapolated OK acetyl ion appearance potential of 10.45 eV to derive several thermodynamic quantities.^{255,256} In these derivations, the kinetic shift in the fragmentation of acetone to form CH_3CO^+ was estimated to be 0.25 eV. Subsequent calculations based on quasi-equilibrium theory indicate that this value is likely to be 0.01 eV or less.¹³¹ Since the present study favors an appearance potential as much as 0.1 eV higher than 10.45 eV, a

cumulative error of up to 0.35 eV for the deduced thermochemical information may have resulted from the low threshold value and overestimated kinetic shift. These thermodynamic quantities are not recalculated since there is no certain means of determining or estimating the OK appearance potential with the apparatus as constructed.

The observed threshold for the dissociation of acetone- d_6 to form CD_3CO^+ is 10.56 ± 0.02 eV. This represents a secondary isotope effect in the appearance potential of about 0.04 eV upon perdeuteration. This effect was clearly observed in three separate measurements of the CH_3CO^+ and CD_3CO^+ onsets. By comparison, a primary isotope effect of 0.092 eV has been seen in the formation of HCO^+ and DCO^+ from H_2CO and D_2CO respectively.¹³⁸

c. Acetone and acetone- d_6 cluster ions

The photoionization efficiency curve for $(CH_3COCH_3)_2^+$ is shown in Figure 16. In contrast to the sharp thresholds obtained in the monomer work, the photoion yield of the dimer exhibits a weak onset and generally increases slowly as a function of excess energy. This behavior has been observed in previous cluster studies^{83,84,90} and is best explained by the possibility of a substantial change in the potential energy surface

upon ionization. For example, Mulliken estimates a 1.55 Å reduction in the equilibrium location of the potential well minimum for $\text{Xe}_2 \rightarrow \text{Xe}_2^+$.²⁸⁹ Under these circumstances, the Franck-Condon factor for direct ionization may be quite small (see Figure 2). Indeed, the possibility exists that the adiabatic transition will not be seen above background.⁸³ Within the sensitivity of the present experiment, the ionization potential of $(\text{CH}_3\text{COCH}_3)_2$ is observed at 9.26 ± 0.03 eV. Much of the fine structure in the dimer ion curve is reproducible; however, specific assignments are not attempted in view of the low resolution employed in this measurement, the obvious complexity in the vibrational structure of this system, and the unknown contribution to the photoion yield above threshold due to fragmentation of higher clusters.⁸³ Because of the ratios of dimer ions to higher cluster ions observed in the present work (see Section IV.B.2.), the latter effect is expected to be small.

The ionization potential determination for $(\text{CH}_3\text{COCH}_3)_2$ permits the calculation of the dimer ion binding energy by consideration of the following reactions:

The sum of the enthalpies for (83), (84) and (85) equals the observed monomer ionization potential of 9.694 ± 0.006 eV. No experimental value for the neutral dimer binding energy has been reported. However, an estimate of this quantity may be made using known second virial coefficient data. Braun and Leidecker have calculated the water dimer binding energy²⁹⁰ (BE) by assuming an ideal two component (monomer and bound dimer) mixture of H_2O vapor for $KT \ll \text{BE}$. Under similar assumptions, the energy of formation $\Delta u(T)$ for Reaction (83) at fixed values of T and P is given by

$$\frac{d}{d(1/T)} \ln [\bar{b}_0 - B_2(T)] = \frac{\langle \Delta u(T) \rangle}{R} \quad (86)$$

where b_0 is the so-called "excluded volume" of the gas, $B_2(T)$ are the experimental second virial coefficients and $\langle \Delta u(T) \rangle$ is averaged over all internal states of the dimer. As T nears OK, $\langle \Delta u(T) \rangle$ approaches the binding energy of the dimeric species. Hence, by plotting the available $\ln[\bar{b}_0 - B_2(T)]$ data for acetone as a function of $1/T$, the binding energy may be estimated from the low temperature slope of Equation (86). This procedure has

been applied to several reported sets of $B_2(T)$ data²⁹²⁻²⁹⁵ as shown in Table IV. Briefly, calculated BE values in the range 1.6-2.4 kcal/mole have been obtained while the data of Anderson *et. al.*²⁹⁶ indicate a substantially higher value. Taking the average of these determinations, a reasonable estimate for the acetone dimer binding energy is about 2.4 kcal/mole or 0.104 eV. Using this value, Reactions (82)-(85) give a dimer ion binding energy of 0.538 eV or 12.4 kcal/mole. The uncertainty in this quantity is probably about ± 1 kcal/mole. In view of the possibility that the dimer adiabatic ionization potential is not observed, 12.4 kcal/mole must be considered a lower bound.

