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FUNDAMENTAL STUDIES OF MOLECULAR MULTIPHOTON IONIZATION*

by

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Fundamental Studies of Molecular Multiphoton Ionization^o

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Abstract. For several years the authors have performed fundamental studies of molecular multiphoton ionization (MPI). We will present a potpourri of techniques and results chosen to illustrate the interesting complexities of molecular MPI. Techniques used include time-of-flight mass spectroscopy, photoelectron spectroscopy, supersonic expansion cooling of molecular beams, harmonic generation, two-color laser MPI, and polarization spectroscopy. Whenever possible the relevance of these results to resonance ionization spectroscopy schemes will be delineated.

1. Introduction

Since the first observation by Veronov and Delone (1965) that tightly focusing a ruby laser into xenon could produce ions (requiring at least 11 photons), the field of multiphoton ionization (MPI) has expanded rapidly. The advent and use of powerful, tunable lasers showed that resonant enhancement at some multiple of the photon energy can increase the MPI cross section by several orders of magnitude. Consequently, detection of ions while tuning such a laser effectively maps out the energies of allowed transitions. Thus, resonantly enhanced MPI has proven to be a versatile spectroscopic tool. Several advantages of MPI include different selection rules for multiple photon absorption, freedom from many experimental difficulties of vacuum ultraviolet (VUV) spectroscopy, the translation of desirable laser properties (bandwidth, coherence, etc.) to the study of high-lying transitions and the high efficiency of ion and electron detection.

It is this last factor that spawned the subfield of resonance ionization spectroscopy (RIS) as defined and described in detail by Hurst et al. (1979). Since ions and electrons can be detected with unit efficiency, if every atom in the laser beam can be ionized with unit efficiency then "single atom detection" is possible. This can be achieved by saturating every bound-bound transition in the excitation scheme and providing a sufficiently rapid ionization. Single atom detection was first demonstrated by Hurst et al. (1977a,b) for cesium.

The extension of ultrasensitive detection techniques such as RIS to molecular systems requires a broad knowledge of conventional molecular spectroscopy and photophysics as well as an understanding of any additional complications due to the requisite use of high-powered lasers.

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In contrast to atoms, molecules possess vibrational and rotational degrees of freedom which complicate and congest electronic spectra. New channels exist for the disposition of excitation energy via these degrees of freedom. High photon fluxes may further complicate the physics and chemistry involved. Offsetting these complications in the development of molecular RIS is the possibility of isotopic selectivity as well as the very practical importance of molecular ultrasensitive detection schemes to societal problems of atmospheric pollution, detection of carcinogens, etc.

II. Experimental

Figures 1, 2, and 3 show the most recent versions of three sets of apparatus used to study various aspects of molecular MPI. The majority of the studies to be described were performed on molecular beams in the apparatus of Fig. 1 or its earlier manifestations (Compton et al. 1980, Cooper et al. 1980, Miller and Compton 1981a,b). The excitation source is an excimer-pumped dye laser (Lambda Physik EMG101/FL2000E) or its doubled or tripled output. Frequency conversion is achieved with an interactive frequency doubling system (Inrad) or by third-harmonic generation (THG) in rare gases. The THG cell is equipped with quartz and MgF₂ optics for the input and output, respectively, and contains a single electrode for monitoring MPI events in the tripling medium. A second, independent, nitrogen-pumped dye laser (Molelectron UV400/DL400) provides two-color capability with the addition of a second lens to the chamber. The molecular beam/cluster source is a pulsed, supersonic nozzle (Quanta-Ray PSV-2) capable of delivering gas pulses of 60-100 μ s duration at backing pressures up to 10 atm and a nozzle temperature of 70°C. The source is typically operated at \sim 10 Hz with a 0.5 mm aperture. The laser is triggered externally after a variable delay with respect to the valve opening.

