

Multiphoton ionization of azulene and naphthalene

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Molecular beams of azulene and naphthalene are irradiated by the output of a tunable pulsed laser and the charged species produced by multiphoton ionization (MPI) are analyzed using a quadrupole mass spectrometer. A study of the ion fragmentation pattern as a function of laser power and laser wavelength permits these two $C_{10}H_8$ isomers to be readily distinguished. Compared to electron impact (EI) ionization, the MPI process can produce more gentle ionization at low laser powers and more extensive fragmentation at high laser powers. The former permits the study of azulene and naphthalene dimers from which their heats of dissociation are estimated. In the case of azulene, two-color excitation yields a mass spectrum that differs from the mass spectrum obtained by excitation with either color, alone. The ionization efficiency of MPI is very high, exceeding that of EI during the time the pulsed laser is on. A qualitative description involving autoionizing states is presented to account for this efficiency and the growth of the daughter ion yield with increasing laser power.

INTRODUCTION

The technique of multiphoton ionization (MPI) is rapidly gaining popularity in molecular spectroscopy and in chemical analysis because of its high sensitivity, based on the detection of charged species.¹⁻¹⁸ As a spectroscopic tool, MPI allows access to states forbidden in single photon excitation, makes more accessible states that could only be reached by VUV excitation, and permits the study of molecular systems having low fluorescence yields. As an analytic tool, MPI provides selective ionization of one species in a mixture in which the ion fragment distribution may be controlled by laser power and wavelength.

As in infrared multiphoton absorption,¹⁹ the successive absorption of optical photons appears also to be a highly efficient process, which is applicable to a wide class of molecules. According to recent work more than ten photons may be absorbed, leading to extensive ion fragmentation.¹⁰ These results raise the question of why MPI is so effective and what affects this efficiency.

In order to answer these questions we have undertaken a study of the MPI spectrum of the two $C_{10}H_8$ isomers azulene and naphthalene. Wavelength and power dependence studies are made and we show that one isomer can be readily distinguished from the other. In addition, low concentrations of azulene and naphthalene dimers are observed, which not only demonstrate once again the sensitivity of MPI but also the ability of MPI to ionize species in a more gentle manner than electron impact (EI). By comparing the MPI signal to that obtained by EI, an absolute efficiency can be derived for the MPI process, showing that during the laser pulse a significantly larger fraction of the species of interest can be ionized. A qualitative model involving autoionizing levels is invoked to explain the high yield of ions in the MPI process.

EXPERIMENTAL

Figure 1 shows a schematic of the experimental setup. The molecular beam machine has been described elsewhere.²⁰ It consists of a stainless steel cross to which a differentially pumped excitation/detection chamber is attached. Inside the cross is the beam source. For noncondensable gases, like glyoxal, benzene, biacetyl, and acetone, the source consists of a stainless steel tube terminating in a 25μ glass capillary array (Galileo Electro-Optics). This array allows us to maintain a large flux of molecules, typically 10^{15} molecules $cm^{-2} sec^{-1}$, while remaining within the effusive regime.

The oven for condensable substances, e.g., azulene, naphthalene, and benzophenone, consists of a stainless steel tube attached by a swagelock connection to the nozzle source. The nozzle source is a stainless steel cylinder with a 0.03 cm aperture. The cylinder is resistively heated using ac current (0-10 A). The body is heated by conduction from the nozzle source. Because the nozzle source is always hotter than the body, clogging is prevented.

The various chemicals in this study were obtained commercially and used without further purification. The

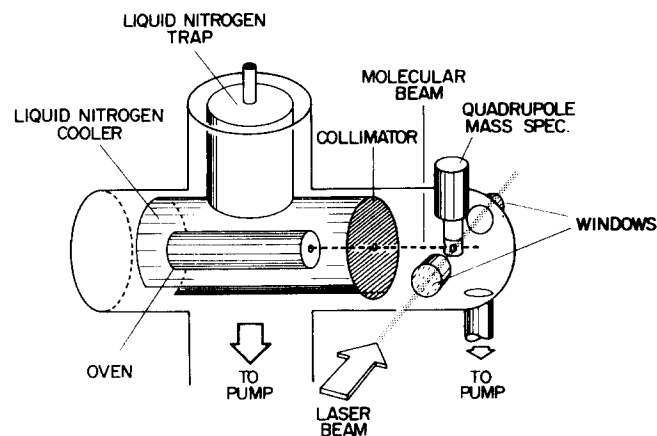


FIG. 1. Schematic diagram of the experimental apparatus.