The photoion yield curve for $(CD_3COCD_3)_2^+$ is shown in Figure 17. Within the resolution of the present work, the measured ionization potential of the acetone- d_6 dimer is identical to that of $(CH_3COCH_3)_2$. The $(CH_3COCH_3)_2^+$ and $(CD_3COCD_3)_2^+$ curves seem to exhibit considerable similarity in their fine structure, suggesting that the observed transitions are fairly insensitive to isotopic substitution. For reasons previously stated, specific assignments are not attempted.

Figures 18 and 19 contain the photoionization efficiency curves near threshold for $(CH_3COCH_3)_3^+$ and $(CH_3COCH_3)_4^+$. Ionization potentials for

Table IV. Calculated Acetone Dimer Binding
Energies from $B_2(T)$ Data.

A. Reference 292.

$T(K)$	$1/T(x10^3)$	$-B_2(T) (\frac{cc}{mole})$	$b_0-B_2(T)$	$\ln [b_0-B_2(T)]$
313.16	3.193	1575	1642	7.4037
323.16	3.094	1375	1442	7.2738
337.16	2.956	1200	1267	7.1444
353.16	2.832	1065	1132	7.0317
368.16	2.715	920	987	6.8947
382.16	2.617	800	867	6.7650
398.16	2.512	700	767	6.6425
413.16	2.420	630	697	6.5468
428.16	2.336	555	622	6.4329
453.16	2.207	455	522	6.2577
473.16	2.113	400	467	6.1463

$b_0 = 67 \text{ cc/mole}$ (Reference 291)

From low temperature slope:

$$\frac{d}{d(\frac{1}{T})} \ln [b_0-B_2(T)] = 1104.5K$$

$$\Delta u = R \times 1104.5K$$

$$= 2.195 \text{ kcal/mole}$$

B. Reference 293.

$T(K)$	$1/T(x10^3)$	$-B_2(T) (\frac{cc}{mole})$	$b_0-B_2(T)$	$\ln [b_0-B_2(T)]$
300	3.333	2000±200	2067±200	7.5321-7.6339-7.7262
310	3.226	1730±100	1797±100	7.4366-7.4939-7.5480
320	3.125	1520±50	1587±50	7.3376-7.3696-7.4000
330	3.030	1350±50	1417±50	7.2204-7.2563-7.2910
340	2.941	1200±50	1267±50	7.1041-7.1444-7.1831
350	2.857	1080±50	1147±50	7.0003-7.0449-7.0870
360	2.778	960±50	1027±50	6.8845-6.9345-6.9819

$b_0 = 67 \text{ cc/mole}$ (Reference 291)

From low temperature slope:

$$\frac{d}{d(\frac{1}{T})} \ln [b_0-B_2(T)] = 1215.5K$$

$$\Delta u = 2.415 \text{ kcal/mole}$$

C. Reference 294.

T(K)	1/T(x10 ³)	-B ₂ (T) ($\frac{cc}{mole}$)	b ₀ -B ₂ (T)	ln [b ₀ -B ₂ (T)]
291.7	3.428	2075.9	2142.9	7.6699
319.4	3.131	1644.1	1711.1	7.4449
329.5	3.035	1527.3	1594.3	7.3742
335.0	2.985	1406.3	1473.3	7.2953
341.4	2.929	1342.2	1409.2	7.2508
351.2	2.847	1257.5	1324.5	7.1888
361.2	2.769	1133.6	1200.6	7.0906
368.4	2.714	965.4	1032.4	6.9396
385.0	2.597	853.9	920.9	6.8254
405.6	2.465	650.5	717.6	6.5759

b₀ = 67 cc/mole (Reference 291)

From low temperature slope:

$$\frac{d}{d(\frac{1}{T})} \ln [b_0 - B_2(T)] = 213.2K$$

$$\Delta u = 1.626 \text{ kcal/mole}$$

D. Reference 295.

T(K)	1/T(x10 ³)	-B ₂ (T) ($\frac{cc}{mole}$)	b ₀ -B ₂ (T)	ln [b ₀ -B ₂ (T)]
323.16	3.094	1560	1627	7.3945
343.16	2.914	1280	1347	7.2056
363.16	2.754	1040	1107	7.0094
383.16	2.610	850	917	6.8211
403.16	2.480	700	767	6.6425

b₀ = 67 cc/mole (Reference 291)

