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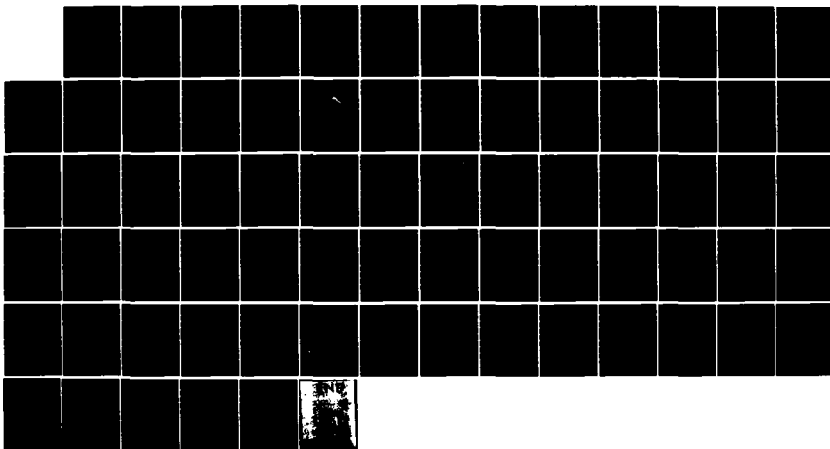
MULTIPHOTON IONIZATION MASS AND PHOTOELECTRON
SPECTROSCOPY(U) INDIANA UNIV AT BLOOMINGTON J P REILLY
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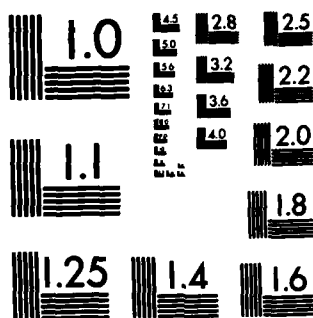
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 17997.14-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Multiphoton Ionization Mass and Photoelectron Spectroscopy		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 Jun 81-31 May 84
7. AUTHOR(s) James P. Reilly		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Indiana University		8. CONTRACT OR GRANT NUMBER(s) DAAG29-81-K-0097
11. CONTROLLING OFFICE NAME AND ADDRESS S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709 MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
		12. REPORT DATE Jul 84
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Multiphoton Ionization
Photoelectron Spectroscopy
Laser Induced Ionization
Ultraviolet Laser Radiation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The experiments that have been performed are of two types. Using a time of flight mass spectrometer, the molecular ions generated by laser ionization have been monitored. Using a time of flight photoelectron spectrometer, the kinetic energy distribution of the electrons simultaneously ejected have also been monitored. The mass spectrometric experiments can be further subdivided into two types. First, those in which samples were introduced via a capillary column gas chromatograph inlet system. Second, those involving laser ionization of molecules adsorbed to metal surfaces.

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FINAL REPORT

MULTIPHOTON IONIZATION MASS AND PHOTOELECTRON SPECTROSCOPY

U. S. ARMY RESEARCH OFFICE

CONTRACT NUMBER: DAAG29-81-K-0097

INDIANA UNIVERSITY

June 1, 1981 - May 31, 1984

PRINCIPAL INVESTIGATOR: JAMES P. REILLY

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Statement of research problem:

Laser induced ionization has been recognized for several years as an extremely sensitive method for detecting atoms in the gas phase. The question naturally arises whether an equivalently sensitive method for detecting molecules can be devised based on this same phenomenon. In order to find out, we have been investigating the two step ionization of molecules induced by ultraviolet laser radiation. From this work we are able to extract information about molecular spectroscopy, photochemistry, and photophysics.

The experiments that we have been performing are of two types. Using a time of flight mass spectrometer constructed during the grant period we have monitored the molecular ions generated by laser ionization. Using a time of flight photoelectron spectrometer also constructed during the grant period we have monitored the kinetic energy distribution of the electrons simultaneously ejected. Our mass spectrometric experiments can be further subdivided into two types. First, those in which samples were introduced via a capillary column gas chromatograph inlet system. Second, those involving laser ionization of molecules adsorbed to metal surfaces.

Summary of important results:

Detailed discussions about the laser ionization experiments that we performed during the grant period are presented in the attached reprints. The most significant results will now be summarized.

I. Laser mass spectrometry experiments

A. Gas chromatography/mass spectrometry

An apparatus interfacing a gas chromatograph with a mass spectrometer was constructed for the first time. A series of aromatic hydrocarbons were introduced into the system. They all ionized, but with a rather wide range of efficiencies. Detection limits in the multi-femtogram realm were obtainable. Light molecules that cannot be electronically excited in the near ultraviolet and that have relatively large ionization potentials are not detectable. Isomers such as chrysene and triphenylene which are very difficult to distinguish using conventional analytical methods are readily distinguishable by laser ionization due to only a few tenths of an electron volt difference in their ionization potentials.

In experiments not yet published we attempted to investigate the simulant DMMP. We find that it ionizes very poorly at 2300 Å, undoubtedly due to its extremely small molar extinction coefficient. Future experiments with this molecule should probably be done with an ArF excimer laser.

When benzaldehyde is laser ionized at 2590 Å, only $C_6H_5^+$ ions are generated. By monitoring both these ions and the photoelectrons simultaneously ejected (see below) we were able to show that this is a consequence of a photochemical rearrangement that occurs in the excited state molecule following absorption of one photon but before ionization by a second photon.

B. Surface Ionization

By proper choice of grid potentials in our laser mass spectrometer ionization of molecules at metal surfaces can be distinguished from that occurring in the bulk gas phase. Surface ionization peaks appear much sharper than their gas phase counterparts. Thus far we have not been able to confirm whether the surface ionization signal has a characteristic wavelength dependence, or if the ionization phenomenon is simply thermal. We have conflicting evidence on this subject. One rather remarkable result is that a series of equally spaced mass spectral peaks can be obtained when a monochromatic UV laser beam impinges on a flat metal surface at grazing incidence. We have shown that this results from standing electromagnetic waves formed reproducibly above the surface during every laser pulse. No practical applications of this phenomenon have been developed. Surface ionization may be of interest to ARO due to the low volatility of agents and the possibility that they could be efficiently collected and then ionized on metal surfaces.

II. Laser photoelectron spectrometry experiments

In this part of our work we monitored not the ions but the electrons generated during the laser ionization process. We found that the electrons are produced with certain discrete kinetic energies, given by the following modified version of the usual photoelectron spectroscopy formula:

$$KE = nh\nu - I.P. - E_{ion}$$

Since in all of our hydrocarbon studies $n = 2$ and the ionization potential of the molecule being probed was fairly well known we extracted information about ion vibrational energy levels. Molecules studied include benzene, toluene, aniline, paradifluorobenzene, nitric oxide, benzaldehyde, acetophenone and DMMP. The benzene study was particularly significant since vibrational spectroscopic information about $C_6H_6^+$ is particularly sparse due to idiosyncracies of its excited states. The long-predicted Jahn-Teller splitting was observed for the first time during these experiments.

Selection rules associated with the photoionization process were also investigated and experimentally verified. This was particularly significant in the case of the rotational selection rule probed by photoionizing NO, since a rotationally resolved photoelectron spectrum of a molecule other than H_2 had not previously been recorded.

As mentioned above photoelectron data enabled us to confirm the mechanism by which $C_6H_6^+$ ions are generated during benzaldehyde irradiation. Photoelectron experiments are beginning to play a role in monitoring other chemical dynamics processes. For example in the case of paradifluorobenzene when vibrational levels 3000 cm^{-1} above the origin of the S_1 state are laser excited, the resulting photoelectron spectrum exhibits considerable congestion, presumably due to rapid intramolecular vibrational relaxation occurring before the ionization step. Future experiments in this area will need to be performed with substantially better time resolution than the two nanoseconds available to us from our excimer pumped dye laser.

