

Molecular Multiphoton Ionization and Ion Fragmentation Spectroscopy

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I. INTRODUCTION

Multiphoton ionization (MPI) has emerged as one of the most powerful methods for molecular detection. MPI spectroscopy is now being used extensively in fundamental research and for a variety of molecular detection applications that demand exceptional sensitivity. From the onset of studies, it was clear that techniques such as resonance enhanced 2-photon ionization had the potential to detect single molecules of many polyatomic species. Further work revealed that MPI could be a very selective detection technique by virtue of the specific optical, mass, and fragmentation properties that can be used to uniquely detect and identify molecules.

In this review we discuss fundamental spectroscopic issues of multiphoton ionization with emphasis on the ion fragmentation processes that are manifested in mass spectra. Several reviews have been published which summarize the field of MPI in general [1-13]. This article provides an update of the field to mid-1987, with particular attention on recent discoveries and applications involving ion photofragmentation. In Section II we introduce some basic concepts and experimental methods that are involved in MPI studies. In Section III we present a review of the classic studies that have led to much of our current understanding of the mechanism of MPI and photofragmentation. In Sections IV and V we discuss recent experimental developments that allow energy- and state-specific ion excitation. The subject of photodissociation spectroscopy is treated in Section IV, and the dynamics of energy absorption and dissociation are examined in Section V. Finally, in Section VI we discuss the enormously successful application of MPI and ion fragmentation spectroscopy to the problem of ultrasensitive molecular detection and chemical analysis.

II. BACKGROUND

Johnson [3, 9, 12, 14-18] and Dalby [19-21] and their coworkers were the first to extensively exploit MPI detection in spectroscopic

investigations. Their work stimulated great interest and shortly afterward several groups were reporting work on molecular MPI [22-43]. These efforts were preceded by investigations of multiphoton processes in atoms and diatomic molecules by physics groups [44-50]. The molecular work had a major impact on spectroscopic research because the method was easily implemented with common laboratory lasers, was applicable to a broad variety of polyatomic molecules, and provided a rich new source of information about highly excited molecular states. A host of new molecular electronic states were accessed, and it became evident that the method provided exceptional sensitivity.

Early in the development of MPI methods, researchers discovered that extensive molecular fragmentation could occur in association with multiphoton ionization. This provided the basis for combination MPI/mass spectrometry (MPI/MS) detection methods for obtaining high molecular selectivity and sensitivity. Initial studies suggested that selective laser-induced fragmentation was nonrandom and a high degree of control could be exerted over fragmentation processes [33-41]. It was also found that the MPI/MS spectra were highly dependent on intensity, whereas there was little control of fragment distributions by conventional ionization methods. These and other similar results created great fundamental interest in multiphoton excitation and mechanisms responsible for laser-induced fragmentation.

A. Multiphoton Excitation and Detection

A variety of multiphoton ionization processes is potentially applicable to molecular species. For resonance-enhanced MPI, it is common to represent the process as $m + n$ REMPI as indicated in Fig. 1, where m denotes the number of photons necessary to resonantly excite an intermediate neutral state and n the subsequent photons required to ionize. 2-Photon resonant, 1-photon ionization was pioneered by Johnson et al. [3, 9, 12, 14-18] for molecular applications, which may be described by $2 + 1$ REMPI. 1-Photon and 2-photon absorption spectroscopies have been well explored. Since these are a crucial component of the overall resonant MPI processes, we review them below. These techniques, by themselves, have important detection applications.

Under conventional ambient temperature conditions, the $1 + 1$ REMPI spectra closely resemble those observed in conventional 1-photon spectroscopy. The $2 + 1$ REMPI spectra frequently resemble 2-photon absorption spectra because the ionization step is effectively saturated at the power levels required to efficiently measure 2-photon processes. This is readily understandable in terms of a simplified rate equation model for the excitation processes [51-55]. A density matrix

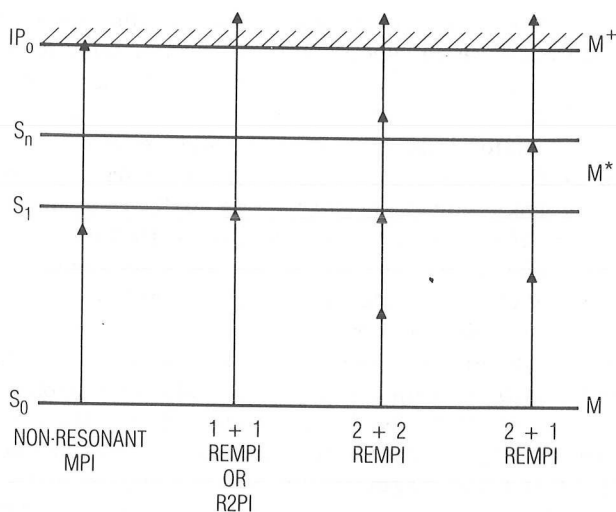


FIG. 1. Examples of various MPI excitation mechanisms.

treatment [54–63] is required for a complete description of resonant excitation with typical laser excitation sources. Unfortunately, results from the density matrix treatment are sufficiently complex to obscure qualitative behavior. Ackerhalt and Eberly showed that the density matrix results simplify to those predicted by the incoherent population rate equations, provided that the ionization cross section exceeds the cross section for the first resonant step [55]. In a similar manner, Schek and Jortner defined conditions for the validity of Block equations and kinetic master equations in describing MPI processes [53]. If the excitation rate is denoted by $R(I, 0)$, where I is the ion and 0 is the initial ground state, we can write down the approximate expression for 1 + 1 REMPI as

$$R(I, 0) \propto \left| \frac{\langle I | \hat{D} | k \rangle \langle k | \hat{D} | 0 \rangle}{(E_k - E_0 - \hbar\omega)} \right|^2$$

where $\hat{D}$ is the dipole operator, k is a resonant intermediate state of energy E_k , and ω is the incident laser frequency. Thus, the overall transition rate is proportional to the product of dipole matrix elements that describe the rates for 1-photon absorption from the ground state times the 1-photon absorption rate between the intermediate state and the ionization continuum. Therefore, the convolution of the normal

1-photon absorption spectrum with the excited state ionization spectrum should roughly approximate the 1 + 1 REMPI spectrum.

As a first approximation, we anticipate that the 1-photon ionization spectra of intermediate states should resemble step functions. For intermediate state resonant frequencies ω , where $2\hbar\omega < E_{IP}$ (where IP denotes ionization potential), there is no 2-photon signal. As the 2-photon energy exceeds the IP, the 1 + 1 REMPI spectrum becomes essentially equivalent to the 1-photon absorption spectrum. Thus, there is no appreciable increase in selectivity for the 2-photon process, although ionization detection can increase sensitivity dramatically with respect to alternative methods (e.g., direct absorption, fluorescence excitation, photoacoustic). When examined in closer scrutiny, a more refined model is required. Franck-Condon effects become important when high vibrational levels in intermediate states are excited [64-66], or if the intermediate state and the ion have substantially different geometries. For Rydberg-like intermediate states, there is little geometry change between the bound state and the ion, therefore changes in vibrational quanta are not probable [67-79]. In other situations, such as for cluster species with weak van der Waals bonds, the bonding coordinate participates strongly in the interaction, and large changes in quanta are required between the bound intermediate and final ion states [80-84]. In this case the spectrum associated with the ionizing photon(s) will strongly influence the overall ionization spectrum.

Intermediate state relaxation processes strongly influence the nature of the resonant multiphoton spectra and the efficiency of the overall ionization process. The relatively well known relaxation channels for aromatic hydrocarbon molecules are shown in Fig. 2. An excited vibronic mode has many opportunities to relax into other states. Electronic relaxation from all vibrational energies of an excited electronic state can occur to lower energy electronic states by the radiationless processes called internal conversion and intersystem crossing. These processes are also mediated by highly excited vibrational levels. If the spin changes, it is called intersystem crossing; if there is no change, it is internal conversion [85]. In the latter case the most important route is complete relaxation to the ground electronic state. A single vibronic level (SVL) can redistribute into a high density of lower energy vibrational modes of the same intermediate electronic state. This is termed intramolecular vibrational redistribution (IVR) and only occurs at higher vibrational energies where the density of combination vibrational modes is sufficiently large that adjacent states lie within the range of the anharmonic coupling strength between modes (i.e., quasi-continuum) [86-92]. All of the relaxation mechanisms mentioned result in mixed vibrational states that have poor Franck-Condon factors for transition to the ionized state.

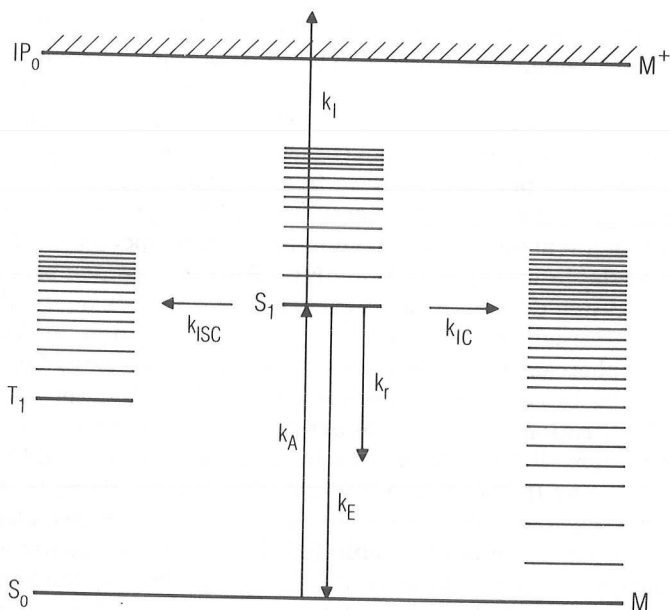


FIG. 2. Common relaxation and decay channels for hydrocarbons and other molecules. The rate constants are defined as follows: k_{IC} denotes internal conversion; k_{ISC} intersystem crossing; k_r radiative decay; k_A absorption; k_E stimulated emission; k_I ionization. Not shown is intramolecular vibrational redistribution k_{IVR} which involves relaxation from a single vibronic level into the vibrational density of states of the same electronic state.

Photodissociation is another important relaxation process. If it leads to products that cannot be ionized by the wavelengths employed, then the efficiency of the overall ionization detection process is diminished [93-95]. This is illustrated by the example in Fig. 3 in which ionization of chlorodimethyl sulfide proceeds efficiently by electron impact but not by MPI. The 2 + 1 REMPI efficiency is about 10^3 weaker than the corresponding process for unsubstituted dimethyl sulfide [93]. The dissociation channel is highly dependent on molecular structure. There are a number of common substituents that dissociate readily due to weak bonds to the hydrocarbon, such as iodine. Heavy substituents also increase interaction between spin states, such that they induce intersystem crossing from the directly excited singlet states of aromatics to the triplet states, which are not readily excited by direct optical absorption. If the bond energy is weak, the highly excited

triplet molecule can dissociate the halogen. If the bond is strong, population can build up in the triplet state, which may not be ionized by the laser source. Generally, the relaxation processes (termed radiationless processes) increase in rate with increased excitation energy. Thus it is common to observe a broadening of spectral transitions as the intermediate state energy approaches the ionization limit [96-98]. However, this is not always true for states such as Rydberg levels. They have unusually weak coupling to dissociative valence states because the Rydberg electron is essentially removed from the bonding and nonbonding electronic structure of the molecule. As an example, recently several

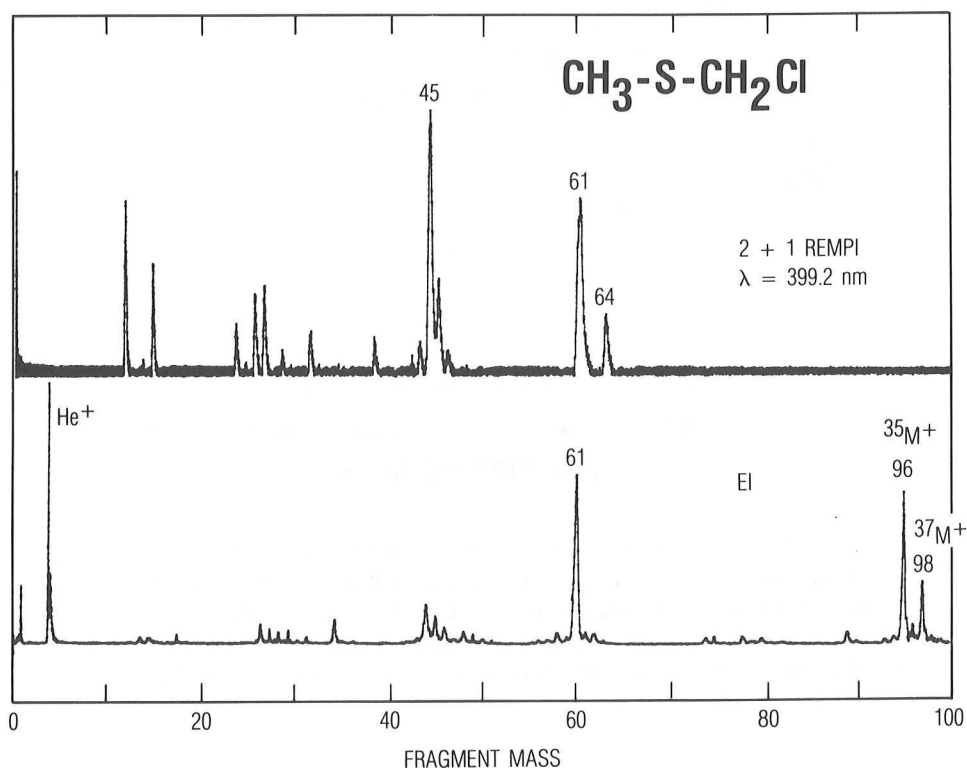


FIG. 3. Time-of-flight mass spectra of chlorodimethyl sulfide in a supersonic molecular beam; (lower trace) EI excitation resulting in parent ion and high signal-to-noise; (upper trace) 2 + 1 REMPI (399.2 nm) resulting in the lack of parent ion and low signal-to-noise due to the faster rate of chlorine dissociation versus ionization from the intermediate level [284].

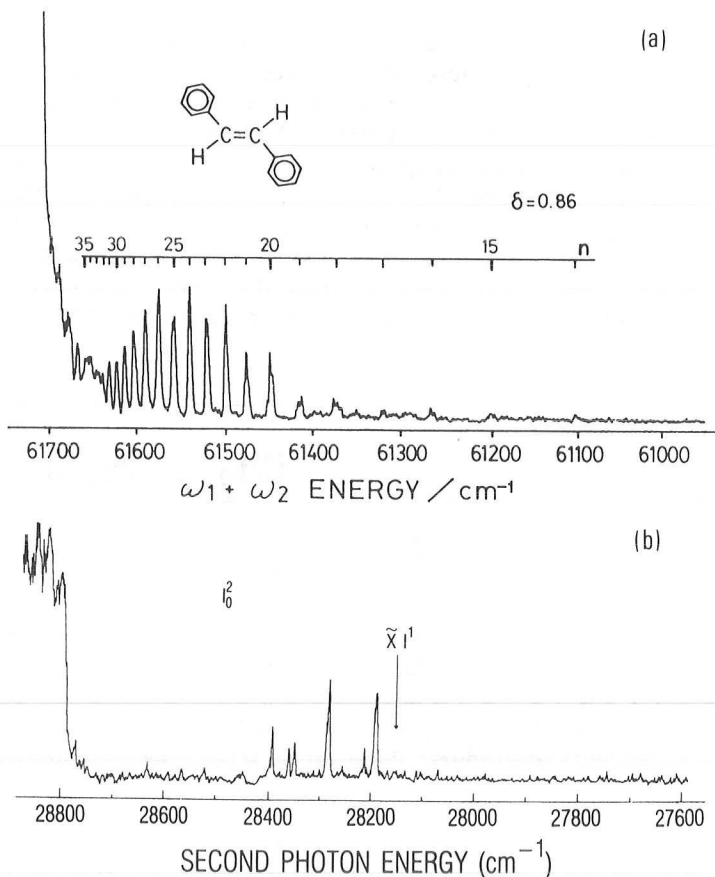


FIG. 4. (a) Two-color jet-cooled autoionization spectra: (a) trans-stilbene; where the ω_1 laser is resonant with the 0_0^0 band of the $S_1 \leftarrow S_0$ transition. The assignment of the Rydberg series is shown by the scale above [72]; (b) aniline; ω_1 laser is resonant with the I_0^2 for $S_1 \leftarrow S_0$. The arrow marks the position of the I^1 vibration in the ionic ground state [69].

laboratories have observed transitions to discrete autoionizing Rydberg states above the first ionization limit of several large molecules [67-73]. These spectra generally show sharp structure as evidenced in Fig. 4.

High intensity laser excitation can strongly influence selectivity of optical excitation processes. In 1-photon absorption, high intensity leads to optical saturation. Generally this is not a problem because

intensity can be maintained somewhat below saturation, without excessively compromising sensitivity. However, for the $1 + 1$ REMPI processes, the cross section of the ionizing process is often much less than for the resonance step. Then at the high intensities required to drive the ionizing process efficiently, the discrete resonance process can become severely power broadened [3]. Power broadening is generally not a significant problem in nonresonant multiphoton processes because the transition rates are slow relative to the short lifetimes of excited states. However, the high intensities needed to drive nonresonant multiphoton excitation can induce significant broadening via the optical Stark effect [3, 9, 99-101]. In these situations the high electric fields associated with the optical excitation alters the energy of the molecular transition. Since excitation pulses are characterized by varying intensity, the net effect is to broaden the observed transition. This leads to increases in linewidth, up to about 1 cm^{-1} for typical laser sources with focused intensities in the range of 10^8 W/cm^2 . (The effect is very well characterized for multiphoton excited atoms, where it is termed Autler-Townes splitting or the dressed atom effect [101-105].) The high intensities required for nonresonant multiphoton processes invariably cause severe fragmentation of the parent ion. This is a major problem if molecular identification is to be based on identification of the parent ion.

Supersonic beam sources have largely overcome the limitations imposed by thermal broadening of multiphoton spectra [106-108]. Molecular cooling of internal energy occurs by expanding a gas mixture, consisting of the compound of interest in a high pressure of carrier gas (typically ≥ 15 psi of a rare gas), into a vacuum chamber through a small orifice. The extent of cooling is such that essentially all molecules are relaxed to their vibrationless level and possess rotation energy corresponding to just a few degrees Kelvin. Cold molecules immensely simplify the 1-photon and resonant multiphoton spectra of large molecules. Time-of-flight mass spectrometry is readily applied to supersonic beam systems, thus providing a combination of extremely high optical resolution with mass spectra of unit mass resolution or better. The cooling improves mass resolution somewhat; however, this is normally not of significant benefit because adequate resolution is attainable at ambient temperature. Figure 5 provides a comparison of spectra recorded for a sample at ambient temperature versus the same molecule cooled in a supersonic beam.