From low temperature slope:

$$\frac{d}{d(\frac{1}{T})} \ln [b_0 - B_2(T)] = 1198.2K$$

$$\Delta u = 2.381 \text{ kcal/mole}$$

E. Reference 296.

$$\Delta u = \Delta H_2 = -3.9 \text{ kcal/mole}$$

these species are observed at 9.10 ± 0.03 eV and 9.02 ± 0.03 eV respectively. Again, it is not certain that these values represent the adiabatic transitions. The extremely low count rates (0.03 - 0.1 count/sec) in these measurements prevent any useful analysis of the fine structure.

With positive ion energetic information available for polymers up to the tetramer, it becomes possible to investigate the relationship between cluster size and bulk properties. For example, it has been observed that the ionization potential for an alkali metal aggregate containing as few as three or four atoms approaches the calculated effective work function of a continuous metal drop of the same size.^{61,297,298} In contrast, the ionization potentials for $(\text{Hg})_n$ do not fall rapidly toward the work function with increasing n .²⁹⁹ For compounds such as acetone, results of this type are likely to be of significant interest in that they have a direct bearing on nucleation and condensation phenomena and possibly even on liquid structure.

In the present study, a smooth and systematic decrease in ionization potential with increasing acetone cluster size is observed. As indicated in Figure 21, the measured ionization energies for $(\text{CH}_3\text{COCH}_3)_n$ fall squarely on a straight line when plotted as a function of $1/n$. It is interesting to compare this functional

Figure 21. Plot of the Observed Ionization Energies for $(\text{CH}_3\text{COCH}_3)_n$, $n=1-4$, as a Function of $1/n$.

dependence to that which would be expected on the basis of a simple independent systems model³⁰⁰ for the cluster ion system. Using a straightforward perturbation approach, the energy levels for the individual monomeric units of a linear cluster ion are considered to undergo splitting due to weak nearest neighbor interactions. Long-range interactions are set equal to zero. The much smaller splittings due to the relatively weak interactions in the neutral cluster are ignored. Under these assumptions, the secular equation describing the degenerate manifold for cluster ion size n should be as follows:

$$D_n = \begin{vmatrix} \alpha - \lambda & \beta & 0 & 0 & \dots \\ \beta & \alpha - \lambda & \beta & 0 & \dots \\ 0 & \beta & \alpha - \lambda & \beta & \dots \\ 0 & 0 & \beta & \alpha - \lambda & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

where α represents the monomer ionization potential and β is the nearest neighbor interaction parameter. It can be shown that the minimum transition energy $\lambda = \alpha - 2\beta \cos \left(\frac{\pi}{n+1} \right)$. To the extent that the above model accurately represents a cluster ion system, this implies a linear decrease of the ionization potential as a function of $\cos \left(\frac{\pi}{n+1} \right)$. Since $\cos \left(\frac{\pi}{n+1} \right)$ is very nearly a linear function of $1/n$ for $n = 2-10$, this model produces a good correlation to our data for the first few members of

$(\text{CH}_3\text{COCH}_3)_n$. Of course, this analysis does not establish a specific structure for the acetone cluster ions; however, it is intriguing that a satisfactory correlation of ionization potential with cluster size can be achieved using this simple picture.

If the ionization energies for $(\text{CH}_3\text{COCH}_3)_n$, $n > 4$, continue to decrease linearly as a function of $1/n$, Figure 21 predicts a bulk ionization potential of about 8.8 eV. A value of 8.86 eV is calculated from a plot of ionization potential vs $\cos(\frac{\pi}{n+1})$. This suggests that the ionization energy of acetone is reduced by about 0.85 eV upon condensation. In view of the uncertainty as to whether our measured cluster ion thresholds correspond to adiabatic transitions, 0.85 eV is probably a lower bound. This value compares favorably to relaxation shifts of 1.0 - 1.65 eV recently observed in the ultraviolet photoemission spectra of seven gases condensed on a MoS_2 substrate.^{301,302}

The photoionization efficiency curve for the final ion investigated in acetone molecular beams, $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$, is shown in Figure 20. Despite the very low count rate for this specie (0.03-0.3 count/sec), a definite onset is seen at 10.08 ± 0.05 eV. This is taken to be the appearance potential for the process

The origin of the very few counts observed between 1230-1240 Å is not certain. The desolvation energy, ΔH_s , of $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$ can be estimated from the enthalpies of Reactions (83), (88) and the following:

Using the experimental appearance potentials for (88) and (89) and -0.104 eV for the enthalpy of (83) as before, ΔH_s is calculated to be 0.544 eV or 12.5 kcal/mole. The similarity between this value and the dimer ion binding energy calculated from Reactions (82) - (85) would seem to suggest that the methyl groups in acetone play a minimal role in the bonding of cluster ions.