The scientific implications of our laser ionization work can best be appreciated by perusing the attached papers. The precise operating conditions and final conclusions from all of our experiments are thoroughly elucidated therein. It is quite clear that whether or not some particular compound of interest can be detected with great sensitivity by exploiting laser ionization depends on a variety of molecular characteristics. The latter are discussed in these papers. Since for most molecules the information needed to make reliable predictions is not available, laser ionization efficiencies must be established experimentally rather than theoretically.

Publications based on this research grant:

1. J. T. Meek, S. R. Long, and J. P. Reilly, "Observation of polyatomic ion vibrational state distribution by laser photoelectron spectroscopy", J. Phys. Chem. 86, 2809 (1982).
2. G. Rhodes, R. B. Opsal, J. T. Meek, and J. P. Reilly, "Sensitive and selective detection of molecules with ultraviolet laser ionization gas chromatography/mass spectrometry", Analytical Chemistry 55, 280 (1983).
3. J. T. Meek, S. R. Long and J. P. Reilly, "Laser ionization photoelectron spectroscopy", Proceedings of the Howard University Conference on Lasers as Reactants and Probes in Chemistry (May 1982).
4. J. T. Meek, S. R. Long, R. B. Opsal and J. P. Reilly, "Laser ionization studies of gas phase and surface adsorbed molecules", Laser Chemistry 3, 19 (1983).
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12. J. P. Reilly, "Laser Photoelectron Spectroscopy", (accepted by Israel J. of Chemistry).

Scientific personnel supported during this grant period:

Principal Investigator: James P. Reilly (summer salary)

Postdoctoral Researchers: Dr. Randy Long
Dr. K. S. Viswanathan
Dr. Warren Wilson

Graduate Students: Dr. Jon Meek (Ph.D. Dec. 1983)
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Laser mass spectrometry

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Abstract

The conjunction of laser induced molecular ionization with mass spectrometry is particularly fortuitous since it enables us to learn more about the former phenomenon by exploiting the latter technique while at the same time we may be able to improve the latter technique by exploiting some of the unique properties of the former phenomenon. One of the most significant features is the potential impact that laser ionization mass spectrometry may have in analytical chemistry. In order to better measure this, we have investigated the ionization efficiency of a variety of organic compounds.

The combination of a capillary column gas chromatograph with a laser ionization mass spectrometer is found to be an ultrasensitive and selective method of chemical analysis. Polyaromatic hydrocarbons can be detected at the multi-femtogram level with parts per trillion sensitivity. In some cases previously unresolvable isomers are readily distinguished. Complementary laser photoelectron experiments have been conducted. While these were originally designed to elucidate ionization and mass spectral fragmentation mechanisms, they are now generating a vast array of new ion spectroscopic data. Our recent results in the previously unexplored area of UV laser induced surface ionization are discussed and their relevance to mass spectrometry is considered.

Introduction

The development of sensitive and selective molecular detection schemes is one of the prime goals of analytical chemists. Much of the success of gas chromatography can be attributed to the existence of detectors which respond particularly well to certain molecules or subgroups and not to others. Ion specific electrodes play an analogous role in electrochemistry. The prospect of selectively ionizing a particular molecular species present in a gaseous mixture is similarly attractive. Because ions can be so easily collected and counted, if the ionization process is efficient, the detection sensitivity will be excellent. Two methods of laser induced photoionization are worth considering. Single photon ionization is simple, causes little or no ion fragmentation and ion currents are straightforwardly interpretable. However as a molecule detection scheme it suffers from a few disadvantages. The short wavelengths of light required (typically below 1200 Å) are inconvenient to handle because of air and window absorption. The only coherent radiation source in this region of the spectrum, the molecular H₂ laser, is rather weak and it operates at a relatively long wavelength (by photoionization standards). A weak light source reduces ionization efficiency because the probability of light absorption is proportional to the product of light intensity and absorption cross section. Finally, since countless molecules absorb and have their ionization thresholds in the 1000 to 1200 Å region, the selectivity of this ionization process is limited.

An alternative photoionization method involves multiphoton or stepwise processes. The most efficient of these is of course two-photon ionization through a resonant intermediate state. This has several advantages over its single photon counterpart. First, the light wavelength can be in the near ultraviolet. This is transmitted by air and numerous optical materials. Second, very intense, easily operated rare gas halide excimer lasers are commercially available which emit radiation at a variety of frequencies within this spectral region. Their light outputs enable one to saturate many molecular electronic transitions and thereby boost their ionization probability. Finally the existence and influence of resonant intermediate states (and other effects to be discussed) cause the ionization probability to fluctuate enormously from one organic molecule to another and this dramatically enhances the selectivity of two-photon ionization.

In a laser mass spectrometer, the conventional electron impact ionization source is replaced by an interaction zone where focussed laser radiation impinges on low pressure gaseous molecules. The ions generated are usually mass resolved by time of flight, since with this technique all of the ions produced by a single laser pulse can be detected. Recent developments in the field of laser ionization mass spectrometry point to a growing role for this technique in the field of chemical analysis. While the earliest suggestion to combine laser ionization with mass spectrometry involved single photon photoionization with vacuum ultraviolet lasers,¹ recent interest has focused on multiphoton ionization processes involving near ultraviolet light sources.²⁻⁴ Laser ionization of atoms has been particularly prominent following the demonstration of single atom detection sensitivity.⁵ Molecular

ionization studies have been motivated more by spectroscopic than analytical goals.⁶⁻⁸ This distinction between atoms and molecules deserves comment. Molecules are certainly harder to detect by laser ionization than are alkali atoms. The former have weaker absorption cross sections and, when excited, can undergo numerous rapid radiationless deactivation or dissociative processes which atoms cannot. Furthermore the ionization potentials of molecules are two or three times higher than those of alkali atoms. For efficient ionization, this requires shorter wavelengths of ultraviolet laser light. As a result background ionization is invariably a more severe problem than it is when ionizing alkali atoms with visible dye lasers. Nevertheless, in spite of these complications we have recently been making substantial progress in demonstrating the analytical utility of laser ionization mass spectrometry.⁹⁻¹⁰ In one of our major projects, we interfaced a capillary column gas chromatograph to our homemade time of flight laser mass spectrometer (see Figure 1).