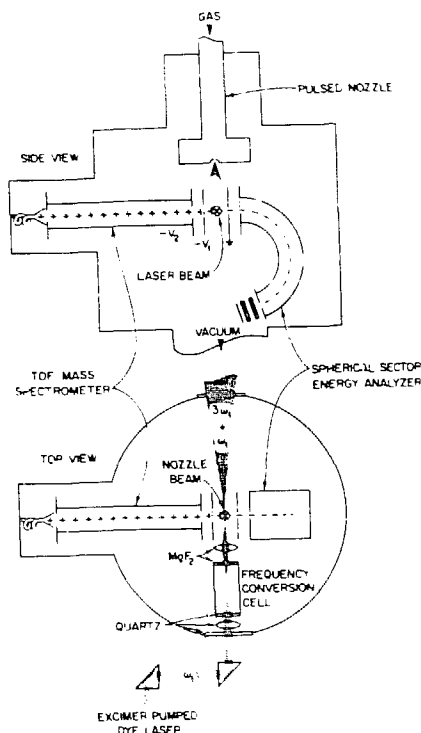


Fig. 1. Schematic of experimental apparatus.

Following either single- or multiphoton ionization the ions and electrons are detected and characterized independently and simultaneously. Ions are extracted with a small electric field and mass-analyzed by time-of-flight techniques with a resolution ($m/\Delta m$) of about 50. The electron kinetic energy distribution (i.e., the photoelectron spectrum) is determined with a 160° spherical sector energy analyzer. Energy resolution ranges from 50 to 200 meV, depending on experimental conditions (ion intensity, analyzer pass energy, etc.). Photoelectron angular distributions may be determined by eliminating the extraction fields and rotating the polarization of the laser beam about the acceptance direction of the analyzer with a double Fresnel rhomb. Signal processing can be in either an analog mode using boxcar integrators or in a digital mode using single pulse counting techniques and a multichannel analyzer. Further details of the ion and electron analysis may be found in previous papers.

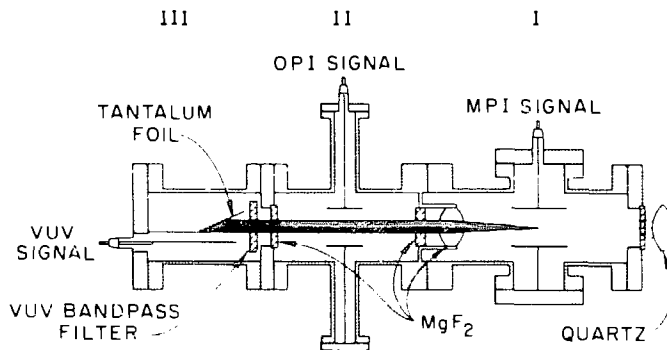


Fig. 2. Schematic diagram of the apparatus used for studies of one-photon absorption and ionization and of two-photon ionization using THG in rare gases. Chamber I is the frequency tripling cell, chamber II is the ionization or absorption cell, and chamber III is a VUV light detector. Each chamber functions as a proportional counter for detecting electrons. See text for details. Chamber I also functions as a cell for conventional MPI studies.

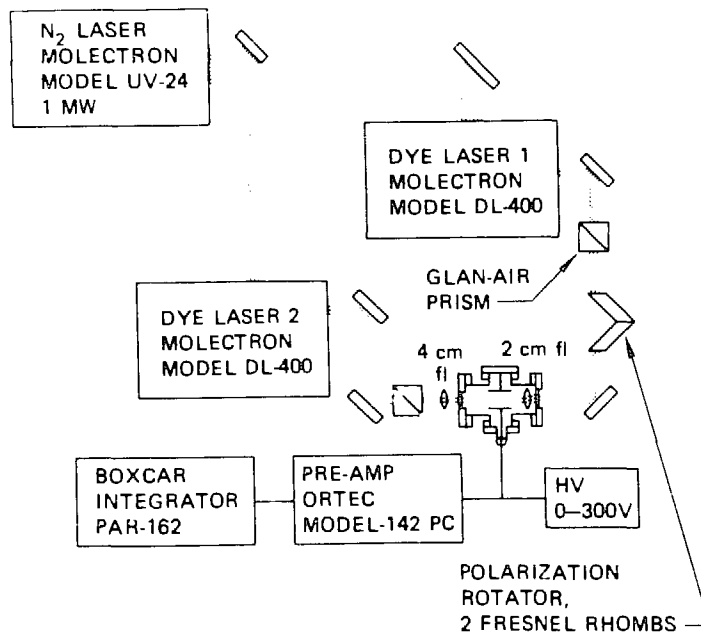


Fig. 3. Apparatus for two-color MPI experiment with the capability of polarization labeling.