C. Preliminary Photoionization Experiments on Carbon Disulfide

As a simple triatomic inorganic molecule, CS_2 may be expected to exhibit significantly different ionization and fragmentation properties than those seen in complex organic compounds such as acetone. These properties, especially the first and higher ionization potentials, have in fact been widely studied by various techniques including vacuum ultraviolet absorption spectroscopy,^{303,304} photoionization,^{45,122,305} photoelectron spectroscopy^{124, 306-310} and photoionization

resonance spectroscopy (threshold photoelectron spectroscopy).¹²³ Because of the intense autoionization features which dominate the photoion yield curve of the parent CS_2^+ ion (see Section II.B.2.a.), photoelectron spectroscopic methods are far superior for the investigation of direct ionization processes occurring well above the initial threshold; however, photoionization mass spectrometry may be profitably applied to the measurement of transitions near the first ionization limit and also appearance potentials for dissociative processes. In particular, it would be worthwhile to use high resolution molecular beam photoionization methods to determine the excitation energies for CS_2^+ ionic vibrational modes and to compare these energies with available values obtained from other techniques.^{123,308,311} Moreover, the photoionization efficiency curve of $(\text{CS}_2)_2^+$ is of interest inasmuch as an analogous experiment has been performed on $(\text{CO}_2)_2^+$.^{83,91} The present study reports a preliminary low optical resolution measurement of the CS_2^+ photoion yield curve between 1200-1240 Å as well as a low resolution determination of the $(\text{CS}_2)_2^+$ curve in the wavelength range 1000-1290 Å.

1. Experimental

Molecular beam sampling of carbon disulfide was accomplished by attaching directly to the gas manifold

a flask containing liquid CS_2 at $20\text{--}25^\circ\text{C}$, thereby sustaining a nozzle stagnation pressure of at least 365 torr. For the dimer study, the CS_2 vapor was seeded in enough H_2 to bring the total source pressure to about 700 torr. A fixed CS_2 vapor pressure was maintained by immersing the liquid sample container in a constant temperature ($\pm 1^\circ\text{C}$) bath. Matheson, Coleman and Bell CS_2 reagent, A.C.S., was used without further purification.

An optical resolution of about $3.75 \text{ \AA}$ (or 30 meV) was employed for both the monomer and dimer photoion yield curves (500 μ monochromator entrance and exit slits). Operating conditions for the hydrogen lamp were very similar to those used in the acetone work; however, the available monochromatic light intensities were significantly below those obtained in the early CH_3COCH_3 measurements. These losses were probably due to the slow collection of oil deposits on the grating or possibly gradual contamination of the end of the discharge capillary tube. In the CS_2^+ investigation, counts were accumulated for 200-300 seconds per data point at $1\text{--}2 \text{ \AA}$ intervals. Ion detection rates varied from approximately 45 counts/second at Lyman α to about 0.2 count/second at threshold. For the $(\text{CS}_2)_2^+$ determination, counts were collected for 300-500 seconds per data point at $2.5 \text{ \AA}$ intervals. Typical counting rates ranged from 0.03

count/second to 3 counts/second. Once again, a reference point was regularly repeated to assure overall calibration.

2. Results and Discussion

The monomer photoionization efficiency curve is shown in Figure 22. Although wide monochromator entrance and exit slits were employed, the resolution of the data appears to be at least equivalent to that obtained in previous conventional photoionization studies at nominally higher resolutions (e.g., see Figure 5).^{122,305} This equivalence illustrates both the deleterious effects of sample internal energy in a room temperature experiment and the power of using molecular beam techniques to provide efficient thermal relaxation of the target molecules. The observed first ionization potential of 10.056 ± 0.015 eV is in excellent agreement with the earlier photoionization measurements. Values from vacuum ultraviolet absorption spectroscopy^{303,304} are about 0.02 eV higher. In addition, there are numerous apparent step-like fine structure features, especially at $250\text{--}820\text{ cm}^{-1}$ and 1500 cm^{-1} above the initial onset. These features probably correspond to low energy vibrational excitations superimposed on structure due to a spin-orbit splitting of about 500 cm^{-1} .^{122,123} Unfortunately, a higher resolution measurement is necessary in order to make specific assignments. Regions of the CS_2^+ curve which contain sharp autoionization peaks might also

Figure 22. Photoion Yield Curve for CS₂⁺ from 1203 to 1239 Å.

be profitably re-examined at the resolutions possible with molecular beam sampling. The value of further work on this system is clearly indicated.