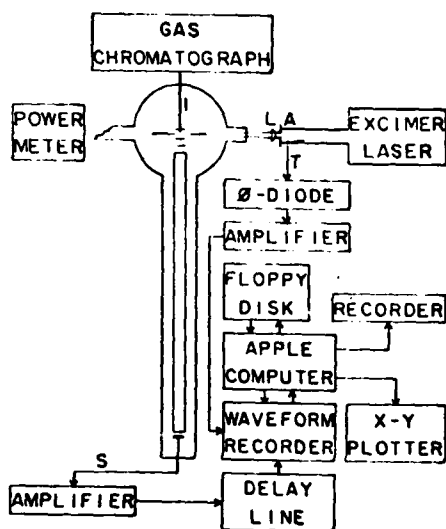


Figure 1. Block diagram of the laser ionization GC/MS apparatus

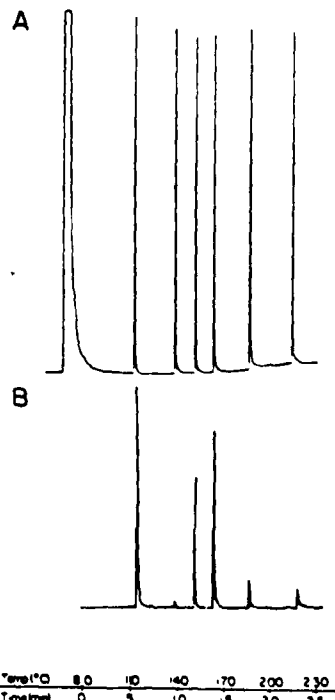


Figure 2. Chromatograms of a polyaromatic hydrocarbon mixture. A: 30 ng each of naphthalene, biphenyl, acenaphthene, fluorene, anthracene and pyrene with a flame ionization detector. B: 500 pg of same compounds with laser ionization detector, monitoring total mass-integrated ion yield

We demonstrated 200 femtogram sensitivity for detecting naphthalene, and between 0.23 and 5.0 picogram sensitivity for polyaromatic hydrocarbons like biphenyl, acenaphthene, fluorene, anthracene, phenanthrene, and pyrene. As an example of the performance of this system Figure 2 exhibits a gas chromatogram of a mixture of 30 ng each of these compounds taken with a conventional flame ionization detector and a chromatogram of a mixture of 20 picograms each of the same compounds recorded with our laser GC/MS system. It is noteworthy that the methylene chloride solvent yields a strong overwhelming initial peak in the FID chromatogram but no peak at all with laser ionization, due to the selectivity of the phenomenon. It is also apparent that detection sensitivity varies greatly from one compound to the next in contrast with FID. This characteristic will be examined below. The linearity of integrated ion yield as a function of sample size was found to be good over a dynamic range of almost five orders of magnitude. One of the remarkable aspects of this study is that our observed detection sensitivity is within an order of magnitude of that which one would predict by the following rough calculation. If λ molecules are injected into a gas chromatograph and they are eluted in a peak having a width of t seconds through an orifice of area A with typical gas kinetic velocity v the average molecular concentration,

c. is then

$$c = \frac{1}{A} \times \frac{1}{t} \times \frac{1}{v} \text{ (molecules/cm}^3\text{)}$$

If the laser cross section is about 1 mm^2 , then 10 mJ of ultraviolet radiation represents a fluence of about 10^{18} photons/ cm^2 which should ionize 10 to 100% of the molecules within the focal volume. For a 1 mm^3 focal volume, at least 10^{-4} c ions per laser pulse are therefore expected. Wessel et al.¹¹ have recently demonstrated that a concentration of about 10^4 naphthalene molecules/ cm^3 is detectable by laser ionization in a cell experiment. With our proposed gas chromatograph using reasonable parameters in the above equation, this would correspond to $\chi = 1 \times 10^7$ molecules ($5 \times 10^{-15} \text{ g}$ at $\text{MW} = 150$) injected into the G.C.. With a 100 Hz laser one would expect about 10^3 ions to be generated from a sample of this size. This is an easily detectable signal. It should be emphasized that this estimate would be even more attractive with higher repetition rate lasers and a less conservative estimate of molecular ionization probability. It is worth stressing, as Lovelock has pointed out years ago,¹² that the theoretical detection limit of a gas chromatograph is determined both by sample ionization efficiency and by carrier gas background ionization. While electron capture detectors are extremely efficient, they induce considerable background ionization. A laser ionization detector may offer the former advantage without the latter problem.

While the ultimate sensitivity of the laser GC/MS system clearly establishes it as a technique with a future, the selectivity of the laser ionization phenomenon is what really sets it apart. As sensitivity improves selectivity is needed to prevent the saturation of any detector. This is particularly true when femtograms of material can be detected. For example it has been estimated that on the order of 100,000 compounds are present in the air at a level of 10 parts per trillion or more.¹³ (This concentration corresponds to about 25 femtograms per cubic centimeter for each species). A number of variables contribute to laser ionization selectivity. These include laser wavelength (in relation to the energies of resonant intermediate states), excited state lifetime, and molecular ionization potential.^{2,14} As an example of the application of this selectivity to a difficult analytical problem, we studied a pair of $\text{C}_{18}\text{H}_{12}$ isomers, chrysene and triphenylene. These compounds have virtually identical electron impact mass spectral fingerprints and yield overlapping peaks in capillary column gas chromatography. They are thus difficult to distinguish with conventional techniques. However through proper choice of laser wavelength we were able to establish conditions such that chrysene ionized and triphenylene did not, (see Figure 3). At other wavelengths both compounds ionize so quantitative analysis of a mixture containing the two species is possible.

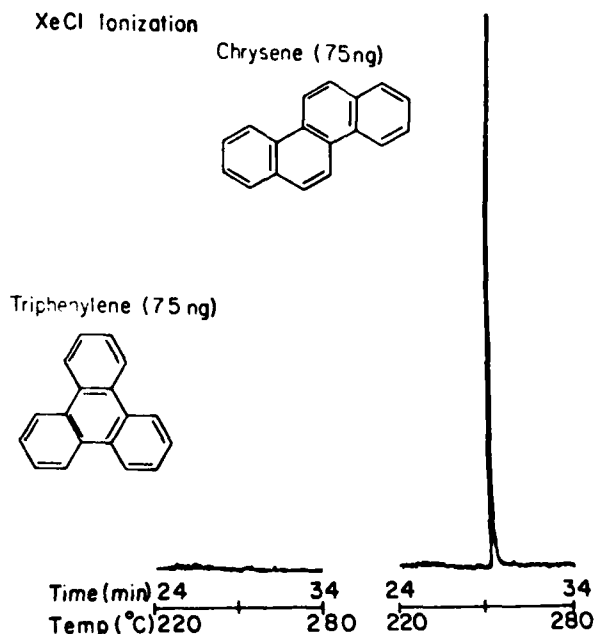


Figure 3. Total ion current chromatograms for 75 nanograms of triphenylene (left) and chrysene (right)

Two of the goals of our multiphoton ionization mass spectrometric studies thus far have been to find out what are the important factors determining a particular species' ionization probability when interacting with a certain pulse of laser radiation, and what, if any, secondary processes occur subsequent to the ionization. Specific molecules have been chosen for study which tend to elucidate the "rules" of multiphoton ionization. What we have learned is that the ionization efficiency depends on the following:

1. the existence of resonant intermediate states;
2. the magnitude of the transition probabilities coupling the intermediate states to the ground state and to the ionization continuum;
3. the occurrence and rate of relaxation or destructive (e.g. dissociation) processes affecting these states;
4. the absolute magnitude of the molecule's ionization potential.

These may be best illustrated by a few examples. Certain olefins such as 1 or 2 butene may be ionized by two photons of either KrF (2485 Å) or ArF (1930 Å) laser radiation. Yet ArF ionizes them much more efficiently because $\pi \rightarrow \pi^*$ transitions occur in the vacuum ultraviolet wavelength region. However, benzene is more efficiently ionized at the longer of these wavelengths even though it absorbs more strongly at the shorter. The reason for this is the existence of fast intramolecular relaxation out of the ${}^1B_{1u}$ state which is excited by the ArF laser radiation. Equivalent relaxation from the ${}^1B_{2u}$ state excited by a single KrF photon is known to be much slower.¹⁵ This difference in ionization efficiencies for benzene at the two laser wavelengths has been quantitatively interpreted with a rate equations model and it leads to the direct determination of intramolecular relaxation rates.² In the benzene experiment, it was also demonstrated that doubly ionized $C_6H_6^{2+}$ is not generated. This fact, along with the unusual abundance of small ion fragments, strongly suggested that the fragmentation mechanism occurring is not a single unimolecular explosion as is the case in electron impact spectra, but instead it involves a succession of single photon ionic dissociations. (By observing the photoelectron energy distribution, as mentioned in the next paragraph, we have verified this model). As an example of the fourth rule, acetaldehyde and butyraldehyde have been studied at the KrF and ArF laser wavelengths. Their ionization potentials are 10.2 and 9.8 eV, respectively. Two KrF laser photons provide 10.0 eV of energy while a pair of ArF photons make 12.8 eV available. We have experimentally observed parent molecular ions with ArF radiation incident upon either molecule or with KrF radiation illuminating butyraldehyde. However KrF radiation is not sufficiently energetic to ionize acetaldehyde. Fragment ions are detectable in all cases. The chrysene/triphenylene case discussed above is a second example of the fourth rule.