The apparatus shown in Fig. 2 is used for single- or multiphoton ionization experiments in high pressure gases (0.1-1000 torr) where THG is required (Miller et al. 1982b). Conventional MPI spectra of bulk gases can also be recorded by using only chamber I (Cooper et al. 1980). The apparatus consists of three separately evacuable chambers, each of which functions as a proportional counter. Electrons produced in such a counter are accelerated toward an electrode maintained at positive bias voltages (10-500 V) and undergo ionizing collisions with other gas molecules causing an electron avalanche. The amplification produced is proportional to the ratio of electric field to pressure (E/P). The gain is finally

limited by dielectric breakdown. The beam of an N₂ laser (Molelectron UV-24) pumped dye laser (Molelectron DL400) is focused in chamber I by a 3.8 cm focal length lens to a spot $\leq 20 \mu\text{m}$, giving a power density on the order of $5 \times 10^9 \text{ W/cm}^2$. Krypton and xenon gases are used as the nonlinear medium and any electrons produced by MPI in the tripling gas are detected with the biased flat-plate electrode (Miller et al. 1980, Miller and Compton 1982a). The VUV light, produced by THG in the focal spot, is collimated with a MgF₂ lens (focal length = 4 cm) and passes through a MgF₂ window into the second chamber (II). Again, any electrons resulting from single- or multiphoton ionization are amplified in the sample gas and detected at the electrode. The VUV beam exits chamber II through a MgF₂ window and passes through a dielectric VUV bandpass filter (Acton Research) to remove the blue pump light. This filter could also be placed between chambers I and II when necessary. Chamber III is a VUV photon detector containing a tantalum foil and a single flat-plate electrode. Photons whose energy exceeds the work function of tantalum ($\sim 4.1 \text{ eV}$) eject electrons which are detected in the proportional counter. Signals from charge-sensitive preamplifiers connected to any two of the three chambers were averaged in a dual-channel boxcar integrator (Princeton Applied Research model 162/165) and displayed on a dual-channel x-y recorder and oscilloscope as a function of wavelength.

The apparatus shown in Fig. 3 has been used for two-color MPI of high pressure gases with the capability of independently varying the polarization of each laser for polarization labeling (Compton and Miller 1984) and collision studies (Compton, Snow, and Miller 1983).

III. Bound State Transitions

The concepts of RIS and single atom detection depend upon bound-bound resonances in two ways. First, these transitions allow selectivity. By tuning the laser to a specific energy level of an atom, one ionizes, and hence detects, only the atom of interest (barring accidental coincidences and using low enough laser power to eliminate nonresonant MPI). Second, these transitions must be saturated (i.e., the rate of absorption equals the rate of stimulated emission) in order to ensure unit ionization during the laser pulse. Finally, the rate of any competing processes (fluorescence, collisional processes) must be kept low as compared to the ionization rate out of the resonantly enhanced state.