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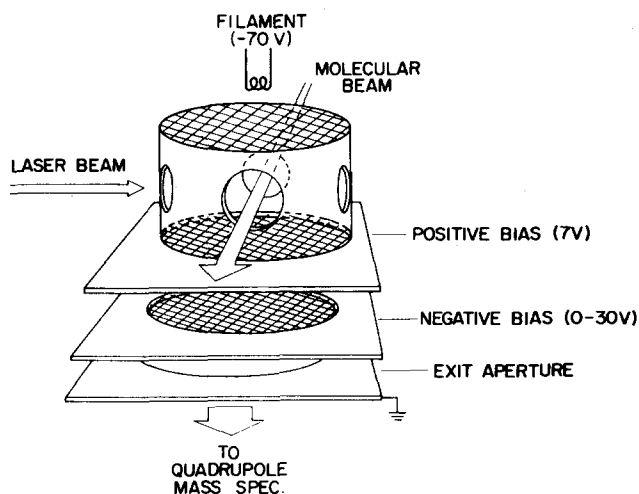


FIG. 2. Ion collection system. Both multiphoton ionization by laser excitation or ionization by electron impact can be studied.

sources are as follows: naphthalene (Fischer Scientific Co.), azulene (Aldrich Chem. Co., Inc.), benzophenone (J. T. Baker Chem. Co.), biacetyl (Pfaltz & Bauer), benzene (J. T. Baker Chem. Co.), and acetone (J. T. Baker Chem. Co.). The glyoxal was prepared from its trimeric dihydrate (Sigma Chem. Co.) before each run.²¹

Inside the excitation/detection chamber there is a quadrupole mass spectrometer (EAI Quad 200). Our ion collection system (see Fig. 2) consists of a cylindrical metal cage with two sets of ports perpendicular to one another. The beam enters the cage through one port and exits through the opposite port. The resulting multiphoton process causes ionization of the molecules in the interaction zone, located inside the cage. The cage functions as an extractor, with a variable positive bias of 7 V which deflects the positive ions through a grid toward the quadrupole mass filter. The grid is used to keep the ions moving in straight lines.²² A focusing element, which is biased negative 30 V, accelerates the ions toward the entrance of the quadrupole. The actual detection of the ions is by a channeltron electron multiplier (Galileo Electro-Optics, model 4770). In order to examine the standard 70 eV mass spectrum we used a filament mounted outside the cage, as shown in Fig. 2. The filament could be turned on and off. When desired a bare ceratron electron multiplier (Murata Corp. of America) biased at -3 kV is used to observe the total ion count.

The excitation source is a Quanta-Ray model DCR-1A Nd:YAG laser which either pumps a dye laser (Quanta-Ray model PDL-1) or is used to generate its second,

third, or fourth harmonics at 532, 353, and 266 nm, respectively. The second harmonic produces 250 mJ of energy, the third harmonic 125 mJ, and the fourth harmonic 25 mJ. The various harmonics can be conveniently separated using the Quanta-Ray harmonic separator, the main component of which is a Pellin-Broca prism.

In order to carry out "pump and probe" double resonance ionization experiments in which a second laser is needed, we use the second, third, or fourth harmonic of another model DCR-1 Nd:YAG oscillator. The two laser beams are aligned in space and a delay is set using a delay generator. The delay generator also triggers the boxcar (Princeton Applied Research, model 162 main frame, 164 plug in). For short delays (< 50 ns) one laser is used that produces both colors. One beam is delayed with respect to the other by changing the optical path.

Table I gives the dye mixtures and the wavelength ranges covered. Note that these wavelength ranges differ from the more familiar ones obtained with a nitrogen laser pump. For the generation of blue and UV light, the frequency-doubled red dyes are used. A Corning 7-54 filter passes the UV light but rejects the red light. Many experiments are carried out with an unfocused beam, but when more power is needed, a 15 cm quartz lens is used.