It is well known in laser ionization mass spectrometry that in addition to parent ions, fragments are also generated with a yield that grows sharply with increasing laser light intensity.^{2,3,16} To help elucidate the mechanism of the ion fragmentation, we undertook photoelectron kinetic energy distribution measurements. According to the formula,

$$KE_e = nh\nu - I.P. - E_{vib}$$

the ejected electron kinetic energy provides an indication of the number of photons absorbed at the time of molecular ionization.

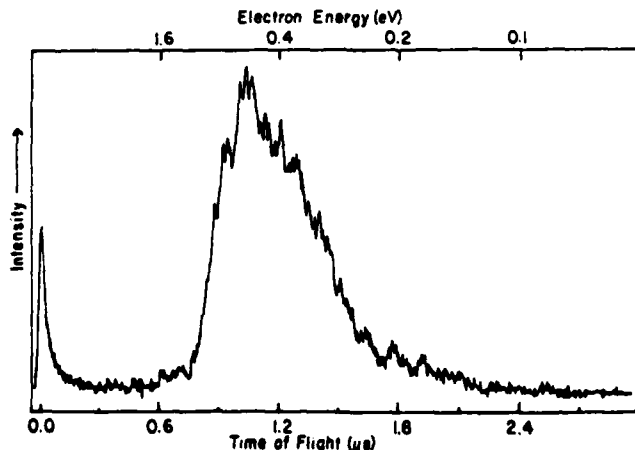


Figure 4. Photoelectron energy distribution resulting from the KrF laser induced ionization of benzene. (Photodiode and electron multiplier outputs are summed by the boxcar averager).

An example of a low resolution photoelectron spectrum induced by exciting benzene with the output from a KrF excimer laser is depicted in Figure 4. The ionization potential of gas phase C_6H_6 is 9.25 eV. Using a photon energy of 5 eV the fastest electrons expected from a two photon ionization process should have a kinetic energy of 0.75 eV. A quick perusal of the observed spectrum indicates that this is indeed the case. In all cases studied to date we have found n in the above formula to be 2. This shows that the mechanism of fragment ion production is two photon ionization to generate molecular ions followed by photofragmentation of these ions (as opposed to multiple photon absorption followed by an "explosion" which yields small ions).

Probably the most unique feature characterizing laser photoelectron spectra is their dependence on light wavelength. The vibrational state distribution of the ions generated in a conventional photoelectron spectral band is largely determined by the overlap between the potential energy surfaces of the ground electronic states of the molecule and ion. It is therefore essentially independent of the wavelength of the ionizing light. However, our case is very different. Laser ionization proceeds through a resonant vibronic intermediate state. The molecular geometry at the time when ionization occurs depends on the vibronic level excited so as this changes with wavelength different ion vibrational distributions (and consequently, different photoelectron kinetic energy distributions) are produced. For example, we have excited ten different vibronic levels in benzene's ${}^1B_{2u}$ first excited singlet state and have recorded ten completely different photoelectron spectra.¹⁷ Some of these are presented in Figure 5. Based on this new data we have measured and assigned two

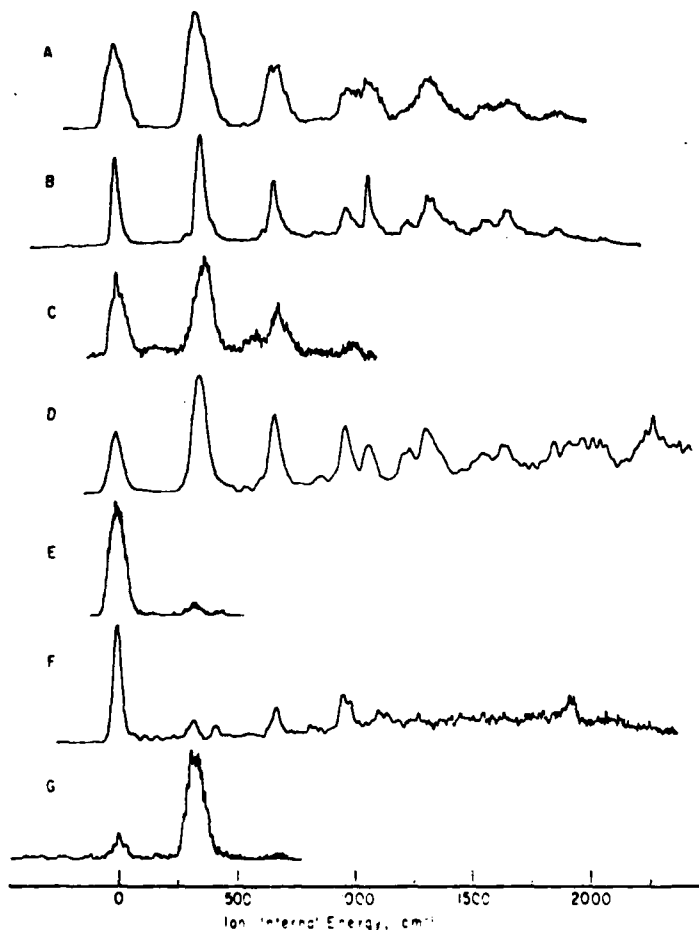


Figure 5. Laser photoelectron spectra obtained by exciting the following vibronic levels of benzene's ${}^1B_{2u}$ electronic state:

- (A) 6_0^1 (effusive)
- (B) 6_0^1 (supersonic)
- (C) $6_0^1 1_1^0$
- (D) $6_0^1 1_0^0$
- (E) 6_1^0
- (F) $6_1^0 1_0^0$
- (G) $6_1^0 16_1^0$

previously unidentified normal mode frequencies of $C_6H_6^+$ and $C_6D_6^+$ and have observed Jahn-Teller splitting in these species for the first time. We also explained how the anomalously large frequency of ν_6 , which had been previously measured with conventional photoelectron spectroscopy, was the result of Jahn-Teller distortion. Finally, we demonstrated that information contained in laser photoelectron spectra can assist in assigning vibronic features in near ultraviolet molecular absorption spectra. We expect to be able to observe virtually all of benzene's twenty normal mode frequencies using this technique. Until now only four have been assigned. This represents a real breakthrough in ion vibrational spectroscopy not only because of the quantity of new spectroscopic data, but also because of the ease of assigning peaks to particular ion vibrations. Many are immediately interpretable based on the well characterized assignments of near-ultraviolet molecular absorption spectra obtained over the past 50 years. As a second example of this work, we have also published similar wavelength dependent photoelectron spectra of toluene.¹⁸ Our laser photoelectron apparatus, with a pulsed supersonic beam source has recently attained a resolution of 3 meV which is comparable to or better than the highest resolution ever attained in photoelectron spectroscopy.