The photoion yield curve for $(\text{CS}_2)_2^+$ is shown in Figure 23. The most interesting portions of this curve were measured at least twice. As in the case of $(\text{CH}_3\text{COCH}_3)_2^+$, the photoionization efficiency of $(\text{CS}_2)_2^+$ rises very gradually from a weak onset. Within the sensitivity of the apparatus, the measured ionization potential for this specie is about 9.63 eV. Once again, the probability for the adiabatic transition may be so small as to prevent the observation of this onset above background.⁸³ A calculation of the dimer ion binding energy may be made in the manner described in Section II.B.3.c. by considering the following thermodynamic cycle:

where IP_1 , IP_2 , D_2 and D_2^+ are defined as in Equation (24). Available second virial coefficient ($B_2(T)$) data for CS_2 ²⁹³ may be employed to derive an estimate for D_2 . These data and calculations are shown in Table V. Using the measured monomer and dimer ionization potentials as well as -0.053 eV

Figure 23. Photoion Yield Curve for $(\text{CS}_2)_2^+$ from 1007 to 1292 $\text{\AA}$.

Table V. Calculated Carbon Disulfide Dimer
Binding Energy from B_2 (T) Data.²⁹³

T(K)	$1/T(\times 10^3)$	$-B_2(T) \left(\frac{\text{cc}}{\text{mole}}\right)$	$b_0 - B_2(T)$	$\ln [b_0 - B_2(T)]$
280	3.571	930 $\pm$ 30	1040 $\pm$ 30	6.9177-6.9470-6.9754
290	3.448	862 $\pm$ 30	972 $\pm$ 30	6.8480-6.8794-6.9098
300	3.333	796 $\pm$ 25	906 $\pm$ 25	6.7811-6.8090-6.8363
310	3.226	740 $\pm$ 20	850 $\pm$ 20	6.7214-6.7452-6.7685
325	3.077	666 $\pm$ 15	776 $\pm$ 15	6.6346-6.6542-6.6733
350	2.857	567 $\pm$ 15	677 $\pm$ 15	6.4953-6.5177-6.5396
375	2.666	489 $\pm$ 15	599 $\pm$ 15	6.3699-6.3953-6.4200
400	2.500	429 $\pm$ 15	539 $\pm$ 15	6.2615-6.2897-6.3172
430	2.326	377 $\pm$ 15	487 $\pm$ 15	6.1570-6.1883-6.2186

$$b_0 = 110 \text{ cc/mole}$$

$$(b_0 = 2/3\pi\tilde{N}\sigma^3, \tilde{N} = \text{Avogadro's number, } \sigma \text{ taken from Table I-A in appendix of Reference 291})$$

From / temperature slope:

$$\frac{d}{d\left(\frac{1}{T}\right)} \ln [b_0 - B_2(T)] = 610K$$

$$\begin{aligned} D_2 = \Delta u &= R \times 610K \\ &= 1.212 \text{ kcal/mole} \\ &= 0.053 \text{ eV} \end{aligned}$$

for the dimer binding energy, the above cycle gives a $(\text{CS}_2)_2^+$ binding energy of 0.479 eV or 11.0 kcal/mole. In view of the uncertainty as to whether the adiabatic transition is observed for the dimer, this value must be considered a lower bound.