Cooling not only facilitates preparation of cold, isolated intermediate quantum states, it also allows production of cold ions for spectroscopic purposes [74-79, 109-111]. This requires some attention to ionization conditions. The intermediate state must not be subject to

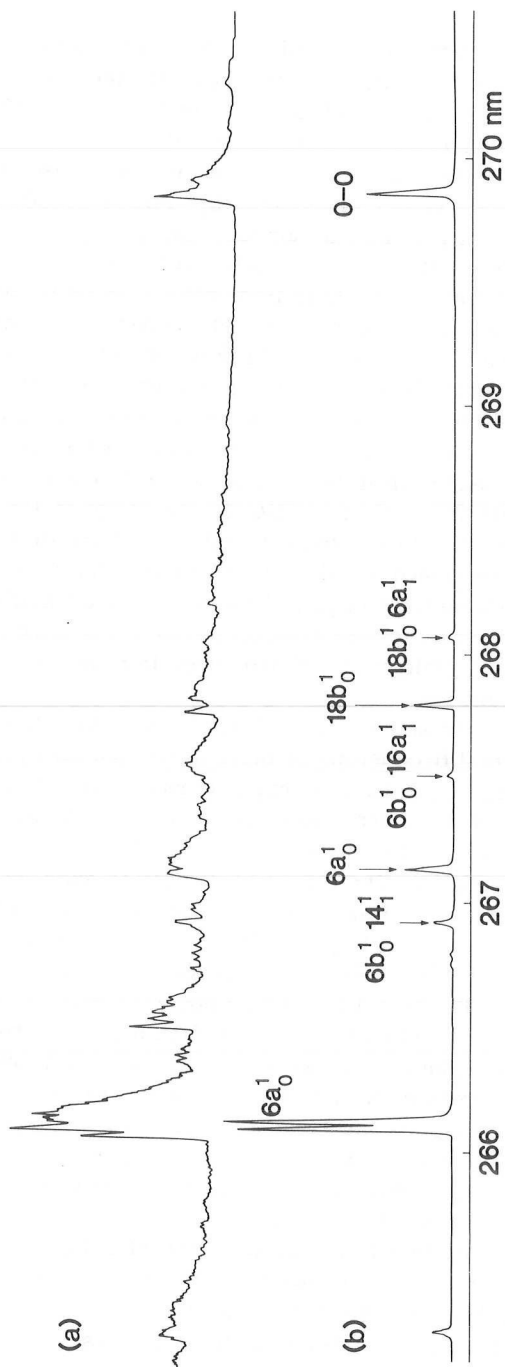


FIG. 5. Parent ion yield spectra of chlorobenzene: (a) room temperature and (b) supersonic jet-cooled [242].

collisional or IVR processes, otherwise a hot distribution of states will result in ionization to a distribution of vibrational states in the ion. Even if SVL conditions are maintained in the intermediate state, it is still necessary to ionize in a way that avoids excitation of vibrational energy in the ion. This can be accomplished by using a low energy ionizing beam, such that only vibrationally unexcited ions may be produced. It is common for the first Franck-Condon active vibration of the ion to be 500 cm^{-1} or more above the lowest ionization threshold. Therefore there is a substantial range of photon energies that will avoid vibrational excitation in the ion. In this case any excess energy above the lowest ionization limit will be imparted to photoelectron kinetic energy. In cases where there is essentially no change in molecular geometry between the intermediate state and the ion, the Franck-Condon factors are diagonal and there is little probability of exciting vibrational levels other than that present in the intermediate state [74-79]. For some molecules a broad range of possibilities exists, so that excitation conditions must be chosen carefully.

B. Instrumental Methods

A wide variety of experimental techniques has evolved out of the basic arrangement of laser excitation and ion mass detection. New methods are designed to emphasize the specific performance objectives of an experiment (e.g., high optical or mass resolution, time-resolved measurements, state- or energy-selected excitation). The unique capabilities for each system will be discussed in context with specific molecular systems in the coming sections. However, it is instructive to generalize and classify the major instrumental approaches from which the specialized techniques derive.

1. Supersonic Molecular Beam, Mass Spectroscopy

The expansion of a high pressure gas into a vacuum through an aperture is termed a supersonic expansion and can lead to substantial cooling of molecular internal energy. The method is well established and extensively reviewed [106-108]. The very narrow distribution of initial rovibrational states in conjunction with laser excitation has many valuable benefits. From a detection and sensitivity standpoint, one can achieve nearly complete molecular excitation using a single wavelength of light. For selective excitation it is possible to populate single vibronic levels in excited electronic states and to form rovibrationally cold ions.

Most molecular beam photoionization experiments employ some form of mass-resolved detection usually using a quadrupole or time-of-

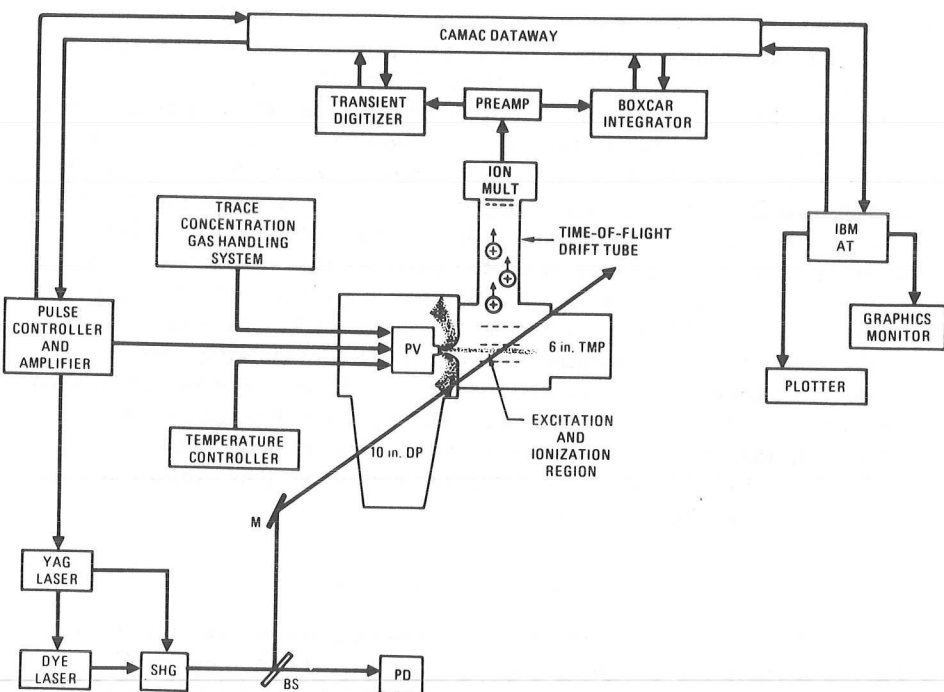


FIG. 6. Schematic of a supersonic molecular beam TOF mass spectrometer apparatus and associated components; where SHG = single harmonic generator, BS = beamsplitter, PD = photodiode, M = mirror, DP = diffusion pump, TMP = turbomolecular pump, PV = pulsed valve [93].

flight (TOF) mass spectrometer. A representative system is the two-chamber TOF system depicted in Fig. 6. The two chambers are differentially pumped; the first chamber containing the molecular beam source and the second chamber the excitation and detection components. A skimmer, situated at the interface of the two chambers, allows a narrow collimated portion of the supersonic jet to enter the second chamber. This arrangement directs the majority of the gas pumping load to the first (source) chamber, allowing the second (detection) chamber to operate at higher vacuum. The standard TOF mass spectrometer employs the Wiley and McLaren three grid space focusing ion source [112]. Ionization is typically by MPI, although electron impact (EI) ionization sources have recently been introduced to pulsed molecular beam TOF spectrometers [113, 114]. The ions are accelerated to constant kinetic

energy in the ion source and then enter a field-free drift region where they spread out in time according to mass. A fast ion detector then records the ion intensities as a function of drift time.

Photoionization mass spectrometry has been carried out in the bulk gas phase; however, the benefits for polyatomic molecules are greatly enhanced using supersonic expansion. Johnson [18], Zare [28], and Letokhov [29, 30] and their coworkers are credited with introducing supersonic expansion to MPI studies. The latter work made use of two lasers in the two-photon ionization mass spectrometric detection [29, 30]. Smalley popularized the use of TOF mass spectrometry for supersonic molecular beam MPI studies [42, 43, 115, 116]. These important advances quickly spurred a proliferation of multiphoton studies in areas relating to one-photon forbidden electronic state spectroscopy and ion photo-fragmentation dynamics. The field will be the subject of later sections.

2. Ion Cyclotron Resonance Spectrometry

Ion cyclotron resonance (ICR) spectrometers have the capability of trapping ions for long periods of time (>1 s) and have therefore proven to be an important tool for the study of metastable ion decay [117-121]. In the conventional mode of operation, ions are formed by EI excitation in a gas of about 10^{-7} to 10^{-8} torr; however, ionization by MPI can also be employed. The ions that are formed and trapped can be irradiated for a desired length of time, and the extent of parent ion disappearance (by photodissociation) detected at subsequent times later. In this manner the wavelength-resolved rates of photodissociation can be measured, thus providing kinetic and spectroscopic information on ions. Mass analysis of the residual ion constituents in the trap volume is obtained in the standard mode using an ejection pulse and a magnetic sector mass analyzer [117]. More recently, a Fourier transform (FT) technique has been introduced for sampling all the masses simultaneously inside the ion trap [118, 119]. A representative FTICR system is illustrated in Fig. 7.

ICR spectrometers can be configured to allow ejection of specific ion masses of interest, thus allowing a variety of selective experiments for elucidating photochemical and fragmentation mechanisms as well as ion-molecule reactions. The axial symmetry of the ICR ion trap cell can also be exploited to measure kinetic energy releases and angular dependences of photodissociation processes [120, 121]. This is possible as a result of the weak electrostatic potential that retains ions along the symmetric axis. The loss of ions along this direction is dependent on the fragment kinetic energy which can be measured as a function of the angle between the laser polarization axis and the ion cell axis.

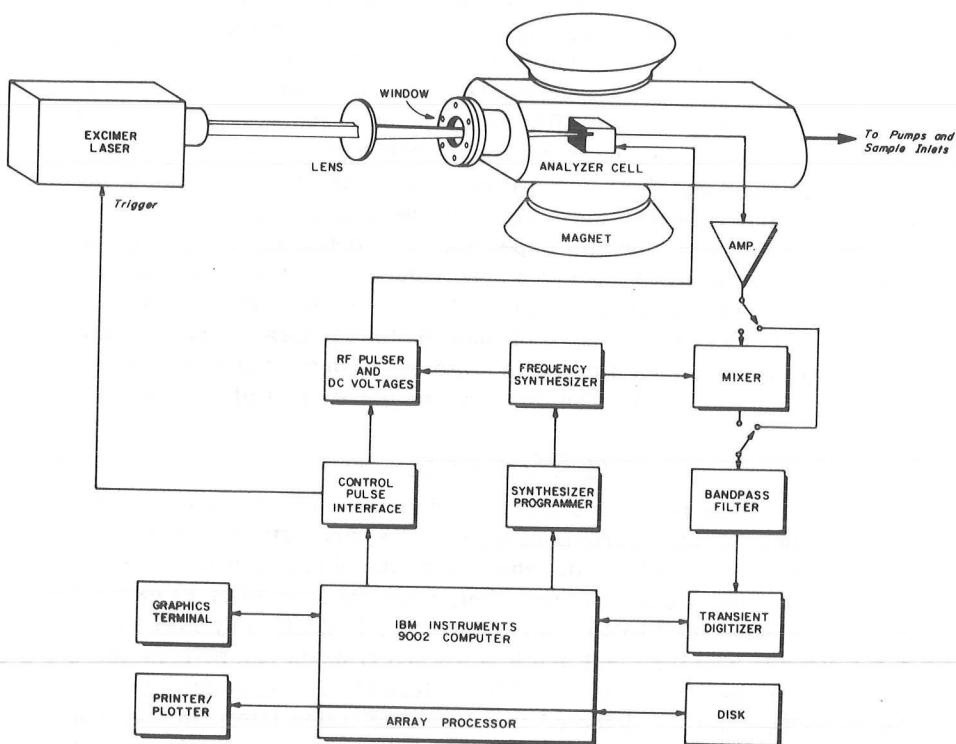


FIG. 7. Block diagram of a Fourier transform ICR spectrometer [267].

3. Fast Ion Beam Spectroscopy

In the typical ion beam experiment, a beam of mass-selected ions is accelerated and directed through a laser interaction region and the resulting fragment ions are then mass-analyzed. Though simple in concept, the collection of electrostatic focusing elements, energy and mass-analyzers, and optical components contributes to a complex and sophisticated apparatus. The complexity, fortunately, is matched by a versatility permitting exceptionally thorough and detailed studies of ion photofragmentation processes. An excellent example of this technology is the apparatus developed by Moseley and colleagues [122] which is diagrammed in Fig. 8. Ions are extracted from an ion source, accelerated to a few thousand volts, and the species of interest mass-selected by a mass filter. The parent ions are then collimated and steered through

an excitation region where they overlap collinearly with a laser beam. The photofragments are then steered to a mass and energy analyzer.

Although ion beam experiments do not generally use MPI as an ionization source, the technique bears directly on the subjects of ion spectroscopy and ion photodissociation. The versatility of the technique is exemplified by the variety of schemes utilized to probe specific details of photofragmentation [122-124]. The collinear (or coaxial) arrangement is used for studying low kinetic energy release processes to a resolution of about 10 meV in the center of mass. A perpendicular (or crossed) configuration is used to measure the angular distribution of the photofragments.

Fast ion beam spectroscopy benefits enormously from kinematic compression, whereby the Doppler velocity distribution becomes an insignificant component of the ion beam velocity at kilovolt energies. This nearly Doppler-free condition dramatically improves optical

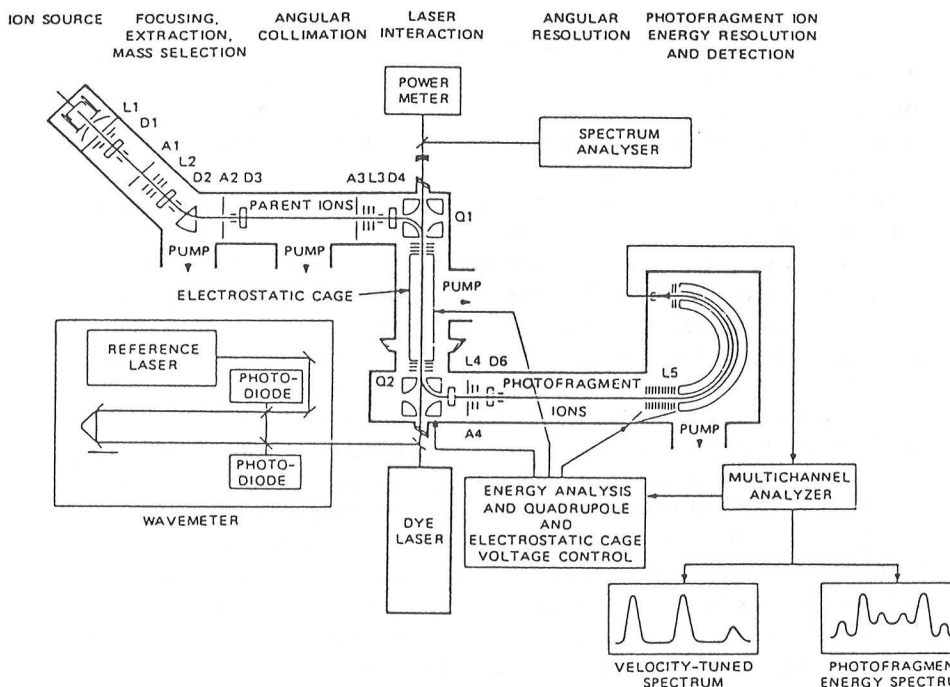


FIG. 8. Schematic of a laser-ion coaxial beams photofragment spectrometer. Experiments using a crossed laser-ion configuration are also possible [122].

resolution to below 100 MHz. Furthermore, by varying the ion beam velocity, it becomes possible to Doppler-tune an ion transition using a fixed-wavelength laser. An analogous effect occurs upon decelerating the ion beam (i.e., kinematic expansion) that considerably enhances the resolution in measuring kinetic energy release in the fast ion beam [125].

4. Photoelectron Spectroscopy

Photoelectron spectroscopy [126, 127] is based on the measurement of the kinetic energy of the electron E_{el} that is detached from a neutral molecule in the process of ionization. In the conventional method, a single wavelength VUV source is used as the ionization source. Ion energies E_{ion} can be determined by measuring the energy of the photoelectron by the relation

$$E_{ion} = h\nu - E_{IP} - E_{el} + \langle E_{th} \rangle$$

where E_{IP} is an ionization threshold and $\langle E_{th} \rangle$ is the thermal energy distribution of the precursor neutral molecule. The accessible states that can be reached by single-photon ionization are determined by the electronic selection rules and the Franck-Condon vibrational factors from the ground state of the neutral molecule. Photoelectron spectroscopy is one of the most productive means for gaining spectroscopic information on the electronic states of ions.

Recently, the methods of multiphoton ionization and supersonic expansion have been introduced to photoelectron spectroscopy, greatly expanding its capability [126, 128-132]. The use of MPI over single-photon ionization has greatly increased the number of accessible ion states by allowing ionization from a variety of resonance intermediate states of the neutral molecules. The latter technique provides molecular cooling which has improved the energy resolution by reducing the $\langle E_{th} \rangle$ distribution. These advances have played a crucial role in understanding the details of multiphoton ion dissociation by providing vibrational and electronic spectroscopic information of the ion. Photoelectron spectroscopy in conjunction with supersonic molecular beam MPI is also proving especially valuable in recent efforts to prepare state-selected ions [74-79, 133-136]. By measuring the photoelectron energies, it is possible to determine the distribution of vibrational excitation in the ion for a particular MPI excitation scheme. By taking advantage of favorable Franck-Condon factors it is possible to populate a single vibration of the ions, thereby permitting a variety of new possibilities for studying the dynamics of ion processes in detail.

III. MULTIPHOTON IONIZATION-DISSOCIATION

A. Mechanisms and Models

The early reports of mass fragmentation in conjunction with multiphoton ionization experiments generated enormous interest. Bernstein and coworkers reported MPI mass spectra with extensive fragmentation [6, 8, 33-36] during the time when there was great interest in bond selective laser chemistry. In an attempt to explain extensive MPI-dissociation (MPID), Bernstein and coworkers proposed that highly efficient multiphoton excitation occurred within the ionization continuum via resonances involving autoionizing states [35]. This suggested the possibility of controlling fragmentation pathways and the course of ion chemistry by choosing autoionizing states through the variation of wavelength. Figure 9(a) represents this early model, which Lubman, Naaman, and Zare termed the autoionization tree mechanism [40]. The

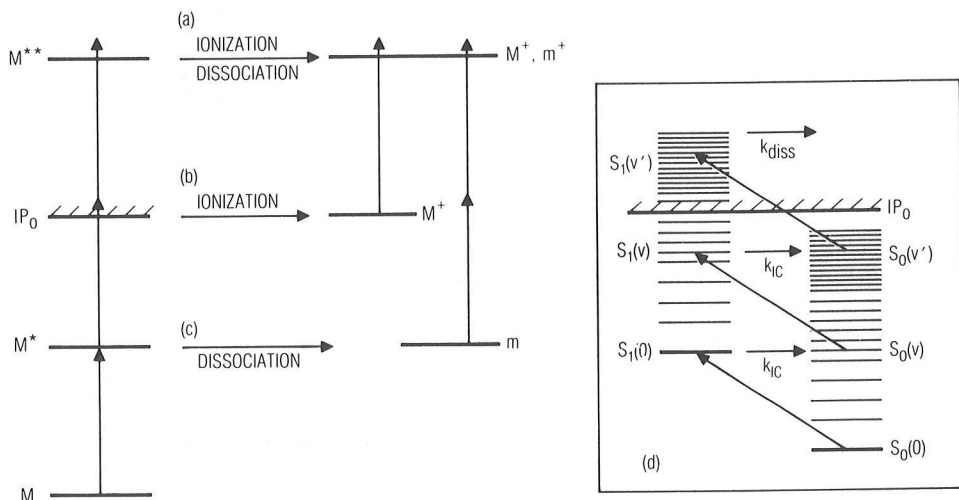


FIG. 9. Various models for MPID. (a) MPI by absorption of photons by neutral excited states above the IP (i.e., autoionizing ladder climbing); (b) multiphoton ionization occurring at the first level above the ionization threshold followed by parent ion absorption and dissociation (i.e., ladder switching); (c) intermediate neutral excited dissociation, followed by fragment ionization; and (d) rapid radiationless decay in the neutral molecule creating vibrationally hot molecules without sufficient electronic excitation to cause ionization. The diagonal arrows represent electronic transitions.