While performing laser ionization mass spectrometry experiments using the homemade TOF system depicted in Figure 6 we observed a remarkable phenomenon.¹⁹ Using a lens we shifted the laser - gas interaction location from the center of region 1 toward grid 0. As this

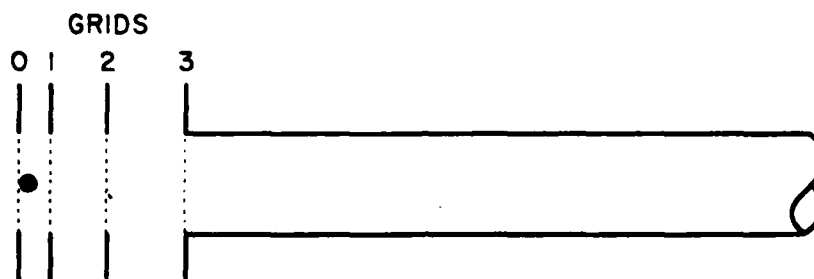


Figure 6. The ionization region and acceleration grids in our laser TOF mass spectrometer

was done the mass spectrum of benzene which we were observing underwent the changes depicted in Figure 7. In 7A only a rather broad gas phase parent ion is observed. In Figures 7B → 7D a remarkably sharp peak develops as the light moves closer toward and eventually

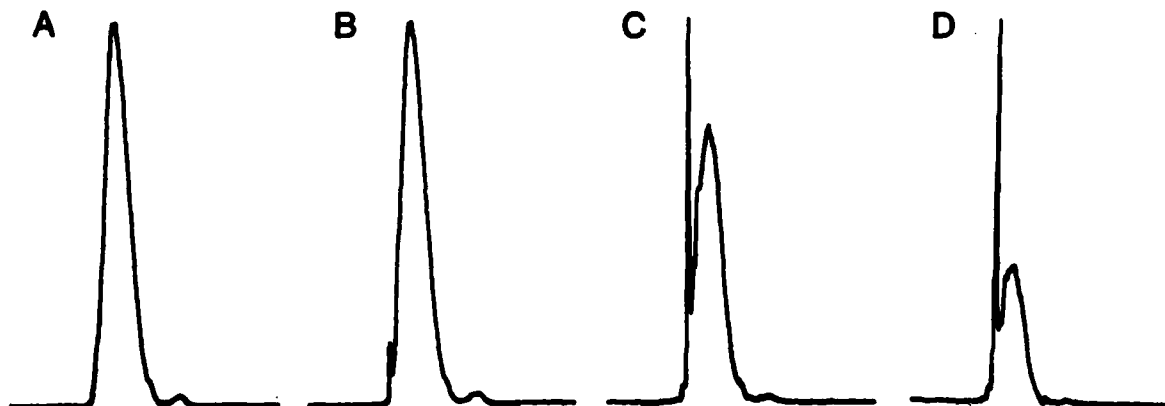


Figure 7. Dependence of mass spectrum on laser position in interaction region (see text)

strikes grid 0. This peak corresponds to $C_6H_6^+$ ions generated at or very near to grid 0. The evidence for this is that the sharp peak only appears with the laser spot near to grid 0, and a computer model accurately predicts the flight times for ions in the sharp peak only if we assume that they are generated on the surface, not in the gas phase. Furthermore when the voltage on grid 2 is increased until it is almost + 1950 V, the broad gas phase peak disappears from the mass spectrum but the sharp peak remains. This is because with + 2000 V on grid 0 and - 2000 V on grid 1, application of a large positive voltage to grid 2 prevents passage of all positive ions except those produced very near (75 microns or less), to grid 0. In order to observe $C_6H_6^+$ generated either at the surface or in the gas phase benzene vapor must be sprayed into region 1 of the instrument. When it is turned off, both the broad and sharp peaks disappear, indicating that neither is an instrumental artifact. The reason for the difference in the two peak widths is fairly simple. The gas phase ionization peak is broad because of the finite width of the laser beam in the ionization region. Ions are generated over this entire width and receive different kinetic energies from the drawout field depending on exactly where they are produced. The surface peak is much sharper because the region over which the ionization occurs is apparently not defined by the width of the laser beam but rather it depends upon the nature of the surface ionization phenomenon itself. The width is affected by both the distance that molecules can be from the surface and still ionize and by the velocity distribution of the ions which are drawn off.

Thus far we have generated surface ionization peaks for a variety of samples including benzene, toluene, alkali metals, phenanthrene, aluminum, 1,2-benzanthracene, perylene and 1,2,3,4-dibenzanthracene, just to name a few. In general, those species which yield strong gas phase multiphoton ionization signals can generate strong surface ionization peaks using relatively low energy (microjoule to millijoule) laser pulses. The tendency to produce substrate ions seems to rapidly increase as the laser intensity is increased. When a stainless steel plate is irradiated K^+ , Ca^+ and Fe^+ ions can all be observed, as depicted in Figure 8.

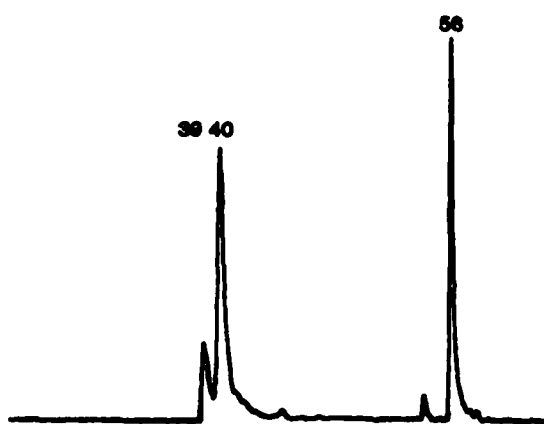


Figure 8. UV laser induced surface ionization TOF mass spectrum of a stainless steel plate

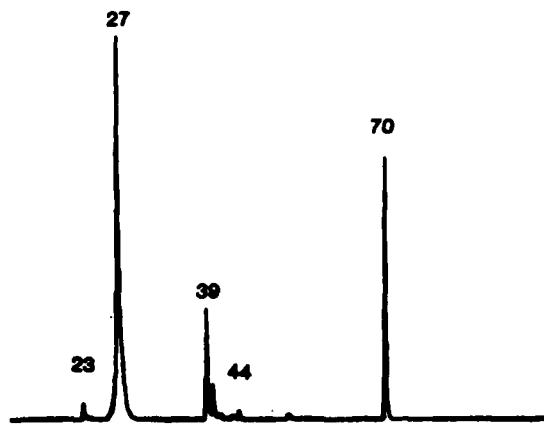


Figure 9. UV laser induced surface ionization TOF mass spectrum of an aluminum coated glass plate

The expected isotope ratios for each of these metal ions based on their natural abundances are preserved. When a hydrocarbon is sprayed on top of the metal surface the metal ion signals become smaller. A particularly interesting mass spectrum which is obtained by irradiating a glass plate covered by evaporated aluminum appears in Figure 9. In this case ions having $m/e = 23, 27, 39, 40, 41$, and 44 , which correspond to various isotopes of Na^+ , Al^+ , K^+ , Ca^+ , are observed. In addition, a strong ion peak at $m/e = 70$ appears. Since it is a sharp peak without a broad gas phase tail we know that it corresponds to an involatile species; however no element which one might expect to observe under these conditions has a mass of 70. We conclude that the peak corresponds to Al_2O^+ , a product of the rapid oxidation of the Al metal surface. Presumably the temporal growth of the Al_2O^+ peak could be quantitatively traced if a fresh layer of Al could be deposited onto the surface *in situ*.