The signal from the quadrupole mass spectrometer is displayed on a strip chart recorder, while the mass filter is scanned slowly. The scan rate is chosen so that at least one laser shot is sampled for each mass peak. Under these conditions the duty cycle is poor compared to what could be achieved using a time of flight mass spectrometer.

RESULTS

Preliminary studies were made on a number of molecules. We are able to ionize molecules such as glyoxal, biacetyl, acetone, benzophenone, and benzene using either the third or fourth harmonics of the Nd:YAG laser. We concentrated our attention on naphthalene and azulene because these compounds have the same mass but different optical properties.

Figure 3 shows the MPI mass spectrum of naphthalene (I. P. = 8.12 eV) using both a focused and an unfocused beam at 281 nm. While the C_{10}^+ peaks dominate in both cases, the fragmentation pattern is much more extensive for the focused beam. We designate the peak conveniently by the number of carbon atoms; the presence of different numbers of H atoms causes the observed split-

TABLE I. Dyes and pumping conditions for MPI.

Dye	λ_{\max} (nm)	λ_{range} (nm)	Solvent	Concentration (mg/liter)		λ_{pump} (nm)	Power (mJ)	
				Oscillator	Amplifier		λ_{\max}	$\lambda_{\max}/2$
R590	560	543-583	Methanol	115	17	532	100	50
R640	600	591-622	Methanol	143	19	532	75	25

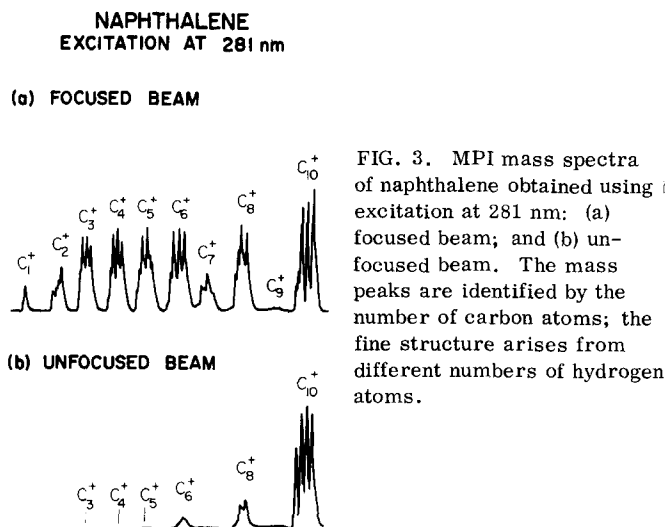


FIG. 3. MPI mass spectra of naphthalene obtained using $\lambda = 281$ nm excitation at 281 nm: (a) focused beam; and (b) unfocused beam. The mass peaks are identified by the number of carbon atoms; the fine structure arises from different numbers of hydrogen atoms.

tings.²³ Figure 4 illustrates how the fragmentation pattern changes as a function of power for an unfocused beam, when different neutral density filters (combinations of glass and quartz plates) are inserted into the beam path. The parent molecular ion peak increases at first and then decreases as the laser power is increased. When the parent ion peak begins to decrease, daughter ions appear. We conclude that saturation exists at high laser powers, even in the unfocused configuration. Increasing the laser power above the saturation threshold increases the extent of fragmentation but does not change appreciably the number of molecules ionized.

Figure 5 presents a study of the power dependence for two fragments resulting from the MPI of naphthalene. In all the power dependence studies an unfocused beam is

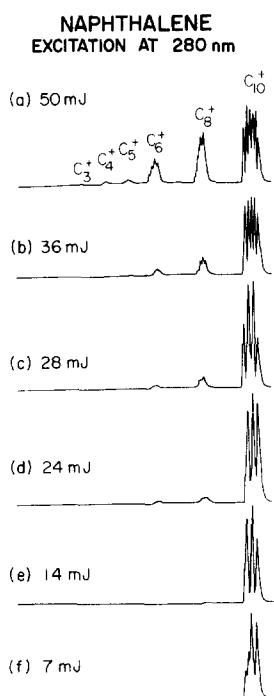


FIG. 4. Power dependence study of MPI in naphthalene using 280 nm excitation (unfocused beam).