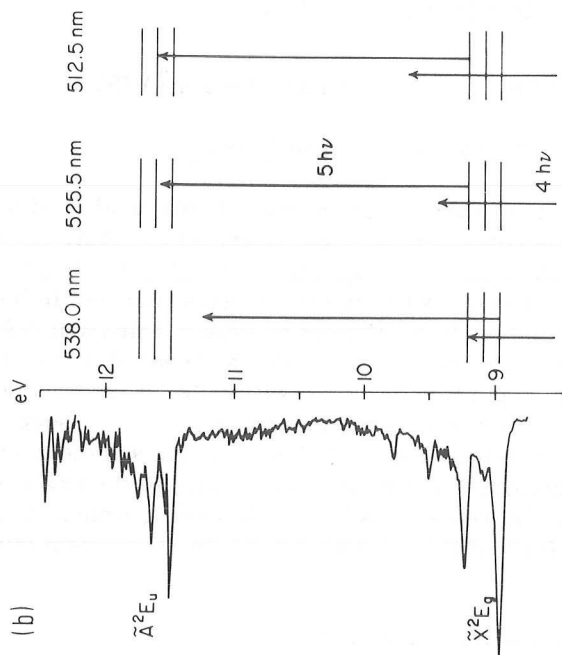
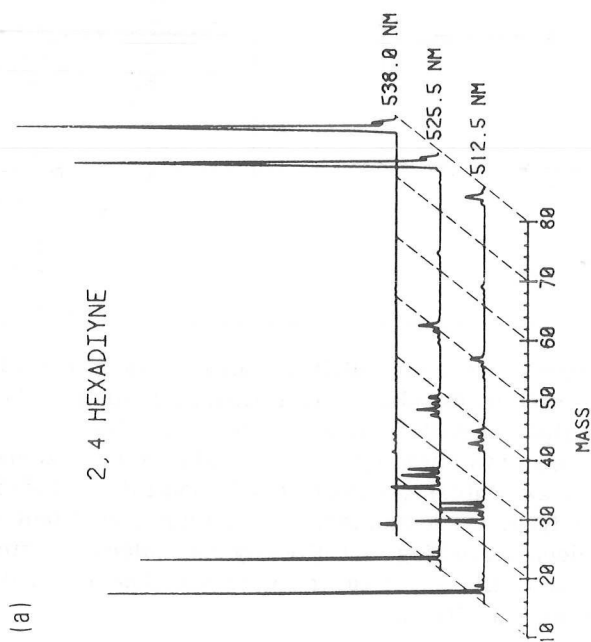


FIG. 10. (a) REMPI mass spectra of 2,4-hexadiyne. Laser pulse energy was $360 \mu\text{J}$. (b) Threshold photoelectron spectrum and four- and five-photon energy levels for the wavelengths in (a) [138].

model has also been referred to as ladder climbing in the neutral parent molecule. In the earliest work, Zandee and Bernstein reported extremely interesting wavelength dependence studies of fragment abundance for benzene MPI [34, 35]. The spectra, recorded by monitoring each mass fragment as a function of ionizing and fragmenting wavelength, were essentially identical for each fragment. Similar results were obtained for other molecules by several research groups [1-6]. It was suggested that the result implied that each fragment was produced directly from the same precursor, presumably the highly excited autoionizing neutral or the parent ion.

In 1980 Boesl, Neusser, and Schlag performed a classic experiment, proving that fragmentation processes (at least for benzene) are independent of excitation within the autoionization continuum of the neutral molecule [137]. Ionization was achieved using a low intensity UV beam, and fragmentation was induced by a high intensity non-ionizing red beam with variable time delay. They discovered that the fragment distribution was independent of the time delay of the fragmenting beam. Since the intermediate states, and states of the ionization continuum of the neutral benzene molecule, are known to have moderately short lifetimes, the experiment implied that the ion, rather than the neutral, is fragmented by the red beam. This completely ruled out the possibility that the hypothesized strong transitions within the "autoionizing tree" could control fragmentation patterns and lead to nonstatistical distributions. Instead, the experiment indicated that if selectivity occurs, it is dependent on processes in ionic species, according to the scheme in Fig. 9(b).

Prompt parent ion formation was soon confirmed by Reilly and co-workers using photoelectron spectroscopy [128]. They showed that the MPI of benzene yielded only low energy photoelectrons, thus indicating that ionization occurs at the lowest energy possible above the ionization potential IP. In fact, kinetic energy analysis of the MPI photoelectron has proved to be a method of vital importance, not only in establishing the energy of the ionization step, but the distribution of vibrational energy in the parent ion [74-79, 128-136] (cf. Section IV-C). An excellent example of the application of MPI mass and photoelectron spectroscopy to the problem of ionization/fragmentation was provided by Carney and Baer [138] shortly after the above-mentioned work of Schlag and co-workers [137]. They observed an abrupt change in the MPI fragmentation pattern of 2,4-hexadiyne as a function of wavelength as shown in Fig. 10(a). By relating their result to the photoelectron spectrum of 2,4-hexadiyne [139], they proved that the abrupt onset of fragmentation occurred at the absorption wavelength of the ground state ion (Fig. 10b).

Shortly after the work of Schlag et al. [137], other groups reported studies involving two-color excitation with variable time delay. Bernstein and coworkers applied the technique to triethylenediamine and reached the same conclusion as in the benzene MPID results, namely that fragmentation proceeds via the ionic pathway [140]. El-Sayed and coworkers devised a novel method for examining the importance of neutral dissociation by using the repeller field of a TOF mass spectrometer to separate the neutral and ionic species following an initial UV ionizing pulse [141]. By varying the magnitude of the repeller voltage, they recorded the fragmentation pattern of benzene- d_6 as a function of ion residence time in the focal volume of a delayed visible pulse. At sufficiently high voltages, no overlap of ions with the delayed visible pulse occurs, thus probing only for neutral fragmentation. Their conclusions also supported an ionic rather than an autoionizing neutral dissociation mechanism. These results also indicate that the neutral fragments did not further ionize under these conditions.

A less common and often overlooked mechanism for ion fragmentation involves ladder switching that occurs in neutrals at energies below the IP. This is described by the diagram in Fig. 2 where a rapid rate of decay from a neutral excited state (e.g., radiationless decay, dissociation, intersystem crossing, etc.) competes with the direct laser ionizing step. For instance, in the case of rapid intersystem crossing, resonant absorption of subsequent photons by the triplet can induce fragmentation, followed by photoionization of the fragment. This situation was actually first identified by Letokhov and coworkers [10, 28] for benzophenone. In that case an interesting kinetic dependence of branching into two different species was observed. It was attributed to the process where ionization and fragmentation occur directly from a higher triplet manifold of the molecule. The neutral fragmentation ionization route is loosely represented in Fig. 9(c). Another possibility exists in which an intermediate neutral electronic state undergoes radiationless decay to highly excited vibrational levels of the ground (or lower lying) electronic state. This behavior, which is illustrated in Fig. 9(d), can prevent electronic excitation from ever exceeding the IP even though the total molecular energy may be sufficient. This mechanism has been invoked to explain evidence supporting neutral fragmentation of highly excited CH_2CO molecules in competition with ionization [142, 143]. Reilly and coworkers, using photoelectron spectroscopy, demonstrated that the $\text{S}_2(^1\text{B}_{1u})$ state of benzene undergoes very rapid (< 20 ps) radiationless decay that prevents it from directly ionizing efficiently [144]. They detected excited state carbon atoms, as have other groups for several polyatomic molecules [143-146]; however, the mechanism of formation from benzene has not been unraveled.

Other evidence has emerged in which neutral dissociation followed by ionization competes with direct ionization and dissociation [93-95]; however, the latter mechanism usually dominates.

Following the work of Bernstein, Schlag, El-Sayed, and others [22-41, 137-141], two theoretical groups proposed theories to describe the MPI/MS experiments. Silberstein and Levine were the first group to propose a statistical model for MPID [147, 148]. In this model the molecule is ionized and the parent ion subsequently absorbs photons. When the ion accumulates energy exceeding the appearance potential for the production of fragments, the parent ion decomposes into all energetically accessible fragments, with a distribution among species determined by the statistical weight of the products and their heats of formation. This description, which is termed the maximum entropy model, did not include any photon interactions in the neutral molecule, above the ionization limit, and thus is also described as the ion ladder excitation route (Fig. 11). The statistical model is similar to the popular RRKM-based quasi-equilibrium theories (QET) [149-151] for unimolecular decomposition. The main difference is that the QET calculate individual rate constants from which branching ratios are derived. In all cases, state-to-state kinetics are assumed to be unimportant in governing product distributions. The justification is that when vibrational excitation becomes sufficient to cause dissociation, the vibrational modes are so highly mixed through anharmonic interactions that their

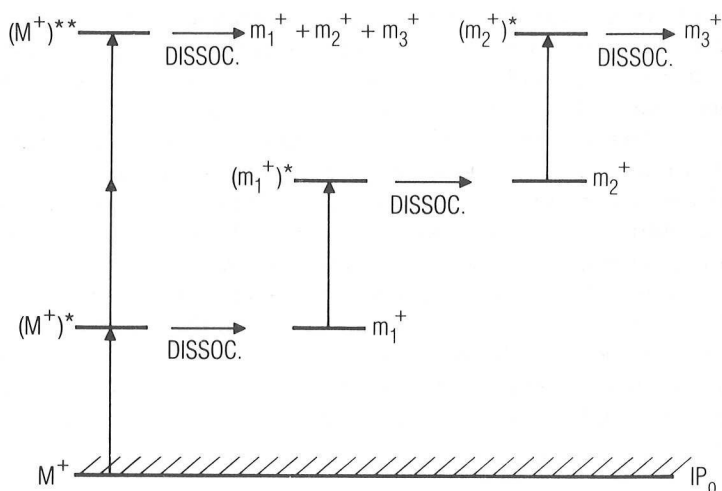


FIG. 11. Ladder climbing versus ladder switching models for parent ion fragmentation.

unique quantum identity is lost and each state behaves as a statistical mixture of quantum states. Thus, only statistics and energetics play a role in product distributions.

The predictive ability of the model requires extensive information on heats of formation and product state entropy. Unfortunately, these are not readily available for many of the fragment ion species. Instead, there is limited data on appearance potentials, which are the energies at which substantial production of the fragment species occurs in mass spectra. Moreover, the ionization and fragmentation in most of these studies were promoted by means such as electron-impact. In favorable cases the appearance potentials are approximately equal to the heats of formation, because the ions dissociate rapidly when they are excited above the dissociation limit. In spite of these limitations, Lichtin, Bernstein, and Newton were able to establish general accord with the Silberstein and Levine model for a variety of molecules [152]. The experimental work showed that the total absorbed energy and not the wavelength is the determining factor for observed fragmentation patterns.

Rebentrost and Ben-Shaul proposed another statistical model which also yielded acceptable fragment distributions [153, 154]. Their model also assumed that no photon interactions occur within the ionization continuum of the neutral molecule. However, they depart from the simple model of Silberman and Levine by proposing that fragmentation can occur sequentially with much of it occurring by multiphoton absorption of the individual fragment species. This is now termed the sequential model for multiphoton fragmentation processes. In its simplest form it assumes that when the excitation energy of the parent ion exceeds the lowest dissociation threshold, it fragments into the next smallest species (Fig. 11). This then absorbs photons, and further fragments. The distribution is then determined primarily by how long the excitation source is able to fragment smaller and smaller species, which depends strongly on laser intensity. This is to be compared with the Silberstein and Levine model in which excitation is presumed to occur primarily in the parent ion and thus to involve upward excitation of this species. The sequential model of Rebentrost and Ben-Shaul clearly requires a large amount of spectral and thermodynamic information for the possible fragment species. Even so, by making reasonable assumptions, these investigators were able to apply it to MPI/MS fragmentation patterns of benzene, and predict carbon fragment distributions with success.

B. Structure-Sensitivity

Although the ionic fragmentation mechanism proved to be rather general [128-131, 137-141], the early studies did not differentiate between a ladder-climbing mechanism and a ladder-switching mechanism in the parent ion (Fig. 11). (This is not to be confused with ladder switching from the neutral to the ion above the ionization threshold, as illustrated in Fig. 9.) In the former case, fragmentation is expected to proceed primarily in the parent ion. The ion is assumed to continue absorbing photons until it reaches an energy level where the fragmentation rate exceeds the excitation rate. The fragmentation pattern would then be determined by the energy of this state, and a number of fragment species could be formed directly from this state. In the latter case a sequential fragmentation process is expected to occur. It is assumed that once enough energy is absorbed by the parent ion to fragment into the lowest energy channel, the ion would dissociate. Subsequent fragment species would absorb photons, and fragment into smaller species.

The original models of Silberstein and Levine [147, 148] and of Rebentrost and Ben-Shaul [153, 154] were rather specific in that they considered only the limiting cases of ladder climbing and ladder switching, respectively. In fact, one can imagine intermediate situations. For instance, whether a vertical (climbing) or horizontal (switching) step occurs depends on the competition between the rates of excitation versus dissociation from a particular excited state. Furthermore, owing to the discrete nature of photon energy, an absorbed photon by a parent ion may place it above the appearance potential for several fragment ions; these ions then form from a common state by a competitive branching mechanism.

An important prediction of the early statistical models [147] was that structural isomers of a molecule should have identical fragmentation patterns, provided the initial distribution of energy in the excited ion species is identical. This was known to be true for EI mass spectra. It was thought that there existed some combination of wavelengths and intensities for which different isomers would have the same mass spectra. It is worth remarking that the question depends on the rate of isomerization of the parent isomer ions versus the rate of dissociation into fragments. The question in turn depends on how these rates differ for EI versus MPID excitation. Lubman, Naaman, and Zare originally presented evidence based on the MPID spectra of naphthalene and azulene which were at odds with the contention that the isomer mass spectra should be similar [40]. Lubman shortly thereafter showed that the naphthalene and azulene MPID mass spectra could indeed be made to be similar, but only for very different excitation conditions [155].

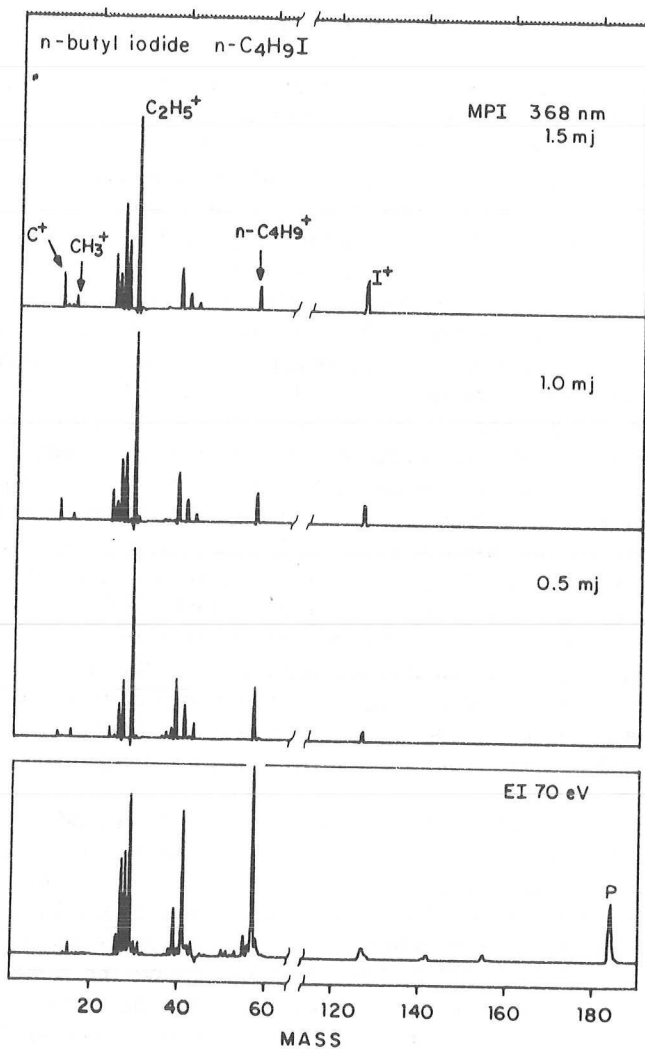


FIG. 12. REMPI dissociation mass spectra for n-butyl iodide and t-butyl iodide as a function of laser pulse energy. Spectra are compared to EI (70 eV) mass spectra [158].

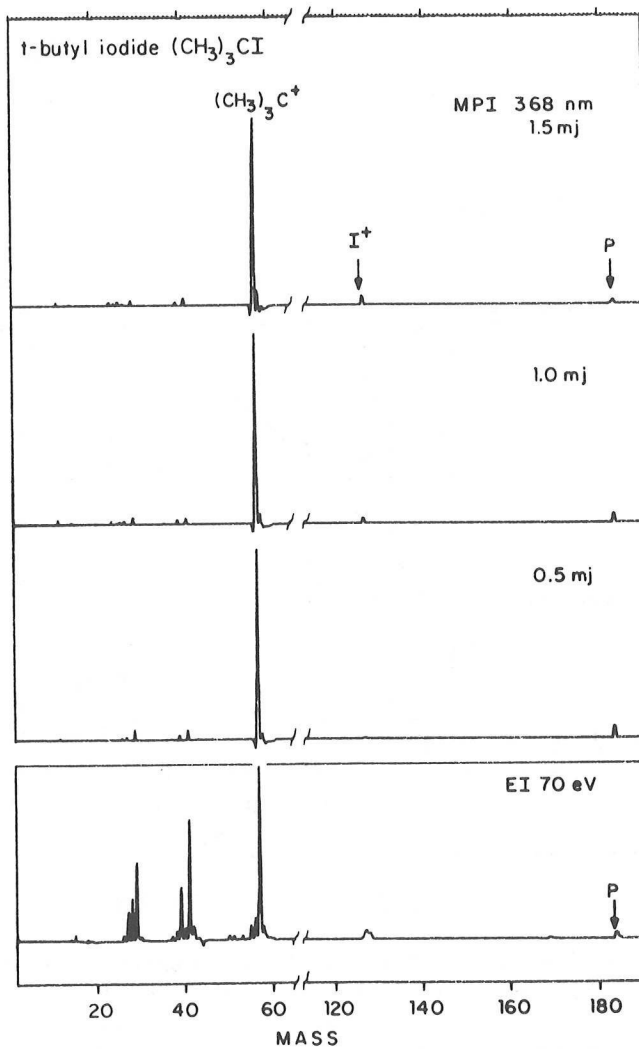


FIG. 12

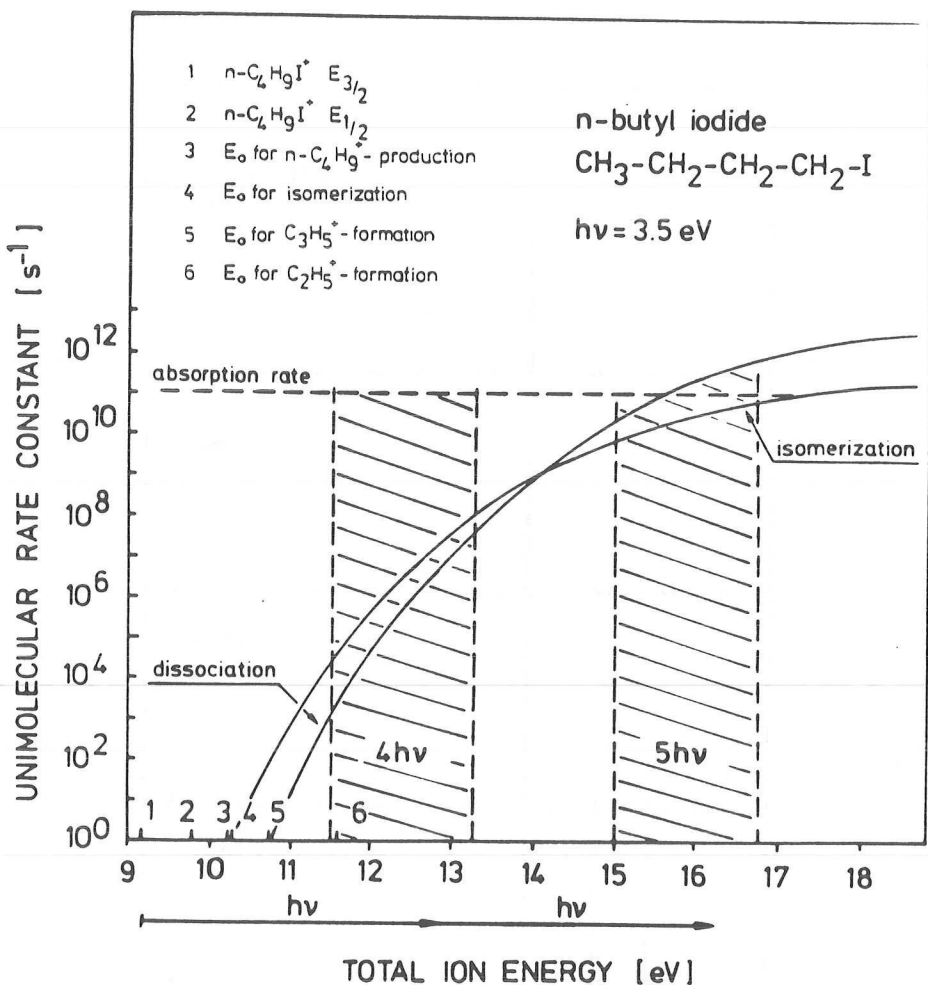


FIG. 13. Schematic $k(E)$ curves for the competing isomerization and dissociation rates of n-butyl iodide. Estimated threshold values for various dissociation and isomerization processes are given on the abscissa; the approximate absorption rate for a light intensity of $5 \times 10^9 \text{ W/cm}^2$ is marked by the dashed horizontal line. Note the "path crossover" from isomerization to dissociation between the four- and five-photon level [160].