The mechanism of the UV laser induced surface ionization remains to be unravelled, but two facts suggest that the phenomenon is selective. First, rather low laser pulse energies are employed in generating these surface ionization peaks. Second, molecules like oxygen, water, nitrogen and small alkanes do not yield surface ionization signals whether they are present alone or along with aromatic molecules which do ionize. This indicates that neither thermal nor electron impact ionization of samples is occurring. These features strongly contrast with the well known technique of infrared laser desorption mass spectrometry which

has been popular for over 10 years.²⁰⁻²⁴ While the UV surface ionization experiment is still somewhat of a novelty in our laboratory, its nonthermal and selective characteristics suggest potentially interesting new applications in mass spectrometry which we would like to look further into.

Under certain operating conditions a periodic but complex pattern appears in our laser ionization mass spectrum. Three examples of these are depicted in Figure 10. In all cases approximately 10 μ J of 2590 Å radiation skidded across an Al plate as benzene was being sprayed onto it. In Figures 10A and 10B a 300 mm f.l. lens was 220 mm from the mass spectrometer plate; the light simply approached the plate at slightly different angles. In Figure 10C the same lens was moved to within 141 mm of the surface. We currently believe

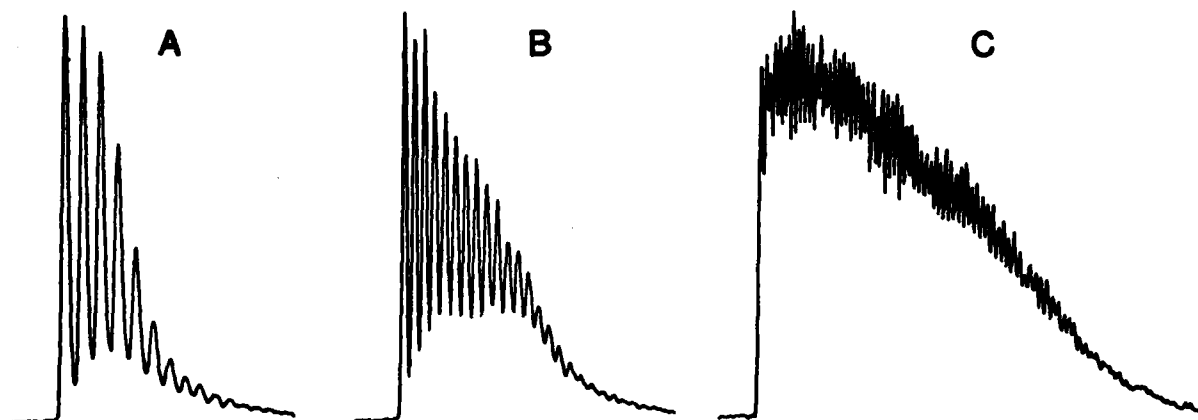


Figure 10. Combined surface and gas phase TOF mass spectra of benzene recorded under conditions which exhibit a spatially periodic laser intensity. (A) laser focussing lens 220 mm from grid 0 (aluminum plate); (B) lens in same position, laser angle of incidence changed; (C) lens moved to within 141 mm of grid 0.

that the interference - like pattern in the mass spectrum is the result of a spatially periodic distribution of light in our laser beam. It unfortunately masks the distinction between surface and gas phase peaks which was so evident in Figure 7.

In summary, the remarkable sensitivity and selectivity of a new type of GC/MS instrument has been discussed. Future work in this area will be devoted to understanding why certain molecules ionize so efficiently while other similar ones do not (e.g. naphthalene vs biphenyl), and to applying the laser MS technique to accomplish photochemical studies on isolated, gas phase molecules which would not otherwise be possible. We have constructed the first high resolution laser ionization photoelectron spectrometer and have demonstrated how it yields ion spectroscopic information which is not extractable using conventional single photon photoelectron spectroscopy. In the future we will be investigating transient species with the same apparatus. Finally, we have recorded wavelength selective, resonantly enhanced UV laser induced surface ionization mass spectra. The mechanism of the ionization process must be unravelled. We are also pursuing the possibility of exploiting this phenomenon as a selective method of introducing non-volatile, thermally labile samples into a mass spectrometer.

Acknowledgments

This work has been supported by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0 and by the U. S. Army Research Office under contract number DAAG 29-81-K-0097.

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This paper was originally published in the journal
Laser Chemistry, Volume 3, pp. 19-28, 1983.

Laser Ionization Studies of Gas Phase and Surface Adsorbed Molecules

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Gas phase hydrocarbons are ionized using the output of UV excimer lasers and frequency doubled dye lasers. The ions generated are mass resolved and kinetic energy distributions of ejected photoelectrons are recorded. Information about the photochemistry and ion spectroscopy of benzaldehyde, benzene and toluene is derived. Molecules adsorbed to metal surfaces are also laser ionizable leading to distinctively sharp peaks in their laser induced time of flight mass spectra.

While the earliest studies of laser induced ionization were performed in the mid 1960s,^{1,2} this field of research has developed and expanded particularly rapidly in just the last seven years. The acceleration is undoubtedly attributable to such exciting developments as single atom detection using dye lasers³ and the application of multiphoton ionization to problems in atomic⁴⁻⁶ and molecular spectroscopy.⁷⁻⁹ Mass spectrometry based on a laser ionization source has been discussed for over a decade,¹⁰ but many of the exciting developments in this area have occurred in just the last few years.¹¹⁻¹⁶ The evolution of commercial laser systems has played a major role in this recent progress. For laser ionization to have a significant impact on mass spectrometry, the ionization process must be efficient. Intense pulsed light sources of high energy photons are therefore needed in order to efficiently induce stepwise two photon ionization. Excimer lasers

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and powerful frequency doubled dye lasers which satisfy this requirement have only been commercially available for a few years.

When considered superficially, the detection of very small concentrations of molecules by laser ionization mass spectrometry might be viewed as a simple extension of previous successful experiments with alkali atoms.³ However, the molecular situation is actually considerably more complicated. First of all, absorption cross sections of molecules are much lower than those of atomic resonance lines. Second, molecular ionization potentials are considerably higher and rarely can be reached with a pair of conveniently available visible dye laser photons. Third, molecules undergo photophysical and photochemical processes such as intersystem crossing, predissociation and isomerization which atoms do not. Since these processes occur following absorption of one photon, they may compete with the second step of a two photon ionization process and thereby reduce the observed ion yield. Finally, because the laser wavelengths required to reach molecular ionization potentials in two steps are so short, background ionization is a major problem which interferes with the detection of low concentrations of hydrocarbons. In spite of these obstacles, we have recently demonstrated multi-femtogram sensitivity for detecting gas chromatograph effluent and selectivity capable of resolving $C_{18}H_{12}$ isomers which cannot be distinguished by either conventional capillary gas chromatography or mass spectrometry.¹⁷