Molecules present several problems with respect to these conditions. Because of the additional vibrational and rotational degrees of freedom possessed by molecules, the density of available rotational, vibrational, and electronic states is much higher than that for atoms. Because the oscillator strength is spread throughout all the available ro-vibronic levels, the laser power required for saturation of a transition from a given v and J level is correspondingly greater. Furthermore, at room temperature, the molecules are distributed according to a Boltzman distribution among the various ro-vibronic levels of the ground state. Hence, a single-frequency laser cannot access all of the molecules at any given time. These points are illustrated in Fig. 4(a) recorded in the molecular beam apparatus of Fig. 1. The spectrum shows the one-photon resonant, two-photon ionization (represented as a 1+1 ionization in the future) spectrum of NO via the $F^2\Delta(V=3)$ state of NO (Miller and Compton 1984). The extended rotational structure is primarily due to the large number of ground state rotational levels populated at 300 K. At this

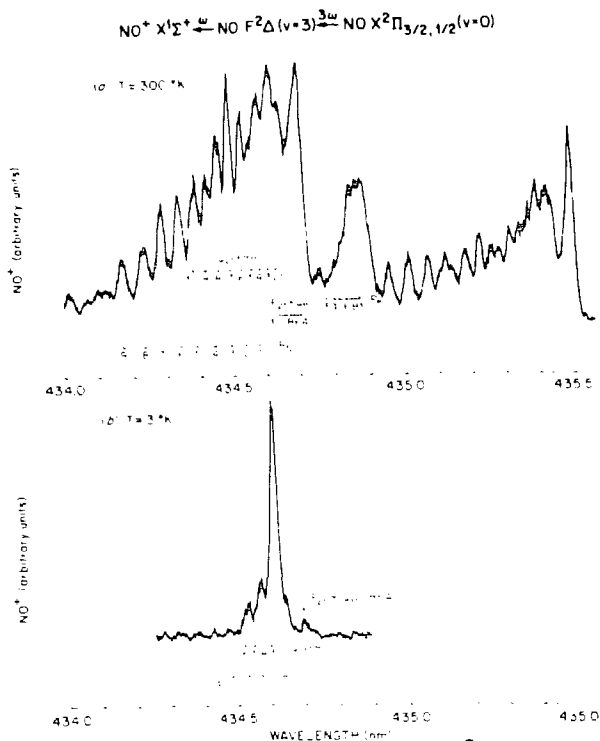


Fig. 4. MPI spectra of the $F^2\Delta(v=3)$ state of NO for (a) room temperature beam, (b) rotationally cooled beam.

temperature 34 levels are appreciably populated (>1%) with the largest number in the $J=7.5$ level of the lowest electronic state (~5%). Additionally, as the ground state is a 2π state, both the $3/2$ and $1/2$ spin-orbit components are populated as seen in the figure. The oscillator strength is spread over four to six rotational branches and a Franck-Condon distribution of five or six vibrational levels, as well as the two electronic states. Thus, the total absorption strength at a given time is reduced by a factor of 10-50 compared to a corresponding atomic transition and the distributed population reduces the sensitivity by another factor of ~20. For an RIS scheme for NO then, one would require more laser power to saturate a given ro-vibronic transition and even then would interact with only that small fraction of the molecules which happen to be in the selected ro-vibronic state at the time the laser is fired.

These factors can be improved in several ways. As shown in Fig. 4(b), the effect of rotational cooling in a supersonic nozzle is quite dramatic. Virtually all of the molecules can be cooled to the $J=1/2, v=0$ state of the $2\pi_{1/2}$ ground electronic state. Temperatures below 1 K can be obtained with more care. At this temperature, 99.85% of the molecules are in the lowest quantum state and any one-photon transition can be easily saturated thus fulfilling the RIS condition. A second way to interact with all of the molecules would be to use a broadband laser tuned to a Q branch band head such as the (P₂₁+Q₁₁) branch shown in Fig. 4(a). A laser bandwidth of about 1 Å would thus encompass all the populated J levels. This would however reduce selectivity against any interfering species which might fall within the bandwidth of the laser.

A second major problem with ultrasensitive detection of molecules involves the possibility of predissociation. Virtually all electronic states can predissociate to some degree. The effect is both to broaden the absorption line (lifetime broadening) and to provide a depletion mechanism against which the ionizing laser has to compete. Figure 5 shows the effects quite clearly. The spectrum shows the (2+1) MPI spectrum of NO via the $v=0$ and 1 levels of the $C^2\pi$ state (Miller and Compton 1981a). In Fig. 5(a) discrete rotational levels are clearly observed (in spite of a compressed scale and moderate bandwidth laser). For the $v=1$ level however predissociation to neutral $N(^4S^0)$ and $O(^3P)$ atoms dominates over ionization for high J transitions which are consequently not observed. Furthermore, all of the low J levels are broadened. Reduced sensitivity is the consequence.