A comparison of the $(\text{CS}_2)_2^+$ photoion yield curve with the $(\text{CO}_2)_2^+$ data of Jones and Taylor^{83,91} reveals some interesting similarities. First, the measured dimer ionization potentials are shifted to lower energy by nearly the same amounts (0.37 eV for CO_2 dimer, 0.426 eV for CS_2 dimer) with both curves lacking sharp initial onsets. Second, the two sets of data predict dimer ion dissociation energies, D_2^+ , which differ considerably from literature values. For instance, the calculated D_2^+ for carbon disulfide dimer ion (11.0 kcal/mole) is significantly below the enthalpy for the $\text{CS}_2^+ - \text{CS}_2$ ion-molecule association reaction ($-\Delta H^\circ = 21.9 \pm 2.5$ kcal/mole) recently determined by Meot-Ner and Field³¹² using pulsed high pressure mass spectrometry. At the same time, the data of Jones and Taylor would appear to indicate a D_2^+ for $(\text{CO}_2)_2^+$ in the range of 9-11 kcal/mole. The enthalpy for the $\text{CO}_2^+ - \text{CO}_2$ ion clustering reaction is once again much higher ($-\Delta H^\circ = 16.2 \pm 1.5$ kcal/mole).³¹² These discrepancies may be due to the inability to observe the $v''=0 \rightarrow v'=0$ transition for the dimer; however, the possibility of

error in the ion-molecule reaction studies (i.e., van't Hoff plots) must also be considered. Finally, the $(\text{CS}_2)_2^+$ and $(\text{CO}_2)_2^+$ photoionization efficiency curves are similar in terms of fine structure. In each case, the dimer curve exhibits one or more autoionization features which resemble peaks occurring in the monomer curve at nearly identical photon energies. By the same token, some fine structure appears to be lost or at least obscured in going from the monomer to the dimer in both systems (e.g., compare the 1050-1150 Å wavelength region in Figures 5 and 23). One detail which seems to be different in the two sets of data is the fact that the most intense autoionization peak in the carbon dioxide curves is much broader for the dimer whereas the peak at 1000-1050 Å in the curves of the carbon disulfide species shows very little, if any, change in width. Observed peak broadening of this type could result from poorer resolution in the dimer studies or possibly from a decrease in the lifetime of the excited Rydberg-like states in going from monomer to dimer.

It should be noted that an interesting application may result from the knowledge of relative peak positions in photoion yield curves of such ions as CS_2^+ and $(\text{CS}_2)_2^+$. If the initial excitation step of an individual autoionizing transition can be correlated

between the parent and cluster molecules (i.e., a given resonance process in the dimer, trimer, etc. can be considered to be identical to a corresponding excitation in the monomer, except for a slight perturbation due to the presence of other monomeric units), the following cycle may be employed:

where E_1 and E_2 are the photon energies at which the similar peaks are observed and D_2^* is the dissociation energy of the process shown. An estimate or measurement of D_2 coupled with the known values of E_1 and E_2 allows the determination of D_2^* . In order to apply the cycle to CS_2 and $(\text{CS}_2)_2$, it would be necessary to perform more careful measurements on both species; however, a cursory examination of the available data (using Figure 5) indicates that D_2 and D_2^* are very similar.

V. RECOMMENDATIONS

With the molecular beam photoionization mass spectrometer as constructed, it is possible to investigate at high resolution the photoionization efficiency behavior of a large number of parent, cluster and fragment ions. Several proposed experiments will be discussed in the present section. Before dealing with this subject, however, a number of possible developments in the instrumental design will be examined. Indeed, there are many improvements which could be made in order to simplify the data collection, increase the photon energy resolution and enhance the ion transmission and detection properties of the mass analyzer. In addition, it would be desirable to extend the energy range of the apparatus so as to possess the capability of studying a wider variety of compounds.

Two fairly simple modifications would serve to make the data collection more convenient. First, it would be helpful to integrate and digitize the voltage output of the picoammeter used to monitor the intensity of the dispersed vacuum ultraviolet light. This step would require an amplifier integrator, together with the appropriate gating circuitry and a provision for displaying and clearing the output. Instrumentation of this

type would eliminate the need to constantly monitor the picoammeter output and would automatically account for any significant short-term fluctuations in lamp intensity. Second, a substantial amount of time could be saved if the entire data collection system were automated. At present, the monochromator grating drive and ion counter are operated manually. Thus, an automated operational mode would involve coupling a stepping motor to the wavelength scan mechanism of the monochromator and providing the necessary circuitry to print out the ion count and integrated photon output after a variable preset time. Upon printing the signals, data collection could immediately proceed by stepping the monochromator to a new wavelength and resetting and restarting the scalars. The long-term stability of the lamp could be monitored by passing the voltage output of the picoammeter to an x-y recorder.