Hudgens and coworkers, likewise, observed similar fragmentation patterns by EI and MPID for *cis*- and *trans*-dichloroethylene [156]. Finally, Wessel and coworkers observed complex fragment intensity dependences for 1-methylnaphthalene and 2-methylnaphthalene that were nonetheless similar for the two isomers [157]. A kinetic model was developed in the latter case that explained the fragmentation behavior on the basis of a sequential fragmentation mechanism involving the methylnaphthalene analogues of tropylium and benzyl ions.

A systematic examination of the role of structure on ion fragmentation patterns was provided by Parker and Bernstein on the MPID patterns of the alkyl iodides [158]. They noted that fragmentation patterns were distinctly sensitive to structure to the extent that isomeric structures were distinguishable on the basis of their MPID mass spectra. These results were in sharp contrast to electron-impact (EI) results in which different isomers were observed to have similar mass fragmentation patterns (i.e., no structure sensitivity) [158]. Schlag and coworkers extended the work on the homologous and isomeric series and alkyl cations [159, 160]. They noted that EI ionization mass spectra for a series of alkyl compounds tend to exhibit similar fragmentation patterns in the low mass part of the spectrum [159]. This represents a propensity for ions (including fragments) in the same mass range to produce similar fragmentation (or breakdown) patterns even if produced from different parents. These investigators established that this pattern of so-called "nested" mass spectra is not reproduced in MPID excitation. Instead, the fragmentation pattern depends strongly on the absorption characteristics for each fragment ion. Consequently, multiphoton fragmentation cannot be modeled by assuming a single mean energy $\langle E \rangle$ as in the original Silberstein-Levine model, but must instead assume a set of independent values $\langle E \rangle_i$ for each fragment ion species m_i^+ produced from the parent ion M^+ [159]. This work, along with the earlier work of Parker and Bernstein, motivated Silberstein and Levine to refine their theory to allow for the possibility of absorption by intermediate ions [161]. The relationship between energy and entropy was still maintained as the governing condition for predicting fragmentation; however, this feature was now applied to more than one ionic ladder. Better agreement with experiment was obtained by this modification, although the authors conclude that under realistic conditions each ion has but one or two major dissociation pathways from which all fragment ions can be assigned.

The work of Bernstein and Schlag and their coworkers on alkyl iodides [158-160] differed from the other studies mentioned [40, 155-157] in that structural isomers were observed to give distinctly fragmentation patterns in the MPID mass spectra, although the EI mass

spectra were very similar. This is illustrated for an isomeric pair, *n*-butyl iodide and *t*-butyl iodide, in Fig. 12. The clear implication is that isomerization occurs before dissociation for EI, but not for MPID. Schlag offered a sensible explanation for this conclusion [160] with the aid of the schematic in Fig. 13. The observed difference between EI and MPID mass spectra for the alkyl cations can be partly attributed to the discrete nature of photon excitation. For the wavelengths employed ($h\nu = 3.5$ eV), ionization of butyl iodide occurs at the 4-photon level (i.e., $4h\nu$). At these low ion energies, the rate of isomerization and dissociation are very slow, although the former process exceeds the latter (Fig. 13). Consequently, in the absence of further ion excitation, as in the case of EI, structural isomers would scramble and equilibrate before dissociating, thereby giving similar fragmentation patterns. In the case of MPID, the absorption rate exceeds the isomerization and dissociation rate at the $4h\nu$ level, hence dissociation occurs at the level or higher. Schlag and coworkers argue that at these higher energies, the rates of isomerization and dissociation have crossed over such that the latter now exceeds the former [160]. In effect, the MPID process never allows the parent ions a chance to isomerize, thus accounting for the structural sensitivity in the mass spectra.

It is probably correct to say that the mechanism of ion photofragmentation cannot be described by broad generalities. Fragmentation behavior depends strongly on the interplay of kinetics (e.g., ion predissociation, metastable decay), energy redistribution (e.g., internal conversion, vibrational redistribution), Franck-Condon effects, and ion absorption rates. These processes can vary widely in importance from one molecule to another. To unravel the details of multiphoton ion absorption and dissociation requires more specific and direct studies on the spectroscopy of parent and fragment ions. Likewise, the rates of dissociation and energy redistribution for state-specific or at least energy-specific excitation are required. In the following two sections we review recent advances leading to direct measurements of molecular ion spectroscopy and dynamics.

IV. PHOTODISSOCIATION SPECTROSCOPY

It is now well established that parent ion absorption plays a dominant role in fragmentation; however, less clear is the role of energy randomization interactions such as radiationless decay of excited ion states on subsequent photon absorption and dissociation. Detailed understanding of these ion processes, however, is often hampered by the lack of basic spectroscopic information on the ion of interest. Until the

1970s, data for electronic state spectroscopy of polyatomic atoms (i.e., larger than triatomics) was virtually nonexistent [162, 163]. The situation has only improved moderately since then. Polyatomic ion spectroscopy is made difficult by several experimental realities: (1) adequate densities are not easily achieved; (2) the ions are often vibrationally and rotationally hot, thereby accounting for spectral congestion; (3) emission detection is often precluded by rapid radiationless decay or dissociation. In fact, it is the last condition that underscores the importance of photodissociation as a spectroscopic tool. First we review other common methods in ion spectroscopy. Our primary emphasis, from the viewpoint of ion photofragmentation is on electronic spectroscopy of polyatomic (larger than triatomic) molecules. However, the lack of a large body of work in this field has prompted us to include some examples involving triatomic molecules. The more established field of IR spectroscopy of ions is not discussed at any length here; we instead refer the reader to recent review articles [164, 165].

A. Gas Phase Ion Spectroscopy—Overview

Fluorescence detection is one of the most common methods used for ion spectroscopy. Resolved emission in discharge sources provides structural information via the measurement of ground electronic state vibrational frequencies. Excited electronic state information is made available using photoelectron spectroscopy, which is usually capable of resolving some vibrational structure [126, 127]. Laser-induced fluorescence (LIF) is likewise gaining favor as a method for recording excited electronic state ion spectra [166]. Recently, Saykally and coworkers introduced an absorption technique in which the ions in a discharge source were driven to undergo velocity modulation by alternating the polarity at the discharge electrodes [164]. The resulting Doppler modulation gives rise to a modulated absorption that is detected using a phase-sensitive lock-in amplifier. The modulation provides a high level of sensitivity and the phase determines the sign of the ion charge. One of the most appealing features of velocity modulation ion spectroscopy is that the neutral species, which are in much higher abundance than the ions, are unaffected by the oscillating electric field and therefore do not interfere with the detected ion absorptions. Although the majority of work using this method has centered on IR spectroscopy, electronic state spectroscopy has been reported [164].

Since ionization is a highly energetic process, the methods available for producing adequate concentrations of ions tend to excite the internal degrees of freedom considerably. Two common methods used besides MPI are electron impact (EI) ionization and Penning ionization.

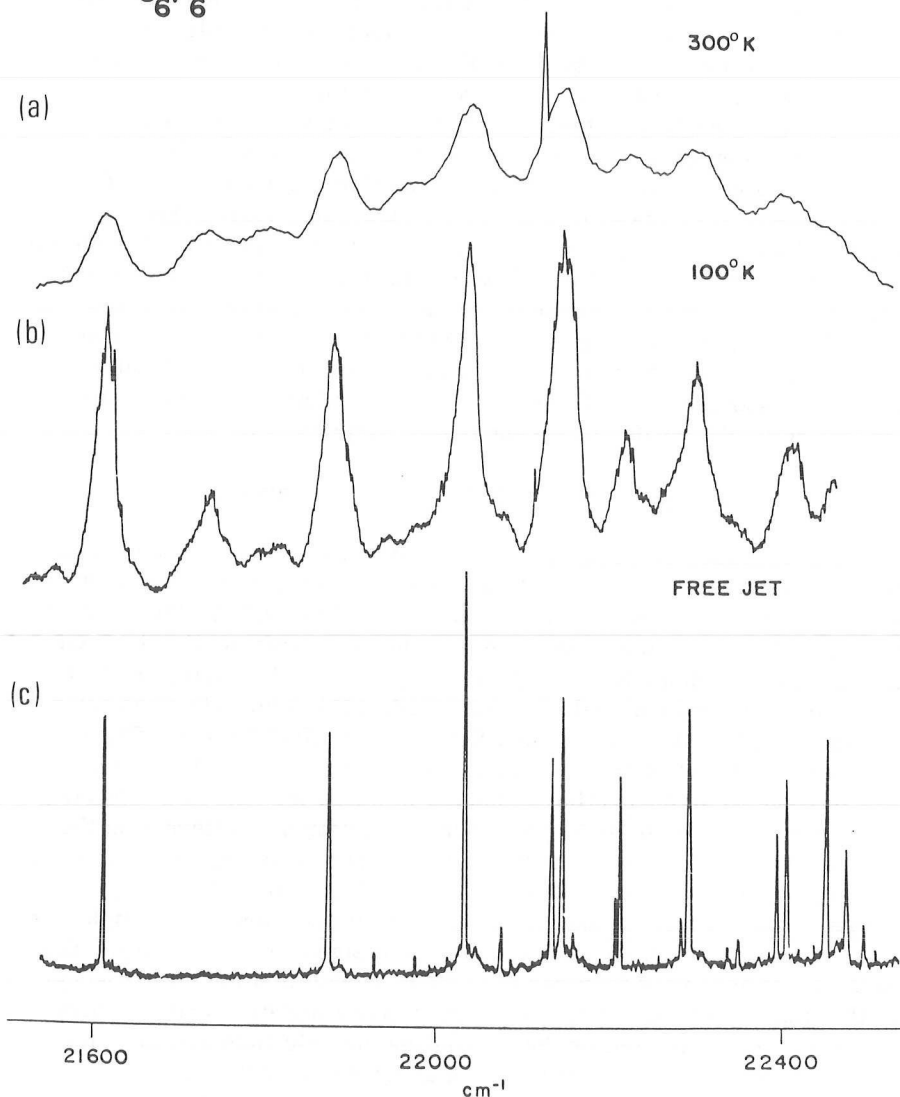


FIG. 14. Laser excitation spectra of C_6F_6^+ . In (a) and (b) the C_6F_6^+ was produced by Penning ionization in a flow system. For (a) the flow was at room temperature, whereas for (b) it was cooled by liquid N_2 . For (c) the C_6F_6^+ was produced by two-photon photoionization through the use of an ArF laser interacting with C_6F_6 seeded in a free jet expansion in Ar. The probe laser linewidth is the same for all three traces. The sharp line in (a) is due to an atomic impurity [166].

EI ionization was applied extensively by Maier and coworkers to generate excited state organic molecular ions that were detected by emission spectroscopy [167, 168]. Leach and coworkers improved on the instrumental resolution of the technique [169, 170]; however, the thermal energy content of the ions continued to pose an obstacle to unambiguous spectral interpretation. A considerable improvement in the EI ionization method was made by Carrington, Miller, Bondybey, and others by exciting molecules cooled in a supersonic free jet expansion [171-174]. Although EI ionization is not an energetically selective process, the resulting ions were observed to be considerably colder when using jet-cooled rather than ambient molecules.

Penning ionization can be induced by exciting metastable electronic states of rare gas atoms such as Ne and He by some form of electric discharge. The energies of these states typically exceed the ionization potential (IP) of most molecules (especially organic molecules). Upon collisions, the metastable can excite the seed molecule to energies above their IP, thus causing ionization. Under certain conditions, ionization occurs without further ion excitation [162]. This creates a non-emitting pool of ions which is favored in experiments relying on LIF detection. In another technique, Miller, Bondybey, and coworkers succeeded in obtaining moderate cooling of ions produced in a discharge by cooling the flow with liquid N_2 [175, 176]. The extent of cooling is illustrated in Figs. 14(a) and 14(b) for the ion $C_6F_6^+$. It is shown in Fig. 14(c) that substantially better cooling is obtained for $C_6F_6^+$ by two-photon photoionization using an ArF excimer laser [177, 178]. In Section IV C, we shall review work involving resonance photoionization for preparing state-selected ions.

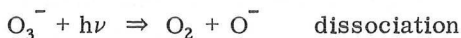
The above work summarizes some recent developments in polyatomic molecular ion spectroscopy including attempts to obtain molecular ion cooling to reduce spectral congestion. Supersonic expansion is shown to be an important method for this purpose. However, those studies involving cold ion spectroscopy were limited to fluorescing ion species and did not employ mass detection. In the following subsections we review recent developments that make use of photodissociation and mass detection as a probe of ion absorption. The ultimate aim is to develop general methods for recording vibrationally resolved electronic state spectra of cold, isolated, and nonfluorescing polyatomic ions.

B. Isolated Ion Photodissociation

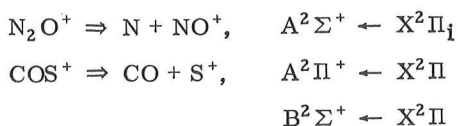
In Section II B three instrumental techniques were highlighted as being important for collisionless ion photodissociation studies: supersonic molecular beams, ion cyclotron resonance (ICR), and fast ion beams. The latter two techniques have a long history of application to

ion spectroscopy and are discussed in this subsection. The molecular beam technique offers the additional benefit of cold ion formation and is discussed in the following subsection on state-selective spectroscopy. ICR and fast ion beam photofragment spectroscopy have their own special attributes as discussed earlier (Section II-B); namely, long ion confinement times for ICR and near Doppler-free optical resolution for fast ion beams. Both techniques are well suited for studying the kinetics and dynamics of photofragmentation and figure strongly in the discussion of the dynamics of photodissociation to follow (Section V). Here we focus on the spectroscopic applications.

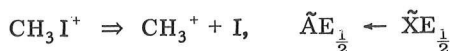
Moseley reviewed the field of ion photofragment spectroscopy in 1985 [122]. The discharge ion sources typically used were best suited for small molecule studies (i.e., H_2^+ , Ar_2^+ , Kr_2^+ , O_2^+ , CH^+ , NO^+ [122]). Studies of polyatomic ions included O_3^+ [179, 180], O_3^- [181-184], N_2O^+ [185, 186], COS^+ [187, 188], CO_2^+ [189], CO_3^- [190, 191], and CH_3I^+ [109, 110, 192-95]. Much of the diatomic work focused on kinetic energy analysis of the atomic fragments. The interpretation of these measurements is more complex for polyatomic ions due to the internal energy in at least one of the fragments. Moseley, Cosby, and Ozenne pioneered such studies using O_3^+ [179]. At visible wavelengths the photodissociation was dominated by the $\text{O}_2 + \text{O}^+$ channel arising from the first three levels of the parent ion symmetric stretch vibration. The vibrational spacings were determined as were the kinetic energy distribution of the two fragments and the rotational energy of the O_2 fragment. The visible photodissociation spectra of O_3^- also showed strong progressions in the symmetric vibration [181, 182]. Cosby, Moseley, and coworkers [181], and Hiller and Vestel [183] measured the total photodestruction cross section. Lineberger and coworkers used both laser photoelectron and photodissociation spectroscopy to study the O_3^- problem [182]. Their tunable laser photodetachment apparatus was capable of simultaneously detecting detachments of electrons and neutral fragments, thereby permitting differentiation between fragmentation and electron detachment processes,



Several groups have employed fast ion beam techniques for the more specific purpose of recording molecular ion spectra [185-188]. Excellent, high resolution fragmentation spectra of N_2O^+ [185, 186] and COS^+ [187, 188] were recorded for the following dissociation and electronic state transitions:



Finally, McGilvery and Morrison were among the first to record the vibrationally resolved electronic spectra of a polyatomic cation [193-195], choosing the system



The CH_3I^+ cation has since been studied by preparing cold ions in a supersonic molecular beam [109, 110] and is discussed shortly (Section IV-C).

The fast ion beam technique has seldom been applied to molecules larger than triatomics; the notable exception is work conducted by Lineberger and coworkers [196, 197]. Their apparatus uses a novel arrangement consisting of devices for detecting low energy electron detachment, ion current, and neutral species. The linear section where the laser beam overlaps with the ion beam is wrapped in a solenoid which causes detached electrons to spiral about the field axis. Detection of a specified range of low energy electrons may be chosen by using an aperture to restrict the detector field of view to electrons with small cyclotron radii. These coworkers applied this method to the electron photodetachment of the acetaldehyde enolate negative ion [197]. The unpaired electron in this species is not represented by a conventional valence state, but rather by a weakly bound dipole state. Although these studies do not involve multiphoton processes or fragmentation, it is a very important advance to the general field of ion spectroscopy and therefore relevant to the spectroscopy and dynamics of photofragmentation. By viewing near threshold electron detachment, Lineberger et al. succeeded in observing rotational autodetachment, which provided detailed structural information on the electron density distribution [197]. Similar but lower resolution photodetachment spectroscopy of dipole bound negative ion states has been reported by Brauman and coworkers using ICR spectroscopy [198-201].