The ultimate reason for seeking a bound-bound transition is to ensure selectivity. The high density of states of most molecules may make accidental spectral overlap the rule rather than the exception. For small molecules (diatomic and triatomic) diluted with other small molecules (say, in air) a region of the spectrum can probably be found which will still provide reasonable selectivity. However, as shown in Fig. 6 (Cooper et al. 1980), a large molecule has essentially a continuous spectrum and analysis of a mixture of such molecules is clearly impossible (e.g., benzene in coal tar).

IV. Photoionization and Photoelectron Spectroscopy

The last element in RIS is the final bound-continuum ionizing step. Again, for molecules new problems may arise in this process.

The relatively low ionization potential of NO allows the use of frequency tripling techniques to perform one-photon ionization experiments. The emphasis of these experiments thus shifts from

Fig. 5. MPI spectra resonant with (a) $v=0$ and (b) $v=1$ levels of the $C^2\pi$ state of NO (Miller and Compton 1981).

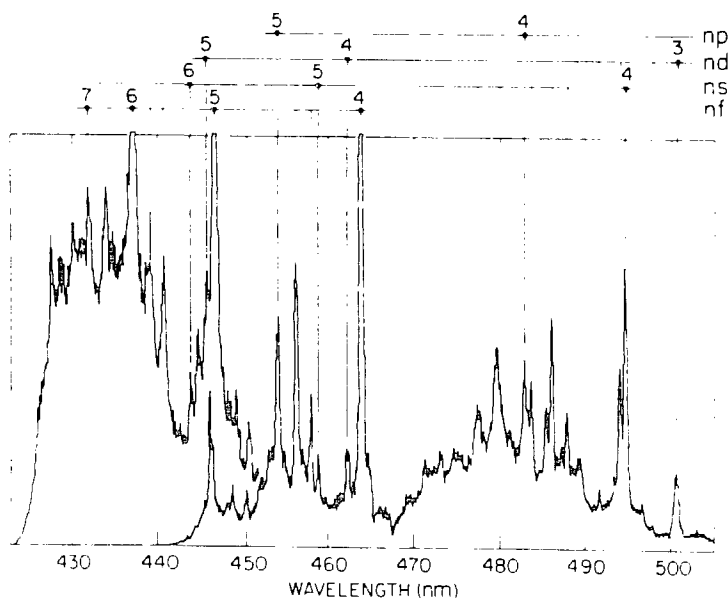


Fig. 6. Three-photon MPI spectrum of pyrrole R (ns), R (nd), and three branches of R (np) series and their vibronic structure. Peak heights do not represent relative intensities (Cooper et al. 1980).

bound states below the ionization threshold to autoionizing states coupled to the continuum. Figure 7 shows the spectrum of NO in the region of 380 to 386 nm obtained by frequency tripling of the dye laser in xenon gas near its $6s'[1/2]^0J=1$ resonance (Miller and Compton 1982a). The

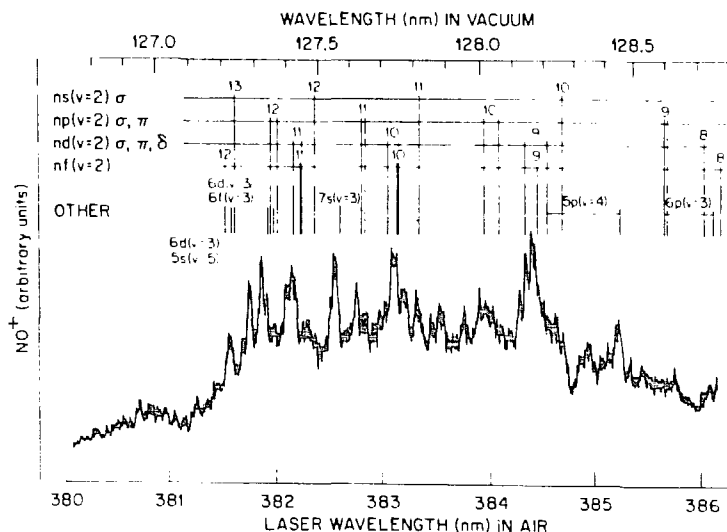


Fig. 7. One-photon photoionization spectra of a rotationally cold beam of NO excited by VUV light produced by THG.