While someone concerned purely with analytical detection sensitivity would view excited state molecular photochemistry as simply an annoying interference to be avoided when designing an efficient laser ionization process, the problem could clearly be turned around and considered from another perspective, i.e., laser induced ion yields must convey information about interfering photochemical processes which should be extractable by someone appropriately motivated. We have recently found this to be the case in a study of the laser ionization mass spectrum of benzaldehyde vapor.¹⁸ Using a KrF laser as photolysis source we found the benzaldehyde mass spectrum to be virtually identical to that of gas phase benzene, with only a hint of the molecular ion at $m/e = 106$. Naturally the question which arises is whether benzaldehyde ionizes and then fragments or, alternatively, does it absorb one photon, fragment to benzene, then ionize? The key to resolving this issue is found in the laser photoelectron spectrum of benzaldehyde. By monitoring the kinetic energies of the electrons

ejected from the ionizing gas we hoped to be able to determine which of the molecules was in fact actually ionizing. The result of our study is that the benzaldehyde and benzene laser photoelectron spectra are identical, indicating that benzaldehyde in fact rearranges to benzene before being ionized. The ten nanosecond time resolution of our pulsed laser is insufficient to resolve this fast kinetic process, but it seems likely that with picosecond ultraviolet laser pulses the time dependence of the collision-free production of benzene from benzaldehyde should be observable. With ionizing pulses which are sufficiently short and intense, $C_6H_6^+$ ions should not be generated from pure benzaldehyde, since the parent ion at $m/e = 106$ is known to be stable from electron impact mass spectra.¹⁹

Another example of how photoelectron studies are of potentially great interest in sorting out the mechanism of a laser ionization process is the laser induced ionization of benzene by KrF and ArF excimer lasers. In the first successful laser photoelectron spectroscopy experiment which we performed²⁰ we showed that the KrF (2485 Å) induced spectrum, which shows a single broad peak (see Figure 1) can be interpreted as a simple two step ionization process without complicating intermediate state effects. However the ArF (1930 Å) induced spectrum, which is also displayed in Figure 1, exhibits two peaks. The second, broader peak decreases relative to the first as the light intensity increases. The first peak corresponds to simple two step ionization of benzene with the electrons carrying off most of the deficit between the photon input energy (12.8 eV) and the ionization potential (9.25 eV). The second peak apparently results from the ionization of some state of benzene formed following single photon absorption. This might be a triplet or isomer state. The benzene ion must be generated in a different geometry or vibrational state distribution, compared with when it is ionized by KrF laser radiation, in order to generate the slow electrons which appear in the second ArF-induced photoelectron peak. Any hope for assigning the excited states involved will require electron energy resolution improvements. Recent developments in this area are described next.

In order to resolve vibrational structure which is obviously masked under the broad photoelectron profiles of Figure 1 (the peaks of which are about 500 meV wide), we switched from a spectrally broad, relatively long time duration excimer laser to a narrow band short pulse dye laser photolysis source. The resulting improvements in

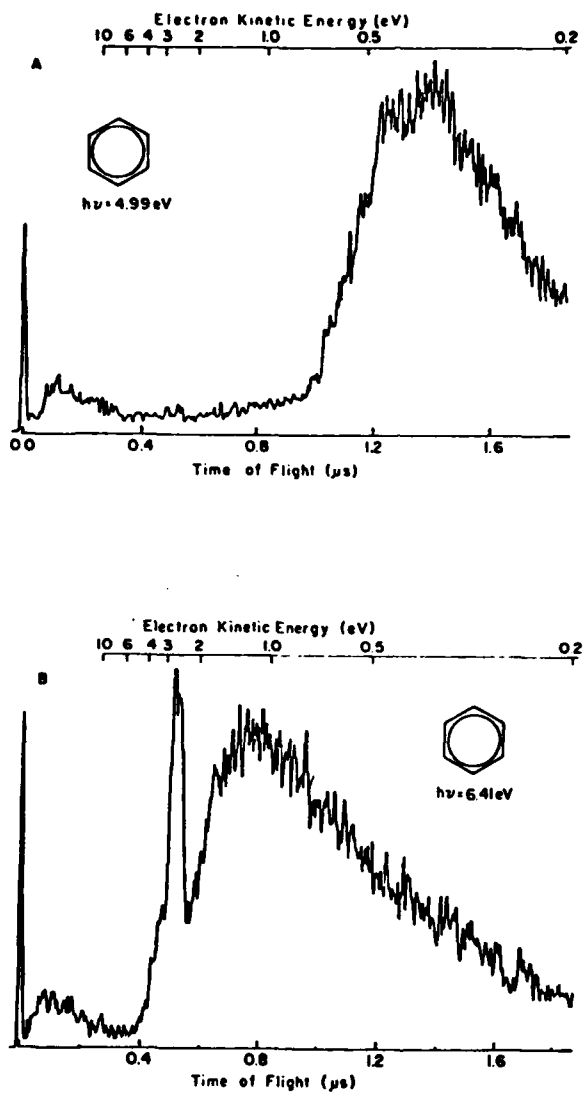


FIGURE 1 Time of flight photoelectron spectra of benzene ionized by radiation from (a) KrF (b) ArF excimer lasers.

photoelectron energy resolution are drastic, as can be seen in Figures 2 and 3. Resolution is now about 7 meV (approximately 60 cm^{-1}) and vibrational structure under the photoelectron band is easily resolved. Most interestingly, the photoelectron energy distribution depends strongly on the vibronic intermediate state excited by the frequency doubled dye laser. Several vibrational states within the ${}^1B_{2u}$ first excited singlet state of benzene have been utilized. When the laser is tuned to the 6_1^0 transition, ions are formed predominantly vibrationally unexcited. When tuned to the $6_1^0 16_1^1$ transition however, virtually all ions are generated with one quantum of excitation in ν_{16} .

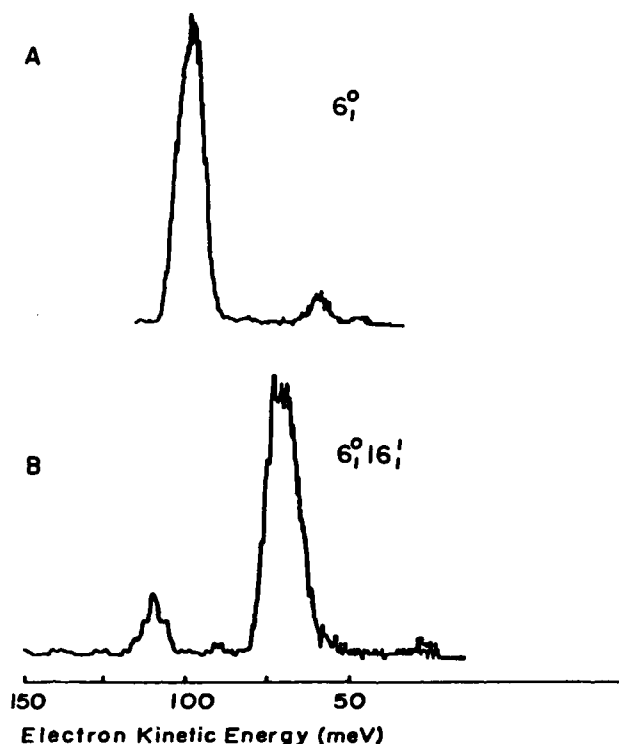


FIGURE 2 Kinetic energy distribution of the photoelectrons ejected from benzene ionized by the output from a narrowband frequency doubled dye laser. The radiation is tuned to the (a) 6_1^0 (b) $6_1^0 16_1^1$ vibronic transitions in the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ absorption band system of C_6H_6 .