The largest contribution to large molecule ion spectroscopy is probably attributable to ICR photofragmentation spectroscopy. This technique, described in Section II-B-2, is operated under low pressure gas phase conditions [117-121], where ionization is usually induced by electron impact excitation and spectroscopy is performed using laser or incoherent light sources. In the ICR technique the absorbed light induces fragmentation of the parent ion, thereby causing a loss of

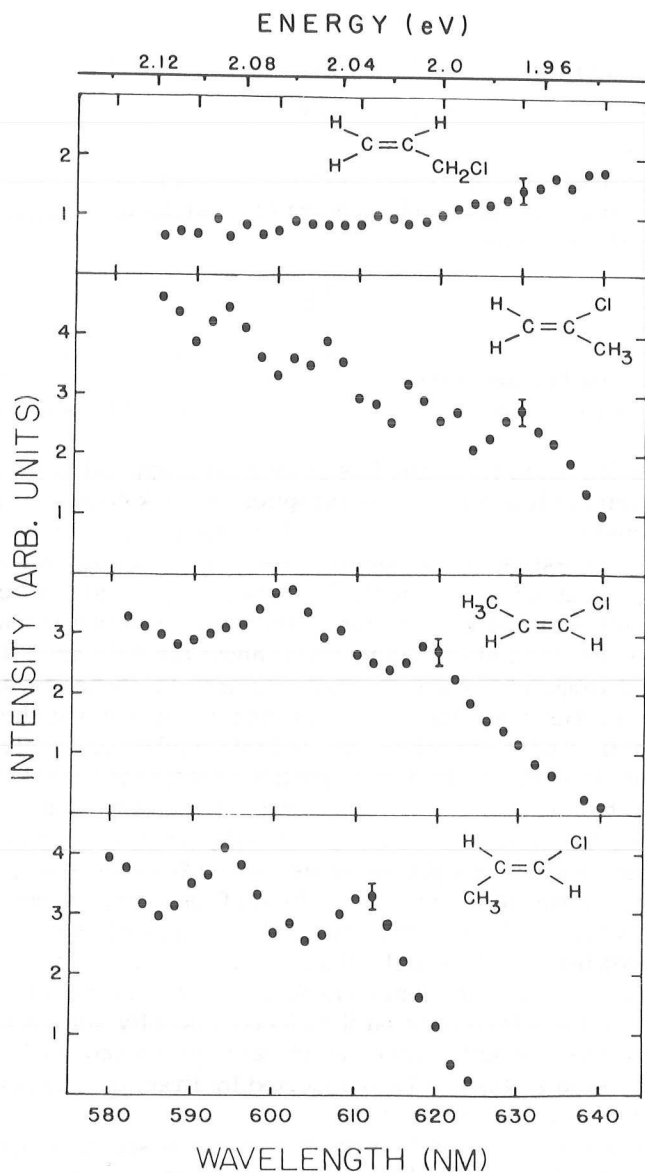
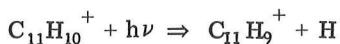


FIG. 15. The high-resolution photodissociation spectra for $C_3H_5Cl^+$ isomers are shown at a resolution of 1 nm. The data were recorded using a tunable CW dye laser [202].

signal. Similar results have also been reported for ambient temperature multiphoton ionization with laser-induced ion fragmentation [157]. Wavelength-resolved ICR photodissociation spectra for isomers of $C_3H_5Cl^+$ are illustrated in Fig. 15 [202]. The spectra are notable for the vibrational structure that is present since ICR spectroscopy does not always reveal this information. As a tool for high resolution ion spectroscopy, the ICR method is limited by the thermal energy of ions. The principal utility of ICR is the kinetic information that may be obtained about the fragmentation process (cf. Section V). In the following subsection (Section IV-C) we discuss developments leading to cold ion photodissociation spectroscopy. First we review recent work leading up to these advances.

Aromatic molecules are a representative group of large molecules that have attracted considerable attention in terms of ion spectroscopy and photodissociation. Andrews and coworkers obtained helium temperature matrix spectra of several aromatic ions that revealed resolved vibronic structure [165, 203-205]. Representative matrix spectra for the 2-methylnaphthalene cation are compared to an ICR photodissociation spectrum in Fig. 16. The aromatic ion spectra are distinctive, with red absorption bands arising from transitions between normally filled molecular orbitals of the neutral species. New blue and ultra-violet band systems were also observed. The linewidths for matrix isolated 2-methylnaphthalene, although considerably narrower than for ICR, were broader than those normally observed for matrix isolated neutral molecules [203-205]. It was not known if this represented homogeneous intramolecular interactions or inhomogeneous matrix-induced broadening. These results gave impetus to gas phase aromatic ion spectroscopy using photofragmentation detection [111, 120, 121, 157, 206-208].

In the simplest cases a single photon provides sufficient energy to fragment the parent ion through the lowest energy dissociation channel. For methylnaphthalene the lowest energy H atom dissociation channel,



occurs for one UV quantum [206]. Thus, the absorption spectrum should govern the efficiency of this simple fragmentation process. For unsubstituted naphthalene, the H atom dissociation energy is greater, thus requiring two UV photons. The absorption of visible light for these molecules requires a proportionately greater number of photons to reach dissociation. Naphthalene photodissociation spectra were recorded in an ICR spectrometer [206-208], in an MPI cell [157], and in a supersonic molecular beam [111]. The first two studies involved ionization of ambient naphthalene molecules and did not reveal any vibrational struc-

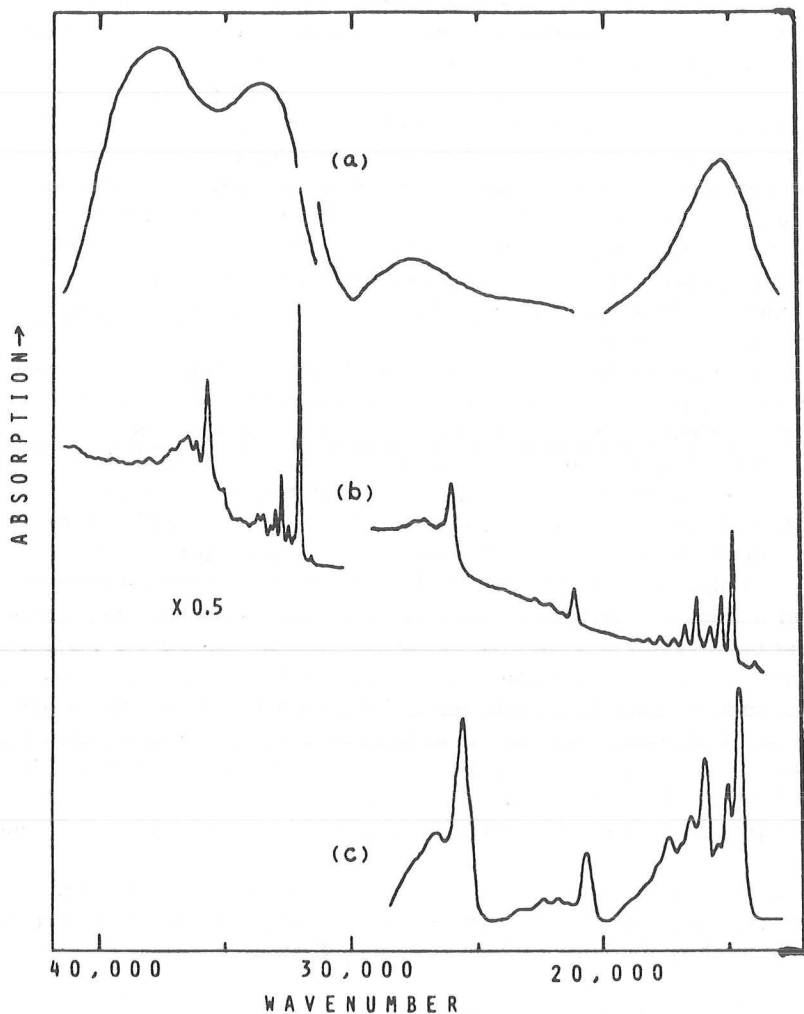


FIG. 16. Comparison of 2-methylnaphthalene cation absorption spectra recorded by different techniques: (a) gas-phase photodissociation spectrum, replotted from Ref. 206; (b) argon matrix absorption spectrum; and (c) Freon matrix absorption spectrum. (Figure reproduced from Ref. 205.)

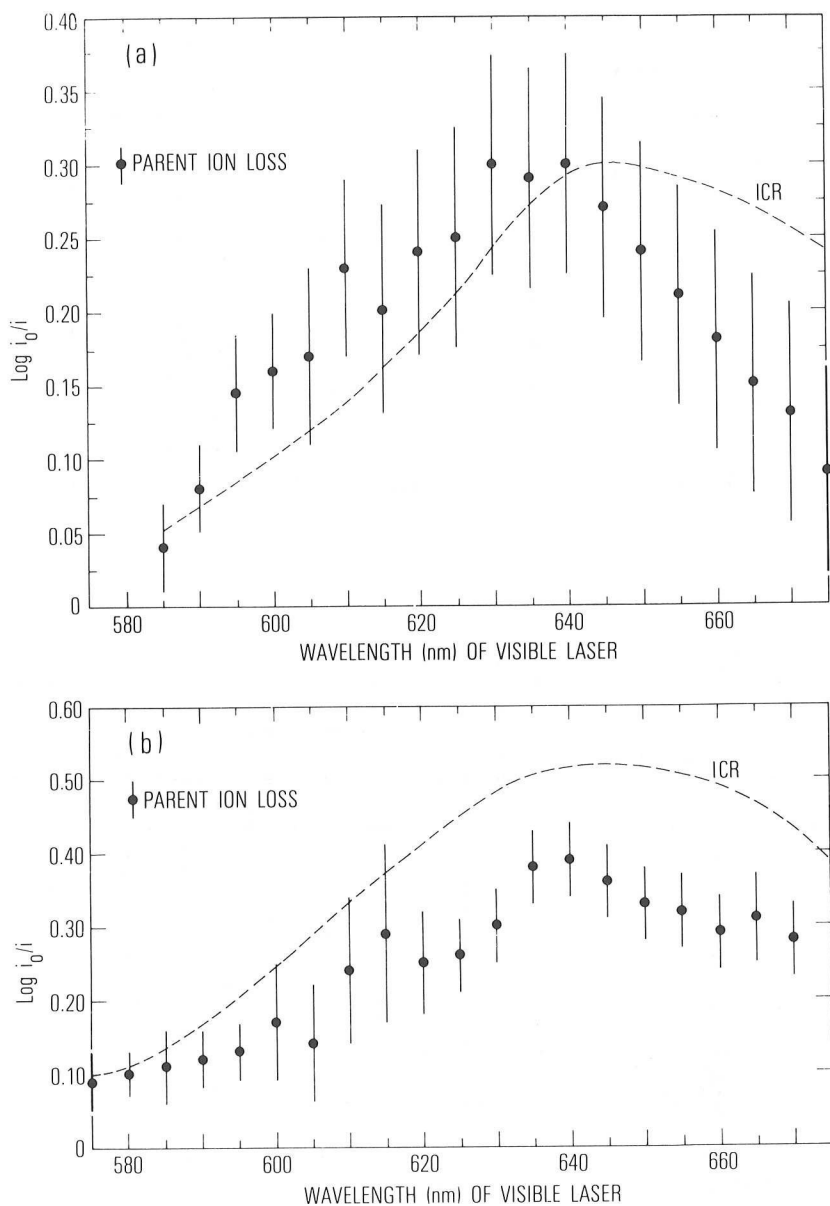


FIG. 17. Loss of parent ion signal recorded as a function of the visible laser wavelength for two-color ionization-fragmentation of (a) 1-methylnaphthalene and (b) 2-methylnaphthalene [157].

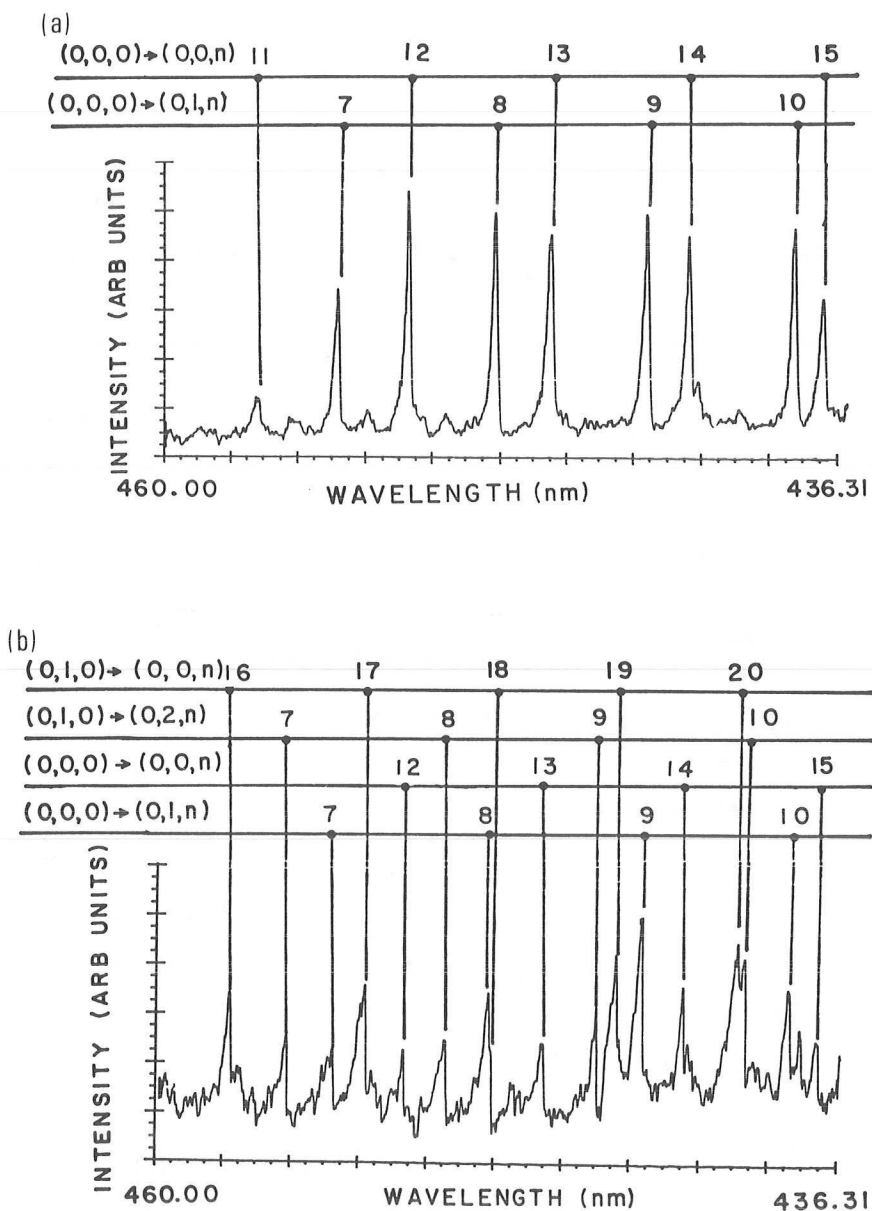


FIG. 18. Photodissociation excitation spectra of CH_3I^+ prepared at ionizing wavelengths of (a) 369.94 nm and (b) 362.59 nm [110].

ture although distinct electronic state absorptions were evident. The 2-photon methylnaphthalene parent ion loss spectra recorded in an ICR spectrometer and an MPI cell are compared in Fig. 17. At the time it was not evident whether the lack of vibrational structure, which appears in the one-photon cold matrix absorption spectra, was due to spectral congestion in the thermal molecules or to some dynamical effects in the 2-photon process. These limitations punctuated the need to generate cold ions, preferably in single vibronic energy states.

C. State-Selected Ion Spectroscopy

The production of cold gas phase ions first requires the removal of the thermal energy distribution in the precursor neutral molecules. A supersonic expansion is the method of choice for this purpose. Cold ions can then be formed by choosing laser wavelengths that promote MPI to just above the ionization threshold (but below the first vibrational level of the ion). A resonance intermediate state of the neutral is preferred for efficient ionization in order to avoid excessive power that might lead to subsequent ion absorption. Excitation of specific vibrational levels of the ion is more difficult since one must contend with the Franck-Condon overlap to lower energy vibrational levels. However, this is controllable to some extent by choosing intermediate electronic states of similar geometry to that of the ion. This enhances the prospect of diagonal ($\Delta v = 0$) Franck-Condon excitation. Hence, the desired ion vibration is first populated in the intermediate neutral state. Rydberg excitation has proved promising in this regard since these electronic states resemble an ion core with a weakly bound electron; hence ionization tends to preserve the ion core vibronic structure. Photoelectron spectroscopy (PES) is indispensable for verifying the selectivity of the ion vibrational excitation process.

Selective ion vibrational excitation by MPI has been studied extensively for diatomic molecules [133-136]. Recently, several investigators successfully prepared vibrationally selected polyatomic ions [74-79]. Colson and coworkers demonstrated using PES the production of vibrationally-selective ions of NH_3 by $3 + 1$ MPI via the C' state [74]. Zare and coworkers investigated the extent of vibrational selectivity for the $2 + 1$ process via the B and C' state [75-77]. Anderson, White, and coworkers achieved state-selective excitation for C_2H_2 [79]. Most of these studies were motivated by the application to ion-molecule reaction dynamics [75-78] and less by the prospect of high resolution spectroscopy. An important exception is the work of Colson, Chupka, White, and Woodward on the positive and negative ions of CH_3I [109, 110]. They prepared state-selected ions by resonance MPI in a molecular beam expansion, verifying the ion vibronic state by PES. A second

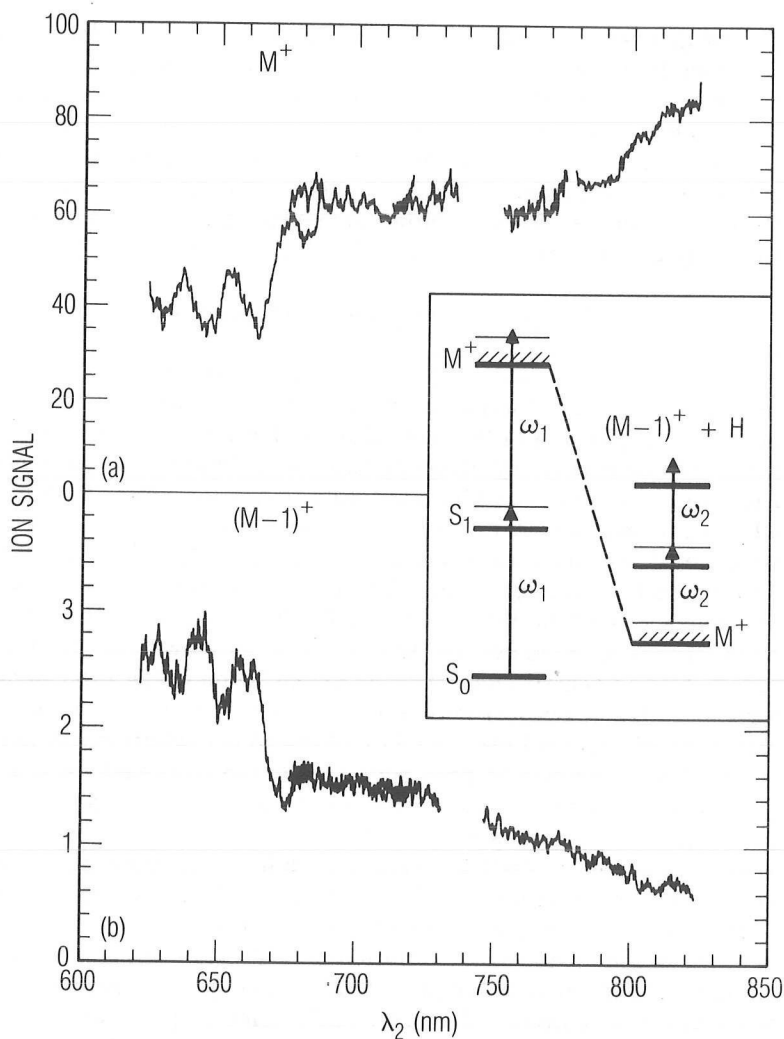


FIG. 19. Resonance ion dissociation spectra of 2-methylnaphthalene cation via low energy electronic states. (a) M^+ molecular ion dip spectrum, and (b) $[M-1]^+$ fragment ion formation spectrum. Two-photon MPI by ω_1 at 308.3 nm populates the ν_8 state of the molecular cation (insert): Delayed excitation by ω_2 reveals a diffuse ion absorption at very low energy and a structured absorption at higher energy [111].

laser was then used to resonantly dissociate the ion by breaking the C-I bond. A portion of their photodissociation is given in Fig. 18.