rotational temperature of the gas is unknown but is probably in the range of 5–10 K based on rotationally resolved spectra taken under similar conditions. The positions of the absorption lines in this region and their assignment (Miescher and Alberti 1976) as listed by Ono et al. (1980) (including some calculated line positions) are given above the spectrum. This spectrum represents the highest resolution (0.007 nm) obtained for the coldest NO sample (5–10 K) reported to date. The previous work of Ono et al. (1980) used conventional light sources with a resolution of 0.014 nm and obtained a gas temperature estimated to be 20 K. Although there is a general correspondence between the spectrum of Fig. 7 and the previous absorption and photoionization spectrum a satisfactory line-by-line match is not obtained with either. The present spectrum should, however, be considered preliminary and work is continuing in this area. More careful calibration and systematic variation in the degree of rotational cooling are necessary to resolve discrepancies. Studies of other spectral regions using THG near the 5s and 5s' resonance of krypton are also possible.

The major point to be made here which is relevant to RIS is that the ionization continuum of molecules (even cooled ones) is highly structured and is composed of several parts – the true continuum due to direct ionization, an effective continuum of numerous overlapped, short-lived (hence broadened) autoionization states, and the relatively sharp, long-lived (forbidden) autoionizing resonances. It is these latter resonances whose long lifetimes allow loss mechanisms such as predissociation and even fluorescence to occur. A comparison of the absorption and ionization spectra (Watanabe 1954) show that the branching ratio between autoionization and neutral dissociation may be as large as 1:5 for NO.

Multiphoton ionization photoelectron spectroscopy (PES) is another probe of bound-continuum processes. For NO where ion fragmentation does not occur, we demonstrated that the distribution of NO⁺ vibrational levels was determined primarily by the Franck-Condon factors connecting the resonant intermediate (A²Σ⁺ or C²π) state and the ground X¹Σ⁺ ionic state (Miller and Compton 1981a, 1982b). Figure 8 gives MPI-PES spectra (2+2) for the

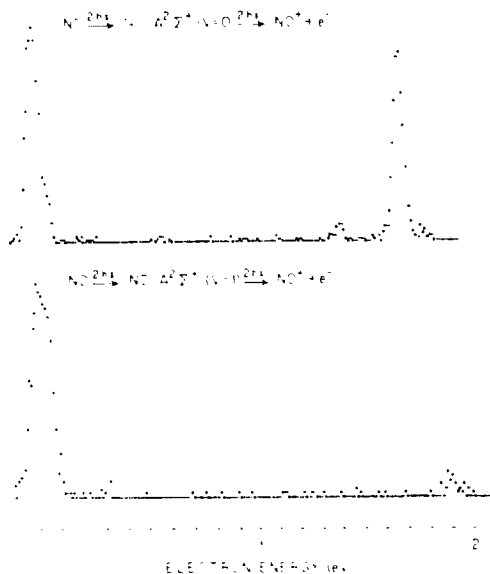


Fig. 8. Resonantly enhanced multiphoton photoelectron spectrum for four-photon ionization resonant with the $v=0$ and $v=1$ vibrational levels of the $A^2\Sigma^+$ state of NO (Miller and Compton 1982).

photon energy level. Since two additional photons are required to ionize the resonant intermediate state, resonances or near resonance in the third-photon region can allow access to different autoionizing states than direct two-photon ionization from the A state. Thus, the large near-zero energy peak was attributed to vibrational autoionization from electronic states populated by transitions originating from the three-photon excited state. Zero energy electrons are not observed when the laser is tuned to the $C^2\pi$ state or $v=3$ of the $A^2\Sigma^+$ state since the third photon is capable of ionization. Very recent results, however, involving frequency doubling in order to eliminate any near resonances, have cast some doubt on this interpretation (Miller and Compton 1984). The origin of these slow electrons is still being actively pursued. Similar MPI-PES spectra have been recorded for NH_3 , H_2 , benzene and I_2 , and provide a unique way to study autoionization and ion fragmentation.