It need hardly be stated that improved mass selected ion transmission and detection would be advantageous in terms of reducing the time required per data point and allowing the investigation of molecular beam constituents which are present in low concentrations (e.g., larger clusters). Despite the discrepancy between the calculated collection efficiency of the present apparatus and

reported values for a similar instrument,^{55,140} it is unclear at this point how the mass spectrometer transmission could be substantially increased inasmuch as several ion box and ion extraction slit designs have been tried with only small observed changes in signal. Also, a check on the mass analyzer alignment indicated that this aspect was fairly well optimized. On the other hand, it would be useful to improve the ion detection system by eliminating the need for the 20db attenuator in the data collection electronics. This step alone would increase the count rate by a factor of about 2.5. In this regard, it is expected that significantly reduced noise levels can be achieved by providing better shielding for the electron multiplier tube and voltage divider arrangement and also by passing the voltage pulse produced at the anode of the multiplier through an electronically isolated connector (i.e., eliminating ground loops).

In spite of the fact that the photoionization mass spectrometer was largely assembled from available surplus equipment, most of the basic instrumentation is quite adequate. However, one major item which could conceivably be replaced is the vacuum ultraviolet monochromator. As mentioned in Section II.D., near-normal incidence monochromators are much better than

Seya-Namioka type instruments in terms of dispersed light throughput and ultimate resolution. Unfortunately, such a change would necessitate redesigning the differential pumping system. The high cost of a 1-m. or 3-m. near-normal incidence device is also a negative factor. In addition, space limitations in the present orientation of the apparatus would be severe enough that the whole instrument would have to be moved and re-aligned.

With or without a new monochromator, a modified vacuum system with much higher pumping speed would be advantageous. In particular, it would be useful to have the capacity for handling the increased gas loads associated with intense helium capillary discharges. The ionization and dissociative properties of many interesting compounds may be studied with the He Hopfield continuum (580-1100 Å); however, relatively high lamp pressures (40-100 torr) are required. Reasonable modifications in the vacuum system might include the use of a larger Roots blower on the first differential pumping chamber and possibly the incorporation of another differential pumping region in the vicinity of the monochromator exit slit. Since the Hopfield continuum is sufficiently excited only in a repetitive discharge, additional electronics would be needed including a high

voltage pulser and an appropriate power supply (about 15kV, 500 mA). For best results below 900 Å, a gold or platinum coated grating with a suitable blaze angle would be employed.

Two possible additions to the nozzle beam sampling system should be briefly mentioned. First, the installation of a time-of-flight correlation chopper would be useful in providing a direct measure of molecular beam temperatures. At the present time, crude temperature estimates may be made only by examining the energy spread of step-like thresholds in the photoion yield curves. Second, enhanced monomer and cluster beam intensities might be realized if the primary skimmer and endwall were cryocooled (see Figure 7). Clogging of the skimmer can be a severe problem in such designs, however. This problem might be especially troublesome in photoionization experiments, since long data collection times are typically required.

The photoionization efficiency curves of a considerable number of ions have been determined using supersonic molecular beam photoionization mass spectrometry. These ions are listed in Table VI according to the investigating group. Many very interesting systems remain to be studied, however. For instance, the present work

Table VI. Ions For Which Photoionization Efficiency Curves Have Been Determined Using Supersonic Molecular Beam Mass Spectrometry.

<u>Investigating Group</u>	<u>Species Studied</u>
1. James W. Taylor <u>et. al.</u> , 79-81,83,91,92 U. of Wisconsin	CO_2^+ , $(\text{CO}_2)_2^+$, CH_3OH^+ , $(\text{CH}_3\text{OH})_n\text{H}^+$
2. Yuan T. Lee, <u>et. al.</u> , 82,84-90,117 U. of California, Berkeley	NO^+ , $(\text{NO})_2^+$, Xe_2^+ , Ar_2^+ , Kr_2^+ , XeKr^+ , XeAr^+ , KrAr^+ , ICl^+ , ArICl^+ , CH_3I^+ , O_3^+ , H_2O^+ , H_3O^+ , $(\text{H}_2\text{O})_2^+$, NH_3^+ , $(\text{NH}_3)_2^+$, $(\text{NH}_3)_n\text{H}^+$, HF^+ , $(\text{HF})_n\text{H}^+$, HCl^+ , H_2Cl^+ , $(\text{HCl})_2^+$, C_2H_4^+ , $(\text{C}_2\text{H}_4)_2^+$, C_4H_7^+ , C_3H_5^+
3. This work.	$\text{CH}_3\text{COCH}_3^+$, $\text{CD}_3\text{COCDD}_3^+$, CH_3CO^+ , CD_3CO^+ , $(\text{CH}_3\text{COCH}_3)_n^+$, $n=2-4$, $(\text{CD}_3\text{COCDD}_3)_2^+$, $(\text{CH}_3\text{COCH}_3) \cdot \text{CH}_3\text{CO}^+$, CS_2^+ , $(\text{CS}_2)_2^+$