The preparation of cold large polyatomic ions for the purpose of resonant multiphoton dissociation spectroscopy was first reported by Syage and Wessel for the naphthalene and 2-methylnaphthalene cations [111]. Using 2-photon resonance MPI in a supersonic molecular beam, it was possible to populate either the vibrationless level of the ion or the lowest optically active vibration ν_8 at about 400 cm^{-1} . A second tunable dye laser was then used to resonantly dissociate the ion. A TOF mass spectrometer was employed to simultaneously detect the signals for the decrease of the parent ion (i.e., ion dip spectroscopy) and the corresponding increase of the fragment ion. The vibrationally resolved 2-photon dissociation spectrum for cold 2-methylnaphthalene cation is illustrated in Fig. 19. A comparison of this spectrum with the ambient ion spectrum in Fig. 17 indicates that considerable spectral congestion results from the thermal energy distribution. However, further observation indicates that a continuum absorption due to a lower energy electronic state overlaps with the discrete structure. Discrete vibronic resonances were also observed for both ions in the UV region [111].

V. DYNAMICS OF ION DISSOCIATION

In this section we explore the dynamics of energy absorption and dissociation. By dynamics, we refer to all time-evolving properties of the photoexcited ion. In particular, we can single out the processes of photon absorption, energy randomization, and dissociation, all of which occur in competition. In Section III the interplay of these processes was introduced and their importance inferred by discussions of ionic ladder-climbing versus ladder-switching mechanisms of photodissociation as well as isomeric rearrangement versus dissociation. Here we review recent work which has attempted to isolate and directly probe in a selective manner each of these processes.

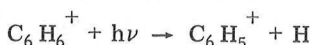
A. Ion Absorption and Energy Randomization

In 1975, Freiser and Beauchamp made the unusual discovery that continuous wave laser light of moderate power could achieve 2-photon dissociation of benzene ions [209]. It was determined that the process was a sequential absorption. The first photon produced an excited electronic state of the ion, which subsequently relaxed to a long-lived intermediate state. The lifetime was sufficiently long for a second absorp-

tion to occur, thus leading to dissociation. These findings stimulated much interest in ion relaxation processes and the new possibilities they offered for collisional and photolytic ion reactivity. Sequential two-photon dissociation has since been observed in other molecular ions [111, 206–208, 210–216]. The cations of benzene and naphthalene have attracted considerable attention as representative aromatic systems; hence, we focus more closely on these model ions.

1. Benzene Cation

Freiser and Beauchamp observed the photodissociation for the reaction



in the energy range of 2–3 and 4–6 eV [209]. We will remark only on the low energy sequential 2-photon process which involves a long-lived intermediate. The origin of the long-lived intermediate can be visualized in Fig. 20(a). Absorption of the first photon was assigned to the second excited ion state, which we designate D_2 (D denoting doublet). Under the low laser power, this state, instead of absorbing further, relaxes by internal conversion to a vibrationally hot set of bath states $\{v\}$ in the ground electronic state, D_0 . Since the relaxation processes available to $D_0\{v\}$ are very slow (i.e., vibrational radiative decay and collisional deactivation), there is ample time in the ICR ion trap cell for a second photon to be absorbed, thus leading to dissociation. The transition is strongly allowed since it involves the same electronic transition, $D_2 \leftarrow D_0$, and favorable Franck–Condon overlap involving the same set of vibrations $\{v\}$ (Fig. 20a). Confirmation of the sequential absorption mechanism was made by noting that the magnitude of the two-photon dissociation signal increased with the interaction duration of the laser.

More recent work has refined the model for the coupling of the second absorbing step with the decay channels in the relaxed intermediate state [213–215]. Most of the ICR work has centered on the lifetime of this long-lived state. Recently, van Velzen and van der Hart reexamined these lifetimes for benzene and substituted benzene [213] and obtained values (i.e., 125 ± 25 ms for benzene at 488 nm) that were shorter than previous determinations [209, 216]. There does not appear to be any measurement of the rate of internal conversion from the low energy excited electronic state; however, it is believed to be rapid on the basis of the failure to observe fluorescence from this level.

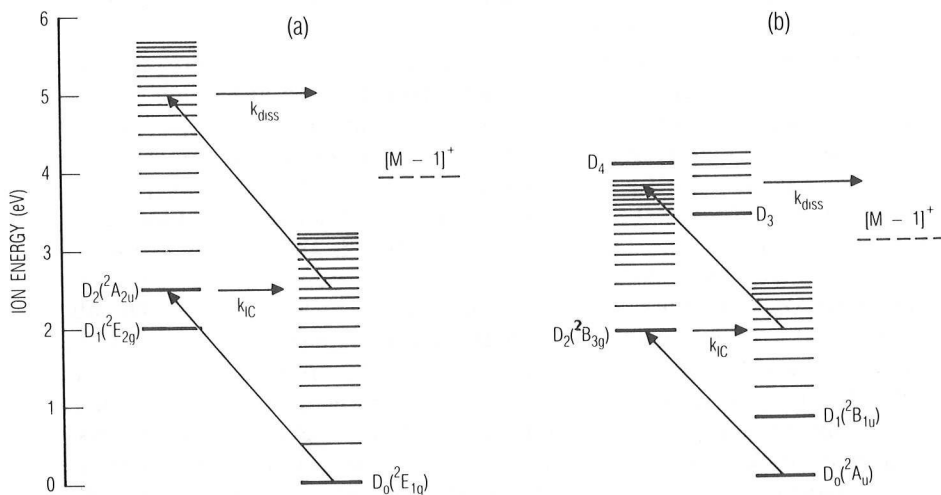


FIG. 20. Energy level diagram and sequential two-photon dissociation mechanism for the cations of (a) benzene and (b) 2-methylnaphthalene. The diagonal arrows represent electronic transitions. The dissociation thresholds are indicated by the dashed lines.

2. Naphthalene Cation

Dunbar and coworkers reported on the sequential multiphoton dissociation of naphthalene and methylnaphthalene for UV and visible excitation in an ICR spectrometer [206–208]. Their photodissociation spectra revealed no vibrational structure in the UV and visible owing to the thermal energy of the neutral precursor (Fig. 16a). An MPI photodissociation spectrum of ambient naphthalene likewise failed to reveal vibrational structure [157]. Syage and Wessel, however, observed vibrationally resolved structure in 2-methylnaphthalene cation by forming cold ions by threshold R2PI in a supersonic molecular beam [111]. A second time-delayed dye laser was then used to record the ion 2-photon photodissociation spectrum shown in Fig. 11 by detecting the lowest energy H atom dissociation channel in a TOF mass spectrometer. (There is some uncertainty regarding the methyl C–H bond energy. Dunbar places the range of value between 3.4 and 5.8 eV [208]. Hence, the overall dissociation may actually be 3-photon; however, the reso-

nance step is a 1-photon absorption). The spectrum, illustrated in Fig. 19, has been discussed before (Section IV-C).

Interesting features in Fig. 19 include a continuous absorption that occurs to low energy of the discrete electronic state at 662 nm and a pronounced power broadening that occurs in the discrete transitions. The continuous absorption is associated with a low energy electronic state D_1 less than 1 eV above the ion ground state D_0 [204, 217] as portrayed in Fig. 20(b). The $D_1 \leftarrow D_0$ transition is formally forbidden in the naphthalene cation, but vibronically active in the vicinity of the D_2 state. The considerable broadening is due to degenerate vibronic interaction between D_1 and D_2 and not simply to power broadening. The absorption of a second photon occurs from vibrationally hot states of D_1 ; the final state is either very high vibrational levels of D_2 (with unfavorable electronic transition moment) or lower vibrational levels of another electronic state D_3 (but with poor Franck-Condon overlap). Unlike the situation for the benzene cation, in which the second photon absorption cross section is similar to the first, the second photon absorption of 2-methylnaphthalene cation is very weak, thereby causing severe broadening in the easily saturable resonance absorption. This model also explains the lack of resolvable vibrational structure for the $D_2 \leftarrow D_0$ photodissociation spectrum of unsubstituted naphthalene cation [111]. The unsubstituted ion has a higher H atom dissociation energy [206–208]. The resultant 3- to 4-photon dissociative absorption requires power levels that saturate the resonant step.

B. Energy-Selected Ion Kinetics

Direct measurements of ion dynamics from specific energy levels provides a valuable source of information for unraveling the important elementary processes in ion chemistry. In Section II-B the sensitivity of photofragmentation to ion structure was examined for a group of structural isomers. It was shown that the rates of dissociation versus isomerization varied with structure and energy, and hence different outcomes could occur depending on the source of excitation (e.g., discrete photon excitation versus indiscriminate electron impact excitation). In the previous subsection (Section V-A) the important issue of energy randomization was discussed in terms of its role on consecutive (ladder climbing) versus sequential (ladder switching) multiphoton ion absorption. Energy randomization is the cornerstone to statistical models for unimolecular decay, and the extent to which statistical behavior occurs is of great interest and of fundamental importance to understanding dynamical processes. In what follows we review work that attempts to follow the specific pathways to dissociation in the midst

of the above competing processes. Excellent review articles, which relate to some of the above issues, have recently been published by Baer [218, 219].

1. More Experimental Techniques

Some of the techniques employed to directly study energy-selected dissociation have been introduced earlier (Section II-B). ICR spectroscopy has the advantage of long ion residence times which has proved important for measuring metastable ion decay. Ion beam methods allow collinear excitation and therefore long ion laser exposure times. Both methods enable studies of the angular distribution and kinetic energy release of fragment ions. We describe two other techniques which have contributed enormously to kinetic studies of ion dissociation: photoion-photoelectron coincidence (PIPECO) spectroscopy and reflectron TOF mass spectrometry.

The PIPECO method allows studies of ions with well-defined energies [218, 219]. If the ionizing photon energy $h\nu$ and the ensuing electron energy E_{el} are known, then the ion energy can be deduced by the photoelectron expression

$$E_{ion} = h\nu - IP - E_{el} + \langle E_{th} \rangle$$

described in Section II-B-4. Energy selection is achieved by two means: (1) using a fixed wavelength (i.e., a He(I) source at 21.2 eV) and studying ions in coincidence with electron energies selected using a dispersive electron energy analyzer; or (2) using a variable wavelength source and monitoring ions in coincidence with zero energy electrons. Recent work appears to favor the latter method, using multiphoton ionization. Minor disadvantages to the PIPECO technique include the thermal energy distribution $\langle E_{th} \rangle$ and the apparent lack of high mass resolution. Dynamical information such as fragmentation rates and kinetic energy release are contained in the ion TOF distribution. An asymmetry results when dissociation occurs while the ions are being accelerated. The slower the rate, the more asymmetric is the signal. The TOF distribution may be deconvoluted to obtain the dissociation rate as a function of specific parent ion energy [218].

The reflectron TOF mass spectrometer, as shown in Fig. 21(a), was designed to correct for the distortions that occur in the arrival times of daughter ions m^+ produced by metastable decay of parent ions M^+ [220-223]. These distortions can be visualized with the aid of Fig. 21, and the understanding that the standard TOF mass spectrometer has an ion acceleration region and a field-free drift region. If ion fragmentation

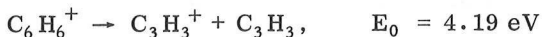
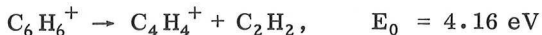
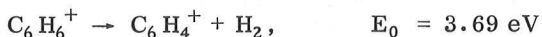
is prompt, then each mass is accelerated to the same energy and therefore travels at a different velocity in the drift region. The different arrival times for each mass give rise to characteristic mass spectra. However, if fragmentation is very slow and occurs in the field-free drift region, there is no way to distinguish parent ions from daughter ions, since the velocities and therefore the arrival times are unaffected by dissociation in this region. (The fragment kinetic energy distributions are insignificant compared to typical accelerated ion energies.) For the intermediate case, where fragmentation occurs during the acceleration period, the m^+ signal exhibits a tailing toward M^+ , which may be analyzed to determine fragment parentage and dissociation rate [41, 219]. For slow dissociation in the field-free drift region, m^+ and M^+ have the same velocity, but they clearly have different energy as a result of their different masses. These masses can then be separated with the addition of a reflecting electric field as shown in Fig. 21. The energy of the reflecting field can be chosen to reflect the lower energy m^+ mass and let the higher energy M^+ mass penetrate the field. The device therefore acts as an energy filter and consequently as a metastable fragment ion analyzer. This feature has been employed extensively in the study of cluster ion dissociation.

2. Case Studies

The recent development in our understanding of ion photodissociation dynamics has been advanced by applying different experimental approaches to similar molecular systems. We examine the new understanding gained by these studies by drawing together a collection of work focusing on the structural isomers of $C_6H_6^+$ and the aniline cation $C_6H_5NH_2^+$.

$C_6H_6^+$ Isomers

The structural isomers of $C_6H_6^+$ take the form of acyclic linear hexadiynes and cyclic benzene and fulvene. Some of the fundamental questions relating to ion dissociation include: (1) whether isomerization to the most stable ion precedes dissociation and (2) whether different fragmentation pathways proceed from common or different energy states and ion parentage. The second issue was addressed by studying the low energy benzene cation metastable decay channels,



where E_0 is the threshold for each ion dissociation pathway [224, 225]. There was some uncertainty whether the H-loss and the C-loss channels originated from different electronic states or occurred competitively from the same state. Baer and coworkers, using the PIPECO method, measured the kinetic energy release for the C-loss channels including the higher energy channels leading to C_2^+ and C^+ (not shown above) [139, 226]. The decay rates for production of $C_4H_4^+$ and $C_3H_3^+$ were determined to be the same for ion energies in the range of 5.0–5.5 eV [139]. Unfortunately, the mass resolution was not adequate to resolve the H-loss channel. Schlag, Neusser, and coworkers, using the reflectron TOF approach, established that the H-loss channels also exhibit the same kinetics as the C-loss channel in the metastable ion energy range studied previously [139, 226]. This was taken as evidence that these dissociation channels occur in competition from the same state. The measured rates were in good agreement with RRKM calculations, from which it was concluded that the dissociation occurs statistically by way of rapid internal conversion of the electronic state excitation into vibrationally hot levels of the ion electronic ground state. Independent evidence for the role of internal conversion is provided by the failure to observe fluorescence from excited electronic states of the benzene cation.

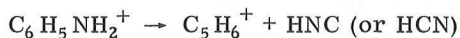
The energy randomization inherent in the statistical model raises questions regarding the competition between dissociation and isomerization for the less stable ion structures. Extensive work has centered on the linear $C_6H_6^+$ isomer 2,4-hexadiyne [227–233]. Unlike benzene cation, the 2,4-hexadiyne cation fluoresces from its lowest excited electronic state, $\tilde{A}^2E_u$, from which a lifetime of about 20 ns has been deduced [230]. Maier and coworkers [230] as well as Dannacher [231] argued that the $C_4H_4^+$ is formed directly from the $\tilde{A}^2E_u$ state. Baer and coworkers, on the other hand, convincingly demonstrated that statistical redistribution to the ground electronic state dominates. The latter group, however, concluded that the vibrationally hot 2,4-hexadiyne cation isomerizes to benzene cation prior to dissociating on the basis of similar fragment branching ratios and decay rates compared to the observed benzene cation dissociation. Bowers and coworkers agreed with internal conversion and statistical dissociation, but took issue with the earlier finding that isomerization occurs before dissociation [232]. These investigators used a laser-ion beam photodissociation apparatus to measure the photofragment angular distribution of 2,4-hexadiyne and showed that the observed large anisotropy is inconsistent with isomerization to benzene cation [232]. Gross and coworkers studied the dissociation of four $C_6H_6^+$ structural isomers using low energy (16 eV) electron impact ionization in an ICR spectrometer [233]. Differ-

ent behavior might be expected at low ion energies since the barriers for isomerization are below the thresholds for fragmentation. They concluded, however, that isomerization did not play a dominant role except for the cation 1,5-hexadiyne.

A series of picosecond pump-probe experiments were carried out by El-Sayed and coworkers on the 2,4-hexadiyne cation [227-229]. They used 266 nm excitation and time-delayed 532 nm probe pulses of variable energy to determine that the $C_6H_5^+$ fragment was formed with more than one characteristic reaction time [228, 229]. This was interpreted as evidence for fragment formation either from different states or from different structures. The results described in the above paragraph indicate that isomerization does not occur at the one UV photon level above the ion ground state; however, the high peak powers of the picosecond pulses along with the ~ 20 ns lifetime of the $\tilde{A}^2E_u$ state can lead to higher electronic state excitation in the parent ion. El-Sayed and coworkers showed that the fast component in the $C_6H_5^+$ rate of formation correlates with increasing laser pulse energy as illustrated in Fig. 22, thereby substantiating the efficiency of the ladder-climbing mechanism to 2,4-hexadiyne [229]. Consequently, the two channels for formation of $C_6H_5^+$ occur from different electronic states (at the one and two UV photon levels) and not from different structures (although the role of isomerization at higher energies has not been established for this cation). These coworkers have also identified ladder-climbing fragmentation pathways at even higher ion multiphoton energy levels [229].

Aniline Cation, $C_6H_5NH_2^+$

A ubiquitous metastable decay channel for aniline cation is described by



This fragmentation process has attracted much interest since it does not involve simple bond breakage, but rather requires some bond rearrangement. Recent work using MPI has helped to understand the kinetics and geometry of the rearrangement process [41, 234, 235]. Zare and coworkers were among the first to apply MPI to the study of unimolecular decomposition of ions [41]. They observed the well-known asymmetry in a fragment ion TOF signal when the fragmentation occurs in the acceleration region of the spectrometer (cf discussion on reflectron TOF in Section V-B-1). Using several wavelengths of light ranging from 266 to 286 nm, they observed changes in the asymmetry that suggested an increasing fragmentation rate at shorter wavelengths. By deconvoluting the peak shape at 266 nm, subject to their acceleration

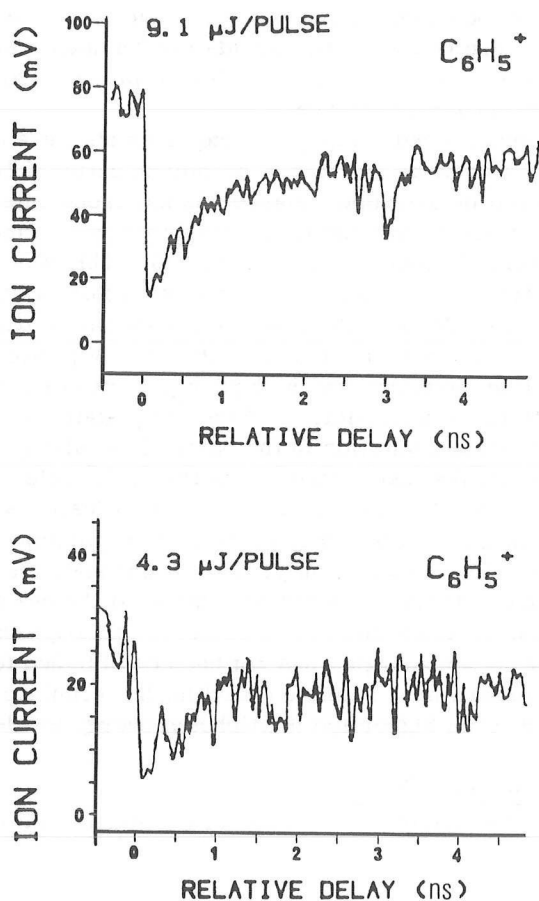


FIG. 22. Ion current for the $C_6H_5^+$ fragment vs delay time between the 266 nm pump and 532 nm probe pulse for two different pump energies. The fragment formation rate at the higher pulse energy is biexponential with a fast 300 ± 100 ps component and slow 20 ± 5 ns component. It is suggested that the slow time arises from the three UV photon state at 14.0 eV and the fast time from the four UV photon state at 18.66 eV above the neutral ground state [228].

conditions, they obtained a unimolecular rate constant of $\sim 2 \times 10^6 \text{ s}^{-1}$. The ion energy, however, could not be accurately determined since the kinetic energy of the ejected electron at the two-photon ionization level was not known.