V. Mass Spectroscopy

The addition of mass spectroscopy to studies of MPI of polyatomic molecules has shown that considerable fragmentation can accompany ionization. In particular, MPI of benzene can lead to extensive fragmentation, with C^+ being the dominant ion, while little or no parent ion is observed (Zandee and Bernstein 1979, Cooper et al. 1980, Boesl et al. 1980). Although at least six photons are energetically required to produce C^+ from C_6H_6 , the reported power indices range from 2 to 3.5. Figure 9 shows such a spectrum for several power levels. The degree of fragmentation is independent of wavelength for benzene; however, for other polyatomics (NH_3 , pyrrole, and furan) (Cooper et al. 1980, Glowia et al. 1982), the degree of fragmentation is highly dependent upon the wavelength (resonant intermediate state). In some regions of the spectrum the parent ion dominates.

Several mechanisms have been invoked to rationalize the production of small fragment ions from benzene and other molecules. In the first, multiple absorption of photons via neutral valence, Rydberg, and autoionizing states leads to superexcited states which subsequently autoionize and dissociate to produce observed fragmentation. The second mechanism

case in which two photons are resonant with either the $v=0$ or $v=1$ levels in the $A^2\Sigma^+$ state. The peaks at high energy correspond to direct ionization, leaving the ion in the $v=0$ and $v=1$ vibration levels, respectively. This single peak is expected from Franck-Condon considerations since the $A^2\Sigma^+$ state is a member of the Rydberg series converging upon the $X^1\Sigma^+$ ionic ground state and hence, these two potential curves are almost identical. We also note weaker photoelectron peaks corresponding to leaving the ion in $v=2,3,4$, etc. These peaks are probably due to electronic autoionization. The intense peak at near zero energy is of particular interest. We have attributed the peak near zero energy to vibrational autoionization as a result of the admixture of another resonant intermediate state at the third-

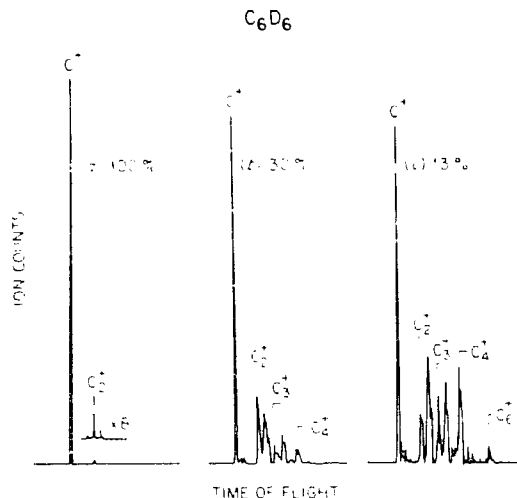


Fig. 9. Ion fragments from deuterated C_6D_6 following MPI at 390.3 nm as a function of laser power (Cooper et al. 1980).

ions must be produced from the further absorption of photons by the parent ion. Furthermore, in the case of I_2 , we were able to measure the kinetic energy for the I^+ ion which corresponded to the reaction $h + I_2^+ \rightarrow I^+ + I$ (Miller and Compton 1981b). For the larger polyatomics, the ion kinetic energies could not provide direct evidence for this model. However, in the case of NH_3 (Glownia et al. 1982) it was possible to show that the extensive fragmentation was due to photon absorption into the first excited state of NH_3^+ which is dissociative. Figure 10 shows the MPI fragmentation of ammonia using 386.6 nm laser light. However, if the laser energy is below about 3.0 eV no fragmentation is observed. At this energy an abrupt onset of fragmentation is observed which is independent of intermediate state. The energy onset for fragmentation corresponds exactly with the onset of the first excited state of NH_3^+ as shown in the one-photon PES.