NAPHTHALENE
 $Y \propto I^n$
 $\lambda = 280$ nm
UNFOCUSED

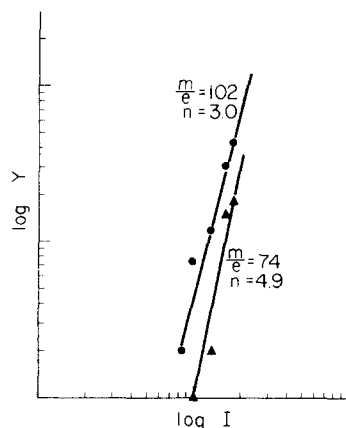


FIG. 5. Log-log plot of the ion fragment yield Y versus laser intensity I (unfocused beam) for the MPI of naphthalene at 380 nm.

used. With a focused beam the power dependence is governed mainly by geometry,²⁴ and the ion current is proportional to the intensity raised to the power of 1.5 to 2. From the power dependence in Fig. 5 we conclude that *at least* five photons are required to generate the $m/e = 74$ ion peak (C_6^+), whereas *at least* three photons are required for the $m/e = 102$ ion peak (C_8^+).

Table II presents the wavelength dependence of the ion fragmentation pattern for naphthalene. At each wavelength a focused beam is used and the power equalized to $\pm 15\%$. No dependence on specific vibronic transitions in resonance with the first pump photon is observed. However, the fragmentation pattern changes even as the laser is tuned by a few tenths of a nm.

Figure 6 shows the MPI mass spectrum of azulene ($I. P. = 7.42$ eV) for different pumping schemes at different laser powers. Whereas the unfocused fourth harmonic produces primarily the parent ion, the focused fourth harmonic produces much fragmentation once again. In contrast, the focused third harmonic produces more daughter ion than parent ion. This is also true for the second harmonic alone. For the combined second and third harmonics, the resulting two-color MPI spectrum is different from either alone.

In analogy to naphthalene (see Fig. 4), the power de-

TABLE II. Naphthalene ion fragmentation as a function of excitation wavelength using a focused beam.

Excitation	$\frac{m}{e}$	C_{10}^+	C_8^+	C_6^+	C_5^+	C_4^+	C_3^+
EI (70 eV) ^a	100	8	12	14	7	1	
303.6 nm	100	13.0 \pm 6	27.0 \pm 6	13.0 \pm 6	27.0 \pm 6	10.0 \pm 5	
301.0 nm	100	17.5 \pm 3	30.0 \pm 3	12.5 \pm 3	32.5 \pm 3	10.0 \pm 5	
299.2 nm	100	29.0 \pm 2	29.0 \pm 2	9.0 \pm 2	26.0 \pm 2	3.0 \pm 2	
298.9 nm	100	35.5 \pm 3	35.5 \pm 3	16.0 \pm 3	29.0 \pm 3	8.0 \pm 3	
298.5 nm	100	30.0 \pm 3	37.0 \pm 3	15.0 \pm 3	26.0 \pm 3	7.5 \pm 3	
286.6 nm	100	47.0 \pm 6	41.0 \pm 6	18.0 \pm 6	29.0 \pm 6	6.0 \pm 5	
286.0 nm	100	62.0 \pm 6	44.0 \pm 6	22.0 \pm 6	38.0 \pm 6	6.0 \pm 5	
266.0 nm	100	82.0 \pm 6	35.0 \pm 6	18.0 \pm 6	41.0 \pm 6	23.0 \pm 6	

^aThis work (see Fig. 2).