Baer and Carney [234] followed the initial MPI work of Zare et al. [41] by measuring the metastable dissociation rate for energy-selected ions using the PIPECO method. The measured rates were obtained from the ion TOF distributions which are asymmetrically broadened as a result of dissociation that occurs while the parent ions are being accelerated (Section V-B-1). The TOF distributions are presented in Fig. 23(a) as a function of specific parent ion energy.

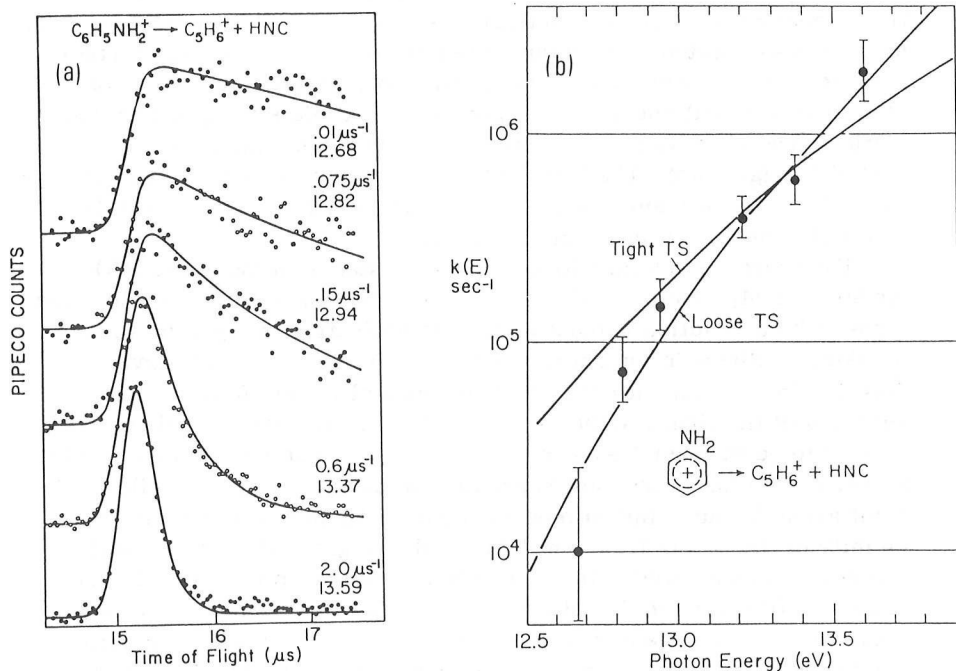


FIG. 23. (a) Coincidence TOF distributions of C_5H_6^+ ions produced from parent aniline ions with the indicated energies in eV. The solid lines are calculated TOF distributions assuming the decay rates indicated. (b) The dissociation rate as a function of the parent $\text{C}_6\text{H}_5\text{NH}_2^+$ internal energy. The solid lines are RRKM calculations assuming tight and loose transition states [234].

The observed energy dependent unimolecular rate constants $k(E)$ were compared to the RRKM statistical rate model [150, 151]. The calculated rates are obtained by the expression

$$k(E) = \frac{\sigma \int_0^{E-E_0} \rho^\ddagger(E') dE'}{h\rho(E)}$$

where ρ and $\rho^\ddagger$ are the densities of vibrational states of the molecular ion and the transition state, respectively, E_0 is the activation energy, and σ is the number of equivalent dissociation pathways. Two models for the transition state were considered; a tight structure which assumes vibrational frequencies that are similar to the aniline molecule, and a loose structure which assumes a set of frequencies characteristic of a linear geometry [234]. The activation energy was not accurately known, hence it was treated as an adjustable parameter. The models further assume that electronic excitation in the ion relaxes by internal conversion to vibrational energy in the ground electronic state prior to dissociation. The observed and calculated rate constants $k(E)$ are represented in Fig. 23(b). The best fit to the data corresponds to a calculation assuming a loose transition state structure and a dissociation at 11.2 eV above the neutral ground state (i.e., $E_0 \approx 3.5$ eV).

Baer and Carney mentioned an inconsistency in the above RRKM modeling [234]. They noted that a loose transition state is usually associated with a reaction without a reverse activation energy. However, the derived dissociation energy of 11.2 eV is significantly above the dissociation enthalpy for the cyclopentadienyl ion at 10.43 eV. The energies of the linear structures of $C_5H_6^+$, on the other hand, are calculated to be at least 1 eV above E_0 and are therefore not likely candidates. Confusion in the past regarding the geometry of the $C_5H_6^+$ fragment arose because initial measurement of E_0 placed the value in the vicinity of the linear fragment threshold energies. However, Lifshitz and coworkers showed that the previous appearance potential determinations suffered from "kinetic shift"; that is, the measurement technique was not capable of detecting very slow dissociation occurring at low energy [236]. Using trapped ion mass spectrometry, they measured a value of $E_0 = 11.26 \pm 0.2$ eV in good agreement with the RRKM result.

Lifshitz and coworkers further proposed an explanation that would allow for a negligible reverse activation energy that is implicit in the loose transition state model. They suggested that the neutral fragment structure is actually HNC which has a heat of formation that is 0.63 eV higher than HCN. The dissociation limit for cyclopentadienyl by this

pathway would then be 11.07 eV, nearly equal to the measured activation energy [236]. The HNC structure for the dissociative fragment of aniline cation is reasonable on the basis of the existing HNC— bond in aniline. However, further support for the HNC structure is provided by the work of Holmes et al. [237, 238]. They generated high kinetic energy neutral fragments (several kilovolts) from the metastable dissociation that occurs after parent ion acceleration of aniline or pyridine. The neutral fragments are then ionized and fragmented by collisions with He atoms. The fragments from pyridine cation led to extensive CH^+ production by this method, which is consistent with an HCN precursor fragment. The neutral fragment from aniline, on the other hand, failed to produce CH^+ , indicating a precursor structure of HCN.

Schlag and coworkers used the reflectron TOF method to identify several other metastable decay channels involving the sequential fragment dissociation of the aniline parent cation [235]. By operating the reflectron device as an energy analyzer (Section IV-B-1), they could identify the parentage of fragment ions, thereby mapping out a plausible sequential fragmentation pathway.

Other Systems

Several recent papers for systems other than C_6H_6^+ and $\text{C}_5\text{H}_6\text{NH}_2^+$ deserve attention. Tai and El-Sayed operated a reflectron TOF mass spectrometer using MPI such that the pulsed extraction field could be delayed with respect to the laser pulse [239]. By varying the delay, a direct measure of the rate of fragmentation could be obtained. The use of a picosecond laser for ionization and ion absorption was considered to offer the advantage of avoiding complications due to ladder-switching mechanisms. The MPID of 1,4-dichlorobenzene was studied and the rate constants for several fragments measured at the 3-photon level of 14.0 eV ($\lambda = 266$ nm). The ion energy is not known precisely, since the electron kinetic energy is not measured and the precursor neutral molecules are thermally excited. However, the measured formation rate constant for $\text{C}_6\text{H}_4\text{Cl}^+$ is in good agreement with the single-photon energy-selected measurements by Baer and coworkers [240] using the PIPECO technique.

Baer and coworkers applied their work to o-, m-, and p-dichloro- and dibromobenzene ions [240]. The measured rates of dissociation to form $\text{C}_6\text{H}_4\text{X}^+ + \text{X}$ indicate that these isomers first rearrange to a common structure, the para isomer. El-Sayed and coworkers, in another picosecond pump-probe experiment, explored the dissociation pathways following further UV photon absorption by $\text{C}_6\text{H}_4\text{Cl}^+$ [241]. The results described above employ neutral precursors at ambient thermal temperatures. Zare and coworkers, as discussed earlier, used the asymmetric

signals that occur in a standard TOF mass spectrometer to derive rate constants for metastable decay [41]. Their work on aniline involved a thermal sample [41]; however, they have more recently studied the chlorobenzene cation dissociation using a supersonic molecular beam source for the neutral precursor [242]. This arrangement in conjunction with MPI excitation and photoelectron analysis allows true state-selected ion dissociation rate constants.

VI. MOLECULAR DETECTION AND CHEMICAL ANALYSIS

A. Overview of Recent Developments

The single atom photoionization detection work of Hurst and co-workers [243, 244] was strong incentive to apply similar techniques to molecules. These investigators were able to detect alkali atoms down to 10 atoms/cm³ in the presence of 10¹⁹ molecules/cm³ of buffer gas. The molecular analog of these studies demonstrated that detection levels of better than a part-per-trillion (ppt) could be achieved for polycyclic aromatic hydrocarbons [245-248]. In the early atomic and molecular detection work, ionization was measured by the simple but extremely sensitive proportional counter, a device capable of detecting individual ionization events. The method, which evolved from earlier applications in nuclear chemistry and physics, exploits the use of a buffer gas, which provides effective amplification of the primary ionizing event by providing secondary ionization by the photoelectrons produced in the primary ionization event. In the presence of a strong electric field, the primary photoelectrons collide with buffer gas atoms and generate a cascade of secondary electrons. This leads to a large, directly measurable current pulse. Unfortunately, the presence of the buffer gas obscures detailed information about the molecular ion created in the process. Thus, the technique is primarily applicable in situations where mass spectra and information about the ions created by the MPI process are not required. Nonetheless, the principal outcome of these investigations was to establish that resonance two-photon photoionization (i.e., R2PI or 1 + 1 REMPI) can provide detection limits for large aromatic hydrocarbons down to about 10⁴ molecules/cm³ in a 1 atm buffer gas environment [246].

As the achievable sensitivity improved, the problem of interference from contaminants became a greater concern. This awareness motivated work to develop methods capable of greater selectivity. Clearly, detection selectivity becomes increasingly important as the intrinsic

sensitivity improves, since the overall measure of detectability is the usable sensitivity. In some of the earlier MPI applications, additional selectivity was introduced by tandem arrangements that included stages such as gas chromatography (GC) to separate the constituents of a mixed gas sample before ionization. Optical selectivity, though not adequate by itself for thermal samples, was used to augment the GC selectivity by taking advantage of the different absorption properties and ionization potentials. Klimcak and Wessel demonstrated high levels of sensitivity and selectivity using such an arrangement for the isomers phenanthrene and anthracene [247]. More recently, Reilly and coworkers demonstrated selective detection using an arrangement based on the use of GC and TOF mass spectrometry [249-251]. This combination provides mass selectivity; however, in an effort to maintain simplicity, they opted for a fixed wavelength excimer laser for ionization, thus limiting their options for optical selectivity.

Some form of mass spectrometry is now used by most detection methods based on MPI. Preparation of gaseous samples by supersonic expansion offers enormous benefits with regard to selectivity and will be discussed at length shortly. However, it can be argued that this improvement comes at the expense of sensitivity since the gaseous sample upon expansion in the vacuum chamber is at a significantly lower density in the region of detection. In order to avoid density reduction associated with low pressure mass spectrometry, Kolaitis and Lubman demonstrated the advantages of atmospheric pressure MPI mass spectrometry in conjunction with an ion mobility drift tube apparatus [252]. Exceptional levels of sensitivity are possible at atmospheric pressures, where part-per-billion (ppb) concentrations correspond to greater than 10^{10} molecules/cm³. The optical selectivity of R2PI, however, is reduced in atmospheric samples and the separability of the ion drift times are limited by diffusion controlled broadening. To overcome this problem, the ions are focused through an aperture into a quadrupole mass spectrometer to enhance the selectivity of detection [252].

Sensitivity can also be improved by accumulating trace molecules on a cooled substrate. After an adequate coverage has been achieved, the molecules can be desorbed by a pulsed laser and then photoionized above the surface [253, 254]. Pulsed desorption and MPI has also been applied extensively to surface analysis of materials [255-257], with much of the development motivated by applications in the semiconductor community. The technique is likewise gaining popularity as a means for introducing nonvolatile or thermally unstable molecules into the gas phase or vacuum [258-263] (which we discuss in further detail shortly).

Efforts to improve selectivity have often centered on advancing the mass spectrometer performance. Mass resolution can be improved by

simply operating two spectrometers in tandem (MS/MS) [264]. However, the most important development for ultrahigh mass resolution is Fourier transform mass spectrometry (FTMS) [118, 119, 265-267]. The basis for this technique is the use of an ion trap cell that derives from ICR spectrometers; hence, the technique is often referred to as FTICR. Resolution is dependent on the residence time of ions in the ion trap cell and can achieve levels greater than 100,000. This capability permits separation of compounds of the same nominal molecular weight but of different molecular structure. An interesting application of FTMS has been reported by which molecular structure can be deduced by consecutive ion photodissociation [267]. Parent ions that are formed in the FTMS detection cell are fragmented by a 193-nm excimer laser pulse. A mass spectrum may be recorded at this stage followed by ejection of all ions except a daughter ion of interest. The daughter ion may then be further photofragmented and the mass spectrum of the granddaughter ions recorded.

Detection methods that improve optical selectivity are understandably based on techniques originally developed for the purpose of high resolution spectroscopy. Foremost among these is the use of supersonic molecular beams. The benefits and applications of this technique to the spectroscopic and dynamical properties of ions have been enumerated extensively in this review. For detection applications, supersonic cooling accounts for excellent sensitivity and selectivity for the respective reasons that: (1) the cold molecules are in virtually the same energy state and can therefore be nearly completely ionized by resonance excitation using a single wavelength of light, and (2) each molecule typically has its own characteristic set of narrow excitation wavelengths that is distinct from that of other molecules. In the following section, recent work is reviewed which demonstrates the enormous enhancement in optical selectivity that becomes possible by supersonic molecular beam detection. However, it should be emphasized that sensitivity is likewise considerable. The potential loss in sensitivity due to the dilution in molecular density that occurs upon expansion is largely compensated by the benefit that results from the very narrow distribution of initial energy states (Point 1 above).

B. Molecular Applications

The field of ultrasensitive detection caters to a wide variety of applications [268, 269]. In chemical analysis, one is often interested in determining the composition of a given sample (i.e., assays) or the extent of contamination. Particular requirements include separating isomers or isotopic substituents in molecules. These applications

usually require high levels of sensitivity and selectivity, but not necessarily rapid analysis times (at least on a real-time basis). Another active area of trace detection is atmospheric monitoring. Numerous applications exist in situations that have high environmental impact (i.e., toxic waste sites, space launch facilities, nuclear power plants). Here, rapid analysis is more important. This statement is particularly true in situations involving toxic and hazardous compounds that might endanger life (i.e., chemical warfare agents).

The value of supersonic molecular beam mass spectroscopy for trace detection was recognized from the start. The molecular cooling accounts for narrow excitation linewidths which contributes to appreciable optical selectivity. For MPI excitation, the selectivity is further augmented by single mass detection. Sensitivity is considerable, owing largely to the ability to detect single ions using modern ion lenses and detectors. Detection is very rapid in the sense that the total transit time of neutral molecules exiting the molecular beam source to ionized particles reaching the detector is well under a millisecond. For chemical analysis, which allows the preparation of samples in convenient carrier gases, impressive detection capabilities for many applications have been demonstrated. The more challenging application is in atmospheric monitoring where the carrier gas is now air at 15 psia (i.e., 0 psig) of pressure. The cooling efficiency of atmospheric air is usually less than ideal, and hence a reduction in the realizable selectivity may be expected. Furthermore, humidity may lead to complexation between water and the trace molecules of interest, causing a loss of wavelength and mass identity. These problems, however, may be overcome. For instance, a recent study using atmospheric expansions of organophosphonates has shown that considerable supersonic cooling can be achieved as evident by the REMPI excitation spectrum in Fig. 24 [93]. It was further shown that water complexation was not significant for various organophosphonates and sulfides. Problems with complexation are often encountered in atmospheric pressure ionization (API) where molecules are ionized by protonation, thus increasing their propensity to undergo hydrogen bonding. This problem is amplified since the ionization occurs at atmospheric pressures and not under the collisionless conditions of a molecular beam.

Sensitive detection relies on finding photoionization processes that are efficient. Aromatic molecules are ideally suited since they involve strong absorption cross sections at convenient wavelengths, require just two photons to ionize, and form relatively stable parent ions. Aromatic molecules have therefore been employed extensively as model compounds for evaluating detection capabilities by REMPI. Other classes of molecules pose more serious detection challenges. Ionization

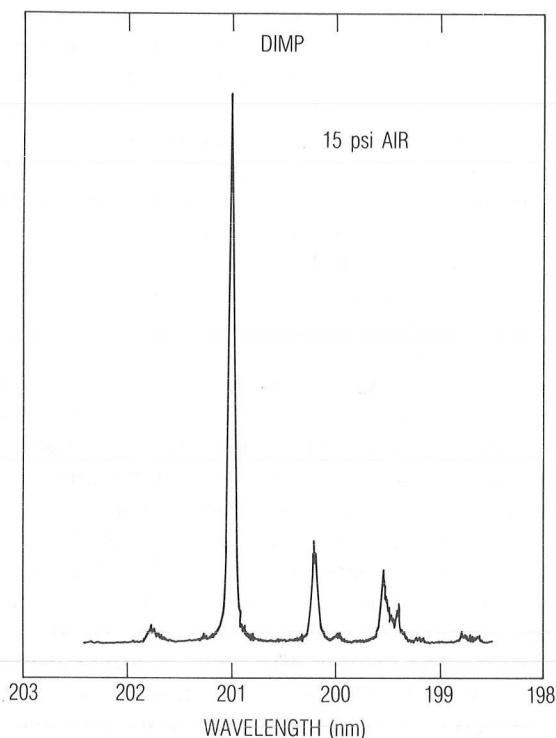


FIG. 24. 2 + 2 REMPI excitation spectrum of DIMP in a supersonic molecular beam using atmospheric room air as the carrier gas (0.5% DIMP in 15 psi air). The fragment ion at $m/e = 43$ was monitored in recording the spectrum [93].

efficiency may be reduced by competitive neutral pathways (e.g., dissociation, internal conversion), inconvenient lasing wavelengths, or ionization requiring more than two photons. Mass selectivity may be compromised by extensive ion fragmentation. Finally, many molecules of interest are nonvolatile (i.e., biological molecules) presenting difficulties in introducing sufficient material into a photoionization source.