could be extended by carefully examining the photoion yield behavior of CS_2^+ from about 900 Å to threshold. At high resolution, it should be possible to identify individual vibrational excitations near the first onset and also to precisely measure the positions of auto-ionization peaks. A better comparison of the fine structure in the monomer and dimer curves could be made. If the intensity of either the dispersed vacuum ultraviolet light or clusters in the molecular beam can be increased, photoionization efficiency curves of $(\text{CH}_3\text{COCH}_3)_n^+$, $n=5,6,7\dots$ could be determined. These measurements would be especially useful in relation to the information contained in Figure 21. The investigation of ionization and fragmentation properties of a wide variety of other compounds is feasible as well. With the H_2 many-line pseudo-continuum, parent and cluster species in nozzle beams of COS, cyclopropane, propylene, 1,3-butadiene, Cl_2 , Br_2 , CH_3Cl , CH_2Cl_2 , H_2S , CH_3SH , etc. may be studied. Experiments on clusters of such aromatic molecules as benzene, hexafluorobenzene and toluene could be potentially very intriguing in comparison with recent electric dipole moment determinations for these compounds.^{313,314} In addition, if the monochromator vacuum system can be upgraded and the necessary electronics

obtained to produce a pulsed He discharge, the photoion yield curves of CO^+ , SF_5^+ , UF_5^+ and many other interesting ions could be measured.

For molecules such as H_2S , molecular beam photoionization studies can lead to the determination of proton affinities (PA) and proton solvation energies (SE). Investigations of this type have already been performed on H_2O , HF and NH_3 .⁸⁴ To calculate PA for hydrogen sulfide, the following thermodynamic cycle may be used:

where AP_1 , AP_2 and D_2 are defined as before (see Equation 31). Since AP_1 and AP_2 can be directly measured, an estimate of D_2 yields the proton affinity. Appearance potential determinations for the dissociative ionization of hydrogen sulfide trimers, tetramers, etc. to form $(\text{H}_2\text{S})_n \text{H}^+$ may also be utilized in appropriate thermochemical cycles such as

where $SE_{n-1,n}$ represents the solvation energy corresponding to the addition of the n th H_2S constituent. For $n=2-5$, these enthalpies can be compared to available literature values.³¹⁵ Analogous experiments could be performed on D_2S .

The photoionization efficiency behavior of many interesting mixed cluster systems remain to be explored. For example, the enthalpy ($\Delta H_{H_3S^+ \cdot H_2O}^0$) for the clustering reaction

has been reported.³¹⁵ Since mixed clusters such as $(H_2S)_2 \cdot H_2O$ can be produced in a supersonic expansion, it should be possible to measure the appearance potential (AP') of $H_3S^+ \cdot H_2O$ and then calculate the $(H_2S)_2 \cdot H_2O$ binding energy ($-D_{2,1}$) from the following cycle:

where AP_2 may be directly measured as in Equation (93). Once again, these experiments could be extended to higher clusters and other isotopes. As another example, photoionization studies of such polymers as $NO \cdot (H_2O)_n$, $O_2 \cdot (H_2O)_n$, $NO \cdot CO_2$ and $NO \cdot N_2$ could be particularly useful inasmuch as their respective ions, $(NO^+(H_2O)_n$, $O_2^+(H_2O)_n$, etc.) are involved in principal chemical reactions in the

D region of the ionosphere.^{316,317} In spite of the vital role which these ions play, very little is known about their vibrational spectra, structures or thermochemistry. It is precisely this type of information which could be at least partially obtained in a sufficiently high resolution photoionization experiment.

Finally, the rapid development of high power lasers of various kinds makes it reasonable to speculate on future utilization of this burgeoning technology in molecular beam photoionization mass spectrometric studies. Needless to say, the most straightforward application would involve the design of tunable high intensity vacuum ultraviolet cw lasers and the use of such instruments as photoionization light sources. Another possible application would be the study of ionization and fragmentation processes using target molecules which are predominantly in excited electronic or vibrational states. The initial excitation step could be accomplished by a laser of suitable wavelength while another laser (tunable) or a conventional light source could be used for the photoionization process.

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