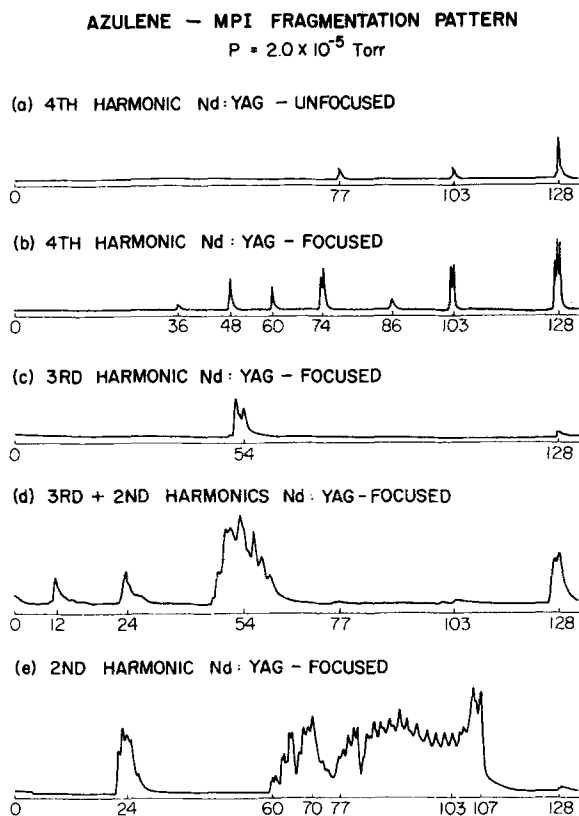


FIG. 6. MPI mass spectra of azulene using various excitation schemes (one- and two-color).

pendence of the ion fragments at $m/e = 74$ and 102 is also measured using an unfocused beam at 280 nm. In both cases a quadratic power dependence is found. The parent ion peak also shows initially a quadratic dependence on laser power, but with increasing laser power saturation occurs, as in naphthalene. Table III presents the wavelength dependence of the fragmentation pattern for azulene using the same experimental setup as in Table II.

As shown in Fig. 6, azulene is readily ionized using the second harmonic (532 nm) of the Nd:YAG laser. However, at the same wavelength no ionization of naphthalene is observed. This permits one to readily distinguish between these two isomers by their MPI spectra.

Upon close inspection of our MPI spectrum, peaks

NAPHTHALENE DIMERS
EXCITATION AT 280nm

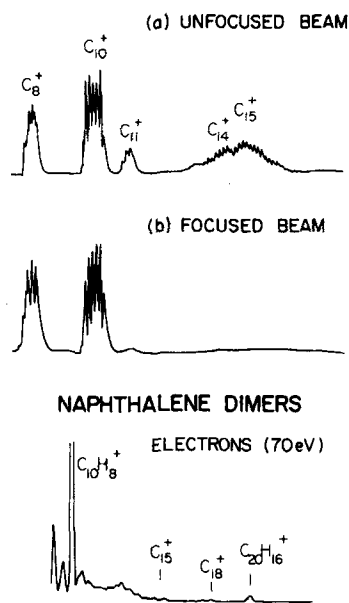


FIG. 7. MPI mass spectra of naphthalene dimers obtained using 280 nm excitation: (a) unfocused beam; and (b) focused beam. The C_{20}^+ mass peak (not shown) has been observed and its intensity is comparable to the C_{14}^+ - C_{15}^+ peaks. For comparison the EI mass spectrum is also shown. The parent ion peak is off scale and the mass scale differs.

were observed at higher masses than the parent ion (see Fig. 7). At first we suspected that they originated from impurities or pump oil contamination. However, these mass peaks are not present in the electron impact ionization spectrum to the same sensitivity, and they disappear as the power of the laser beam is increased using the focused beam. We assign these peaks as originating from the dimers of naphthalene and azulene. The detection of these dimers using the unfocused beam illustrates the "softness" of the multiphoton ionization process. The signal produced by electron impact is about four orders of magnitude smaller than with the unfocused laser beam.

Since we use an effusive molecular beam, the dimers in the beam reflect the concentration of dimers in the oven. We studied the dimer fragment ion signal as a function of oven temperature (see Fig. 8). We find the following heats of dissociation:

$$\Delta H_{d1s}(\text{azulene dimer}) = 5 \pm 1 \text{ kcal/mole}$$

and

$$\Delta H_{d1s}(\text{naphthalene dimer}) = 4 \pm 1 \text{ kcal/mole ,}$$

TABLE III. Azulene ion fragmentation as a function of excitation wavelength using a focused beam.