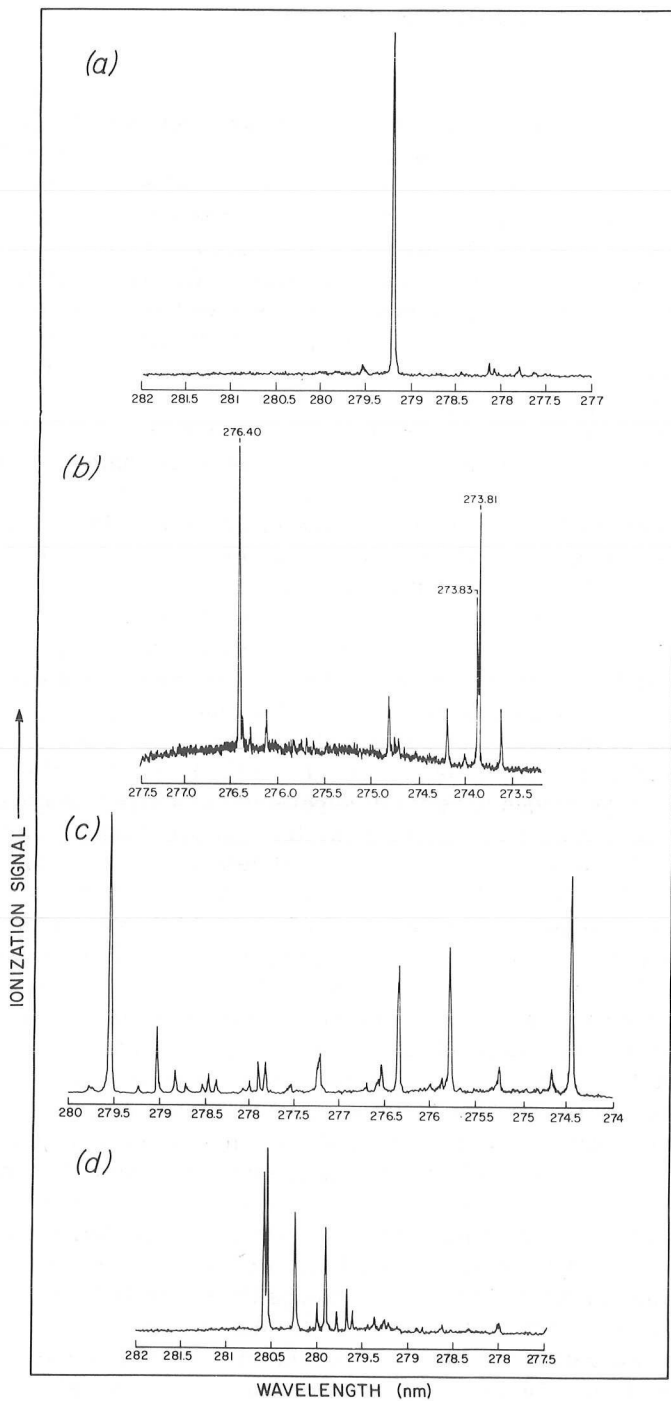
1. Aromatic Molecules

Aromatic molecules are of considerable interest since they include carcinogenic components of combustion products, pesticides, and other toxic compounds. Aromatics are a favorable group of molecules for detection owing to their R2PI excitation through a strong intermediate

(π, π^*) transition. Moreover, these transitions usually occur in the near UV where high output is available from commercial pulsed dye lasers. Finally, the intermediate resonance states are typically stable to decay processes (i.e., internal conversion, dissociation) that might compete with the ionization step. However, there are exceptions to this situation, such as the presence of substituents that accelerate the rates of radiationless processes. The R2PI efficiencies for many aromatic and large unsaturated hydrocarbons have been measured for tunable laser excitation in a molecular beam [270] and excimer laser excitation in an ambient vapor cell [271]. Predicted sensitivity in the former study was as low as 2 ppb.

Lubman and coworkers made major contributions in demonstrating the detection capabilities of supersonic molecular beam, MPI mass spectrometry [269, 272-276]. They addressed several issues concerning aromatic molecular detection. The problem of radiationless decay processes competing with ionization is a severe one since it reduces detection efficiency. These investigators studied a series of mono- and o-, m-, p-disubstituted halogenated hydrocarbons and identified conditions under which radiationless decay processes operate [272]. A qualitative model was presented that is useful in predicting the effect of substitution and isomeric structure on the ionization potential, (π, π^*) transition wavelength, and radiationless decay rate. These properties are important since they bear strongly on the ionization efficiency.

One of the unique benefits of supersonic molecular beam spectroscopy is the narrow transition bandwidths that occur due to molecular cooling. This provides a level of optical selectivity not available by other gas phase methods. Lubman and coworkers initiated a series of experiments to determine the extent of separability attainable by molecular beam MPI mass spectrometry [269, 273-276]. They considered the optical separability of (1) structural isomers [272, 273], (2) molecules of similar mass [274], and (3) isotopic substituents [275]. Figure 25 shows that the R2PI excitation spectra for structural isomers of dichlorotoluene are dramatically different, allowing a sensitive optical means for separation that is not available by mass detection alone [272]. A similar study was conducted for the o-, m-, and p-cresol isomers [273]. These experiments were notable since they actually considered the separability of the isomers in supersonic expansions of air samples, where cooling is not as effective. Nonetheless, discrimination limits between 10^2 and 10^3 were achieved and a theoretical detection limit of 20 ppb was reported [273]. Other groups demonstrated optical selectivity for isomers without the aid of molecular beams. These include the selective ionization of either anthracene or phenanthrene using excitation at either 285 or 310 nm [247]. Another example is the selective ioniza-



tion of chrysene over triphenylene using XeCl excimer excitation at 308 nm where the two-photon energy exceeds the IP of chrysene (7.8 eV), but not triphenylene (8.1 eV) [249]. Although optically selective excitation has been emphasized in the above study of isomers, it is also possible to obtain mass selectivity by identifying different fragmentation patterns as a function of ionizing wavelength. The related challenge of separating molecules of similar or of the same nominal mass is less demanding than the isomer problem since the parent masses can often be separated and the optical and fragmentation properties tend to be more different for less similar molecules.

Isotopic separation of atoms by optical means is difficult since the shifts due to changes in the electronic states are small. In molecules, however, the isotopic shifts are due to changes in vibrational frequencies which can be reasonably large ($\geq 1 \text{ cm}^{-1}$) compared to electronic shifts. Separation of molecules containing isotopic substituents (i.e., naturally occurring ^{13}C) was demonstrated using R2PI in a supersonic molecular beam; however, these studies relied more on mass than on optical selectivity [277, 278]. Lubman and coworkers demonstrated that considerable optical selectivity was possible in a supersonic molecular beam [275]. Figure 26 shows the TOF mass spectra for the three possible isotopic combinations of 2,6-dichlorotoluene for four different (but closely spaced) wavelengths. The optical selectivity for the chlorine isotopes is reported to be of the order of 60, which enhances multiplicatively the selectivity by mass selection alone [275].

As detection limits improve, the requirements for selectivity become greater. Hence, efforts are underway to gain additional stages of selectivity from the single optical/mass methods described above. Syage and Wessel have been exploring the potential for two levels of optical selectivity using two-color double resonance excitation augmented by TOF mass detection in a supersonic molecular beam system [73, 96, 111, 279]. Several variations have been examined involving a second resonance excitation from the intermediate neutral state to discrete vibronic states that are: (1) above the IP (i.e., Rydberg auto-ionization) [73, 279], (2) below the IP (using ion dip detection [280–283]) [96, 279], and (3) in the electronic ground state using stimulated emission pumping and ion dip detection [279]. The excitation mechanism

FIG. 25. Resonant two-photon ionization spectra taken in an expansion of 1 atm backpressure of Ar of (a) 2,4-dichlorotoluene, (b) 2,6-dichlorotoluene, (c) 2,5-dichlorotoluene, and (d) 3,4-dichlorotoluene. Only the molecular ion is monitored in these spectra using a TOF mass spectrometer [272].

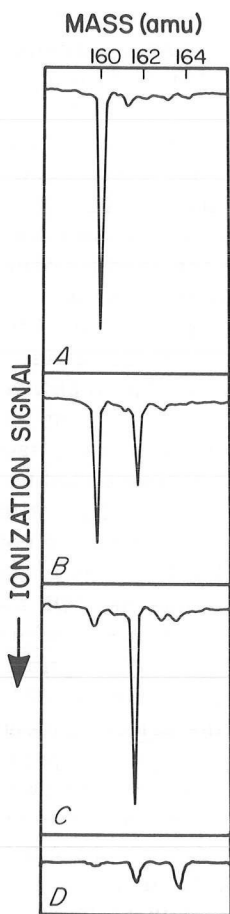


FIG. 26. Time-of-flight mass spectra of 2,6-dichlorotoluene obtained as a function of wavelength: (A) 273.812 nm, (B) 273.822 nm, (C) 273.836 nm, (D) 273.85 nm [274].

for the first two processes is portrayed in Fig. 27, and an example of the double resonance ion dip signal for aniline according to the scheme in Fig. 27(a) is illustrated in Fig. 28. This method of detection can be exceptionally selective since the ω_1 and ω_2 resonant frequencies and the detected parent ion mass are highly specific. Another double optical resonance technique has been investigated in which the parent ion is formed by one-color R2PI followed by resonance ion dissociation through a single dissociation channel (cf., Fig. 19). The second step

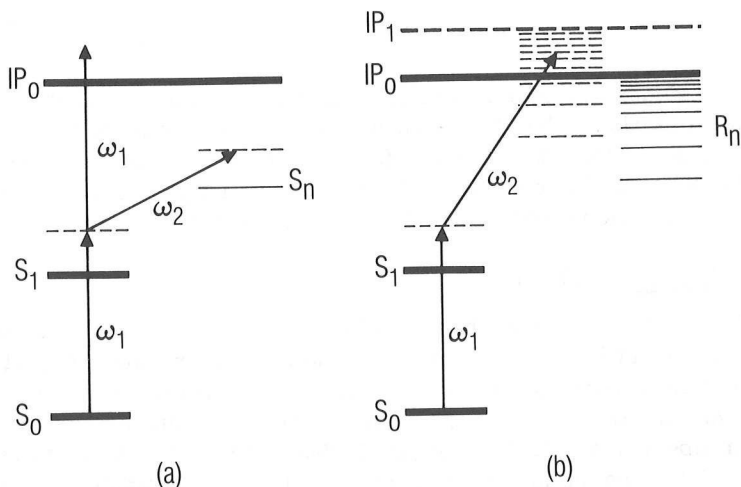


FIG. 27. Double resonance excitation scheme for higher excited electronic state and Rydberg detection. (a) Excitation to final states below the ionization potential, IP_0 , using ion dip detection. (b) Excitation to final states above IP_0 that undergo autoionization [279].

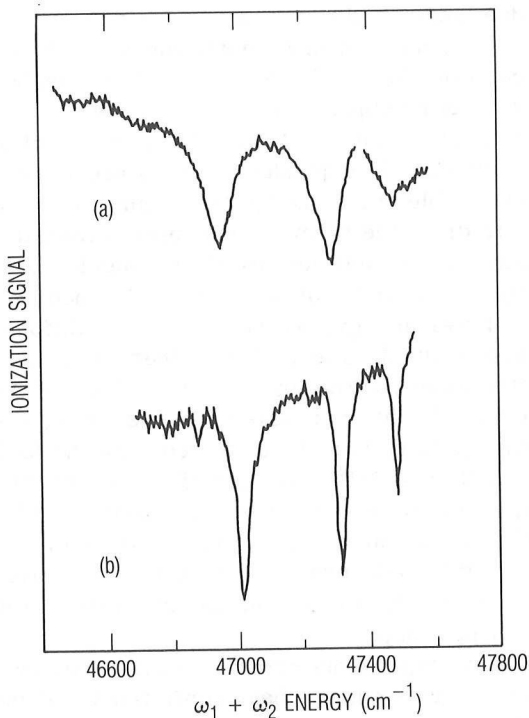


FIG. 28. Ion dip spectrum for the $S_n(v) \leftarrow S_1(v=0)$ absorption of aniline and aniline- d_5 . Ion dip intensities are plotted relative to the ion signal level in the absence of the ω_2 beam [279].

has been demonstrated for 2-methylnaphthalene using resonance UV and visible excitation. The visible absorptions in the aromatic ions are very selective since they do not occur for the neutral molecules. Resonance ion dissociation also offers double mass selectivity (parent and known fragment ion) along with the double optical discrimination.

2. Challenging Applications

Many molecules present special challenges for sensitive detection. Often, the most hazardous molecules, which demand the greatest levels of detection sensitivity, are poorly understood spectroscopically. A good example are the organophosphates and phosphonates which represent groups of insecticides and pesticides, as well as chemical nerve agents. VUV absorption spectra indicate that strong single photon absorptions occur only at relatively high energies (i.e., wavelengths of about 200 nm and shorter) [284]. This situation also characterizes many organosulfide molecules [93, 284, 285]. The spectroscopy of these compounds poses problems for sensitive detection since adequate pulse energies are difficult to generate for these wavelengths using conventional pulsed dye lasers and nonlinear crystals.

Syage, Pollard, and Cohen recently conducted a study of the spectroscopy and detection limits for a variety of organophosphonate and sulfide molecules using supersonic molecular beam, MPI, TOF mass spectroscopy [93, 284]. The 2 + 2 REMPI spectrum of diisopropyl methylphosphonate (DIMP) expanded in air is presented in Fig. 24. Since sufficient tunable pulse energy at 200 nm was not available, it was necessary to drive the formally one-photon transition using two photons. Although not an optimum excitation mechanism for sensitivity, a detection limit on the order of 50 ppb was obtained. A 1 + 2 REMPI excitation via a lower energy, but very weak and diffuse state at about 265 nm, was also studied. Interestingly, there was no resemblance in the mass spectra when exciting by these two different routes. There is some evidence that the 200-nm state may dissociate, thereby altering the fragmentation pattern in addition to reducing the ionization efficiency [93, 284]. The REMPI detection efficiency of dimethyl sulfide was, likewise, hindered by the necessity to drive an otherwise single photon transition (at 195 nm) using two photons in a 2 + 1 REMPI excitation. However, this state proved to be nondissociative over the 5 ns laser pulse, led to stable parent ion, and resulted in a detection limit on the order of 1 ppb [93].

The above case represents detection difficulties owing to unfavorable spectroscopic properties. These limitations will mostly be overcome by new developments in laser and crystal technology (e.g., broadly tunable ultrafast dye lasers and solid state lasers, β -barium

borate crystals) as well as more extensive spectroscopic studies to identify more efficient excitation methods. Another challenging application that has been attracting much interest recently are molecules that are nonvolatile (e.g., biological molecules) [269]. The objective is to develop methods that can introduce sufficient amounts of material into a photoionization source. If the molecules are thermally stable, then low volatility can be overcome using ovens or heated molecular beam valves [286, 287]. However, when the large molecules are thermally fragile, as is often the case, other methods are required. A number of successful methods include (1) thermospray deposition onto a hot surface [288–290], (2) laser desorption [258–263], and (3) supercritical fluid injection [291–294].

Thermospray deposition and laser desorption are based on the same premise, that rapid heating can volatilize a large molecule before

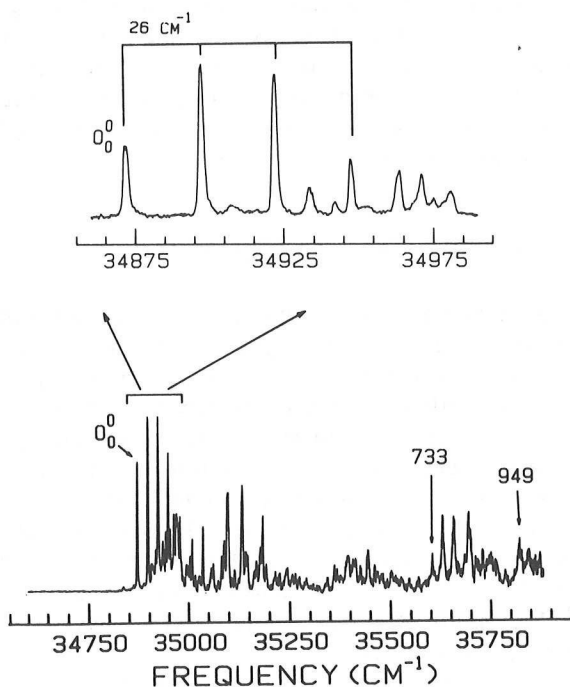


FIG. 29. R2PI excitation spectrum of tryptophan in a molecular beam using the thermospray pulsed molecular beam source. The source temperature was 230°C and the carrier gas is argon at a backing pressure of 1.4 atm [289].

it decomposes. Levy and coworkers used the former technique by injecting a solution containing the molecule of interest onto a hot surface in a molecular beam valve [288-290]. The material would then be immediately swept away by the carrier gas and expanded into the vacuum system. In this way, these investigators were able to record high resolution R2PI excitation spectra of a variety of amino acids. The spectrum of tryptophan is given as an example in Fig. 29. Lubman and coworkers demonstrated remarkable success in using laser desorption to introduce large biological molecules into a supersonic expansion for laser photoionization detection [258, 262, 263]. Using R2PI they observed only the parent ion for several polynuclear aromatic hydrocarbons as well as for adenine and cytosine [258]. For other larger and more important biomolecules, only minimum fragmentation was observed to occur [262, 263]. The use of supercritical fluid injection for a supersonic expansion was first reported by Randall and Wahrhaftig [291]. Under high pressures and low temperatures, many gases (e.g., CO_2 and N_2O) can be liquified. The supercritical fluid has the advantage of being able to dissolve many large molecules and then expand into a vacuum chamber as a gas, thereby providing supersonic cooling. Lubman and coworkers investigated this method as yet another important way to introduce polynuclear aromatic hydrocarbons and small biological molecules into a supersonic molecular beam mass spectrometer [292, 293].

VII. CONCLUSIONS AND OUTLOOK

The importance and extensiveness of MPI is inescapable. We have made no attempt to cover the field in general except as it applies to the subjects of ion fragmentation dynamics, ion spectroscopy, and molecular detection. We have also focused primarily on work of the last five years. In this period of time the area of MPI has shown a pronounced maturing; the basic mechanisms have been unraveled and now efforts along these lines stress more selective and detailed probes. It also appears that the number of studies that simply make use of MPI now exceeds the number of mechanistics studies of the process itself. The demystification of MPI has led to a broadening of its base and an increasing impact on other fields of science. Applications have become a very large part of the MPI literature.

We feel incapable of making any revelations about the future of MPI, although important new fields are certain to occur. We have not reviewed the subject of molecular clusters; however, this is one of the most rapidly growing fields using MPI. However, at this time, this field still struggles with the difficulty of probing specific cluster sizes,

particularly neutral clusters. Ionic clusters are more easily separated by mass and hence should attract considerable effort for selective studies of cluster spectroscopy and photodynamics. However, photodissociation studies of cluster ions are still rather unrefined in terms of the nonspecificity with regard to cluster size and energy, and the inability to monitor specific decay channels.

It seems reasonable to expect further refinement of experimental methods. The ability to form state-selected ions for large molecules by MPI excitation in supersonic molecular beams and to verify the ion state distributions using photoelectron spectroscopy is a very important advance. The combination of these methods should prove indispensable to the study of high resolution ion spectroscopy and photodynamics in much the same way that supersonic expansions are relied upon for molecular dynamics and spectroscopic studies of neutral molecules. Results of state-selected polyatomic ion-molecule reactions are just being reported and should generate enormous interest. Surprisingly, the use of tunable picosecond excitation on cold ions has yet to be exploited and will probably attract some future interest.

It is certain that MPI will stress applications in the future. The molecular detection work reviewed here has demonstrated that unmatched performance can be obtained by molecular beam MPI mass spectroscopy in terms of speed, selectivity, and sensitivity of detection. Development of the technique as a viable broad-based analytical tool only awaits future development of rugged, compact, and widely tunable sources of laser pulses (e.g., tunable solid state lasers). MPI is now being used for many diagnostic applications, just a few of which include studies of flame ignition and propagation, propulsion dynamics, plasma physics, and surface analysis. It is certain that applications involving MPI will continue to push along many fronts.

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NOTE ADDED IN PROOF

Although many important studies have been published since this article went to press, we reference two recent papers that report on resonance multiphoton dissociation of cold molecular ions.

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