The PES of the two larger molecules studied at ORNL, CH_3I and benzene, also show that fragmentation follows creation of the parent ion. A major conclusion of our MPI-PES studies is that in every case studied thus far the fragmentation is due to absorption in the ionic manifold. No evidence for absorption in the autoionization manifold has been observed in any molecule but NO where a minor ionization pathway involves absorption of one photon from an autoionizing state. The detailed physics of the ionic photodissociation processes is still under investigation.

Clearly, any proposed RIS scheme for a particular molecule will have to take into account possible fragmentation and its origin. On the other hand, fragmentation may provide a "fingerprint" of the molecule being ionized which could add selectivity to RIS.

IV. Two-Color and Polarization Spectroscopy

Two-color MPI experiments (i.e., use of independently tunable dye lasers) offer a number of significant advantages over those using a single laser. Williamson and Compton (1979) pointed to the utility of multiple-color MPI spectroscopy in a study of molecular iodine. The major such advantage is the spectral simplification which arises from selecting a single rovibronic level with the first laser. The second laser will then only interact with these excited molecules and a simple PR branch or PQR branch structure will emerge in the probe laser spectrum. This simplification is complementary to, but perhaps more versatile than, that provided by

assumes that the parent ion is initially produced by MPI, and then absorbs further photons to reach dissociative or predissociative ionic states. A third possible mechanism involves neutral dissociation followed by MPI of these fragments. Iodine, ammonia, and hydrogen sulfide are three simple systems which show intense fragment ions resulting from MPI. In each case the PES shows directly that the initial ionization step results in the formation of the parent ion, I_2^+ , NH_3^+ , and H_2S^+ (Miller and Compton 1981, Glownia et al. 1982, Miller et al. 1982a). The fragment

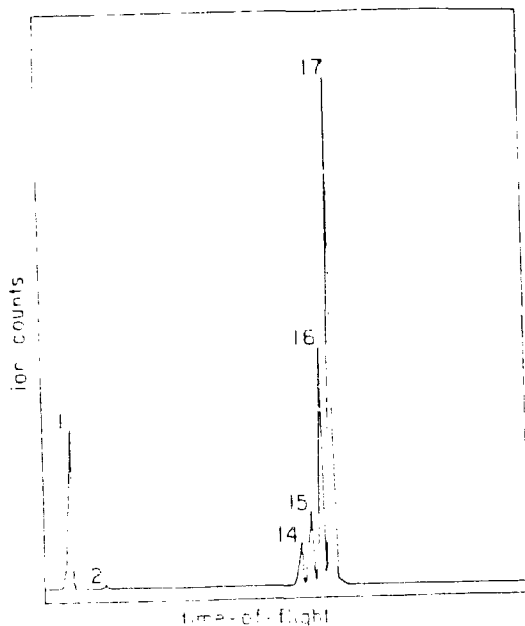


Fig. 10. Mass spectra produced by MPI and fragmentation of NH_3 molecules with 386.610 nm laser light as measured by TOF method.

VUV light from THG. Two-color MPI has also been used for collision studies of excited states of NO (Compton, Snow, and Miller 1983).

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supersonic cooling. Furthermore, by defining additional resonances in the MPI scheme (i.e., replacing virtual states with real states) the ionization cross section is increased and the experiment is better defined. Also, different selection rules may allow access to different states with sequential two-color excitation than with simultaneous multiphoton excitation. Finally, varying the relative polarization of the two lasers provides additional information about assignments. Several groups have previously published two-color spectra of NO (Ebata et al. 1983, Seaver et al. 1983). We have observed several additional two-color MPI pathways and plan to use this very powerful excitation technique to simplify and characterize PES. In addition, we hope to demonstrate two-color MPI where one excitation involves