Excitation	$\frac{m}{e}$	C_n^+								
		C_{10}^+	C_8^+	C_7^+	C_6^+	C_5^+	C_4^+	C_3^+	C_2^+	C_1^+
EI (70 eV) ^a	100	14	4	27	20	3	11	6
355.0 nm	100	650
286.6 nm	100	71	21	67	50	71	29	4
280.7 nm	100	64	18	70	57	68	50	4
280.0 nm	100	59	23	68	50	64	45	4
266.0 nm	100	65	...	17	61	30	48	59
355.0 nm + 532.0 nm	100	176	...	59	53	...

^aThis work (see Fig. 2).

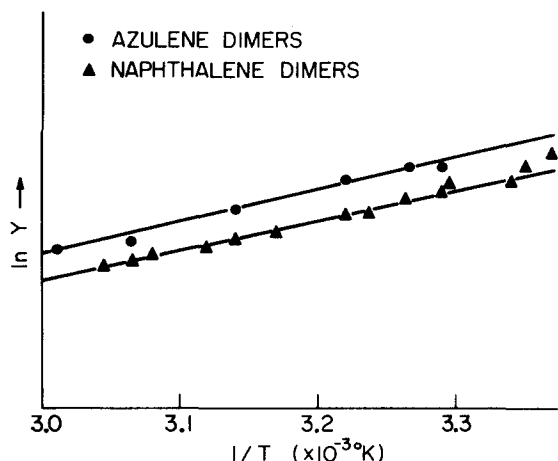


FIG. 8. Plot of the logarithm of the yield Y ($m/e=154$) for ions from azulene and naphthalene dimers versus the reciprocal of the absolute temperature. Both the monomer and dimer concentrations change with temperature; the yield Y is normalized to the parent ion peak (C_{10}^+).

where we ignore possible changes in ionization efficiency with internal excitation of the dimer as the temperature of the source is varied. With a reasonable estimate of the entropy of dimerization it would appear that less than 1% of the effusive beam contains dimers. However, as seen in Fig. 7, the dimer MPI signal is about 5% of the monomer, indicating that the unfocused laser beam ionizes the dimer with a much larger efficiency than the monomer.

The use of a two-color ionization scheme has also been investigated. For azulene we use the bare channeltron to detect total ion current. No significant ionization is observed with the unfocused second or third harmonics of the Nd:YAG laser alone. However, when the two beams are combined both in time and in space a very strong signal results. The second harmonic is in resonance with the first excited singlet state (S_1) and the third harmonic with the second singlet state (S_2). Two possible mechanisms appear plausible: (1) resonant pumping to S_1 followed by two UV photon ionization; or (2) resonant pumping to S_2 followed by two visible photons or visible photon plus UV photon ionization. If the two laser beams are delayed so that there is no overlap between them, then no ionization is produced. The same investigations have been carried out on benzophenone. Here we use the third harmonic (low power) to excite the molecule to S_1 . After a variable delay the same harmonic from a second laser is passed through the excitation/detection cage. Again no signal is observed when the two beams do not overlap. It is also worth noting that Antonov *et al.*¹² investigated the ionization of benzophenone using a dye laser to pump S_1 , and an H_2 laser to cause ionization. They also observe a signal only if the two laser pulses overlap.

Finally, a comparison is made of the MPI technique with electron impact (EI) mass spectrometry. Our experimental setup allows both to be studied under identical conditions.²⁵ With the electron flux inside the cage

at 0.2 mA we observe a signal height which we define as one unit in the case of naphthalene. Using the laser excitation at 280 nm (50 mJ 10 Hz), the corresponding signal is 10^{-4} units. However, the duty factor of the laser is 6×10^{-8} . Therefore, the fraction of the beam ionized by the laser when it is on is some 1700 times larger than by EI. For some purposes it is useful to speak of phenomenological cross sections for MPI. If one assumes a quadratic power dependence, then the cross section is found to be 4.4×10^{-21} cm², based on an assumed EI ionization cross section of $\sim 2 \times 10^{-15}$ cm². Although the MPI process depends on both laser wavelength and laser intensity, the above estimate shows that the ionization efficiency for MPI can readily exceed that of EI if both have the same duty factor.

DISCUSSION

By choosing two molecules of identical mass, we are able to assess the potential of multiphoton ionization (MPI) for chemical analysis. Our data on azulene and naphthalene show that one can readily distinguish these isomers. Moreover, the MPI process is extremely sensitive and has the capability of selectively ionizing species as a function of laser wavelength or wavelengths (multicolor schemes). In addition, the fragmentation pattern, which dramatically differs from that of electron impact (EI), can be varied from the parent ion to fragments as small as CH_n^+ by increasing the laser power.

We have also examined the efficiency of the MPI process by comparing it to EI using the same experimental arrangement. MPI is more efficient than EI in ionizing the gas sample during the time of the laser pulse. This high efficiency cannot be explained by direct excitation into a photoionization continuum. Instead, our data support the hypothesis of Bernstein²⁵ and others² that the MPI process proceeds through resonant or near-resonant autoionizing states that are connected to each other by electric dipole transitions, which we call the "autoionization tree." Autoionization states are known to play often the dominant role in ion production. Because the density of autoionizing states increases with energy, the resonance condition becomes more readily satisfied, enhancing the pumping rate to cause fragmentation.

Our two-color laser experiments further support the concept of an autoionizing tree, as opposed to subsequent pumping of parent ions and their first daughter ions or neutrals. We found in azulene that the simultaneous excitation by the second and third harmonics of the Nd:YAG laser produced an altogether different ion fragment pattern than excitation by either harmonic alone. If only "colored" ions or neutrals were involved in producing the smaller fragment ions, then the simultaneous excitation by both harmonics would have resulted in a superposition of their individual MPI spectra. Because an autoionizing tree is involved, it is easy to understand how the fragmentation pattern changes with laser wavelength and with laser power. The latter implies that the rate of up pumping (climbing to higher branches) is faster than the rate of autoionization (twig snapping).

The two-color setup also allows us to investigate the role of electronic relaxation in the intermediate state by delaying one color with respect to the other. In both benzophenone and azulene we observed no ion production when the two colors did not overlap in time. Two explanations are possible. Either electronic relaxation causes the second color to be ineffective in climbing the autoionization tree, or the resonant pumping by the first color of S_1 does not start the ascent of the autoionization tree. In the case of benzophenone, the intersystem crossing lifetime is about 100 nsec,²⁰ and the delay of the second laser with respect to the first was varied from less than 10 nsec to more than 1 μ sec without ion production. Thus, we conclude in the case of benzophenone that pumping S_1 does not initiate the MPI process. This also explains the similar observation by Antonov *et al.*¹² However, in the case of azulene we were not able to delay the two lasers on a time shorter than the radiationless lifetime of S_1 and thus no conclusion can be reached. It would seem that such studies on other molecular systems would be a fruitful area of research.

The concept that the MPI process can in some cases be pictured as the climbing of an autoionization tree also helps to explain the difference between EI and MPI. Because only a specific branch is selected in MPI, the distribution of fragment ions need not follow the quasi-equilibrium theory,²⁶ which has enjoyed some success in predicting the EI fragmentation pattern. The intensity-dependent studies reported in this work prove that coherent excitation, in which more than one photon is absorbed simultaneously, can control the overall rate of ion production. Consequently, for many molecular systems a simple stochastic model of MPI involving master equations appears not to be adequate in simulating the observed phenomenon. The nonlinear intensity dependence of the fragment ions in the case of naphthalene (see Fig. 5) further supports the model of an autoionization tree, although there is no *a priori* reason to expect that the MPI mechanism need be the same for all molecules.

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²²J. Millman, *Vacuum-Tube and Semiconductor Electronics* (McGraw-Hill, New York, 1958). The low bias voltage suppresses additional ionization from secondary electrons. Under our pressure conditions, ion-molecule reactions are negligible.
²³We can resolve individual peaks so that the valley is at least 10% of the average adjacent peak heights. Since the increase in resolution is achieved at a loss in sensitivity, the spectra

reported here are taken under low resolution.

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²⁵A similar study was performed by L. Zandee and R. B. Bernstein [*J. Chem. Phys.* **71**, 1359 (1979)], in the case of

benzene. They found comparable efficiencies for the MPI and the EI process. We are grateful to R. B. Bernstein for communicating this work to us prior to publication.

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