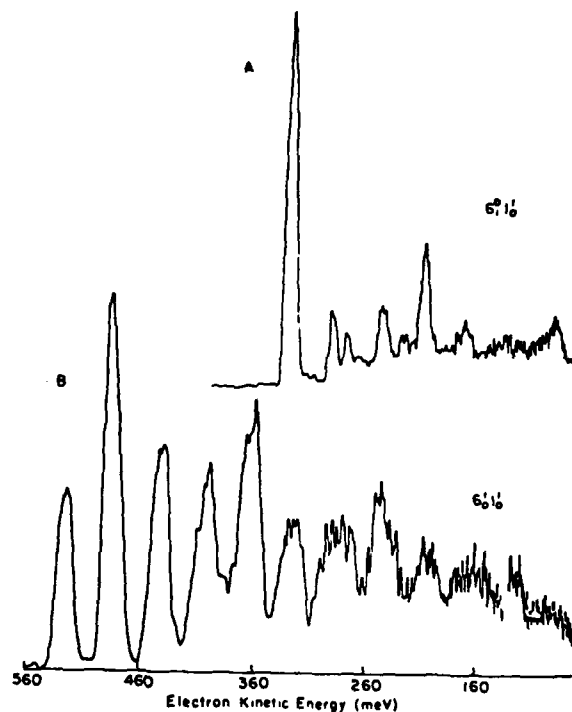


FIGURE 3 Same as Figure 2 except that the vibronic transitions involved are (a) $6_1^0 1_0^1$ and (b) $6_0^1 1_0^1$.

(The assignment of this ion peak, which has never been observed in a conventional photoelectron spectrum of benzene, follows from three mutually conclusive bits of data: First, the vibronic state from which the benzene ionizes in this experiment has been previously assigned as $v = 1$ of ν_{16} .²¹ Second, in the Rydberg spectrum of benzene a vibration of comparable frequency has been assigned to ν_{16} .²² Third, isotope substitution experiments which we have performed with benzene yield the correct frequency ratio.) When the transition $6_1^0 1_0^1$ is excited, $v = 0$ ions are preferentially formed, but the second most populated vibrational state is 122 meV above the ground vibrational state. This peak appears in the conventional photoelectron spectrum of benzene and has been previously assigned to $v = 1$ of ν_1 .^{23,24}

Considering the vibronic state which we pass through to obtain this spectrum, this work represents strong corroboration of the earlier assignment. Finally, when the transition $6_0^1 1_0^1$ is excited, a photoelectron spectrum with 12 peaks is generated as displayed in Figure 3. This is quite remarkable considering that the conventional single photon photoelectron spectrum of benzene contains only four or five peaks. More ion vibrational states can apparently be accessed when benzene is photoionized from a vibrationally excited S_1 state rather than from the vibrationless S_0 ground state. The Franck-Condon principle can be invoked to rationalize the observed trends, although calculations of the potential energy surfaces of the neutral and ion electronic states will be required to quantitatively interpret relative peak heights. A complete analysis of the benzene data is being prepared for publication.²⁵ We have recently obtained and published analogous results for toluene.²⁶ Similar vibronic state dependences are evident. In summary, laser photoelectron spectra contain information about what species is ionizing, how many photons are required to induce ionization and what the vibrational frequencies and state distribution of the product ions are.

A very recent development in our work in this area has been the observation of laser induced ionization of hydrocarbon molecules absorbed to metal surfaces. We originally observed this with gas phase benzene which was being sprayed onto a Ni grid. Similar results have now been obtained with heavy polyaromatic hydrocarbons. Briefly, when a UV light pulse is focussed into the interaction/ionization region of our laser mass spectrometer, depicted in Figure 4, ions are formed in the gas phase by two step ionization. A TOF mass spectrum of benzene is displayed in Figure 5a (at low intensities, only a single peak at mass 78 is observed). As the laser beam is shifted towards a metal surface in the ionization region, a second, much narrower peak appears in the mass spectrum, as seen in Figures 5b-5d. This peak results from ionization of benzene molecules at the surface. This hypothesis was confirmed in the following ways:

- 1) The peak appears only when the laser focussing lens is moved so as to illuminate the region near grid 0 and it disappears when the lens moves back toward grid 1.
- 2) A simple computer model which calculates ion flight times based on their mass, initial velocity and position and fragmentation dynamics

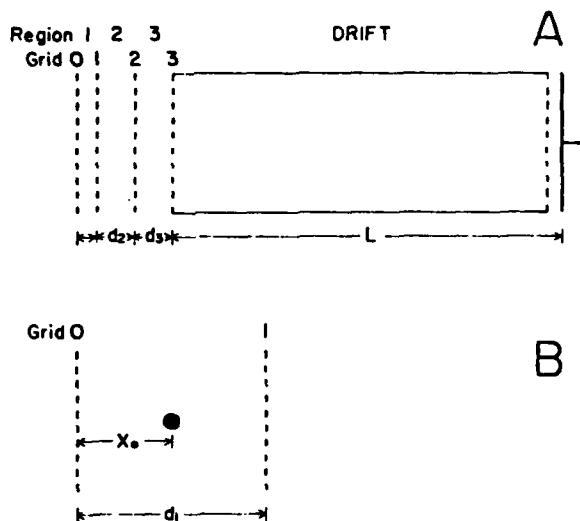


FIGURE 4 Basic ionization region and flight tube design of our home-made laser TOF mass spectrometer.

accurately predicts the location of the sharp peak *only* if we assume that the ions originate at the surface, not further to the right in the gas phase.

3) Shifting the lens position moves the laser focal spot around within region 1. When this is done the broad (gas phase) ion peak shifts in time, but the narrow (surface) peak, when it appears, always appears at precisely the same time. These dependences on lens position are exactly what one would expect for ion peaks resulting from gas phase and surface ionization.

4) The above data were recorded with +2000 volts on grid 0 and -2000 volts on grids 1, 2 and 3. Setting the voltage on grid 2 to +1950 V should prevent passage of all ions except those formed within 75 microns of grid 0. When this is experimentally tested the broad peak disappears from the mass spectrum but the sharp peak remains. Details of the ionization mechanism remain to be established, but electron transfer may be occurring from an excited absorbed molecule to the metal surface. Whether or not this phenomenon will

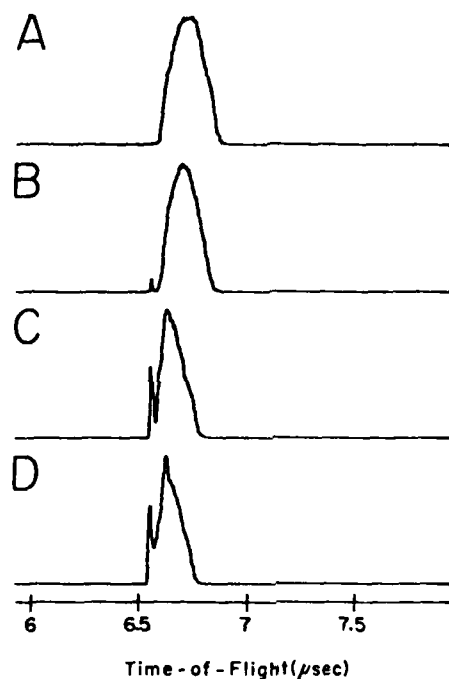


FIGURE 5 TOF mass spectra of benzene ionized with low intensity KrF laser radiation. Only the region near $m/e = 78$ is displayed. In (a) the light irradiates gas phase molecules between grids 0 and 1 (see Figure 4). In (b) $\rightarrow$ (d) the laser focal spot is moved progressively closer to grid 0.

enable us to record electronic spectrum of surface adsorbed species simply by tuning the laser wavelength depends on the exact ionization mechanism and at the present time remains to be seen. Due to the narrowness of the mass spectral ion peaks, we are currently interested in the potential of this technique as a method of sample introduction in mass spectrometry.

Acknowledgements

This work has been supported by the US Army Research Office under contract number DAAG29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0.

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The laser photoelectron spectrum of gas phase benzene

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(Received 20 May 1983; accepted 24 June 1983)

Benzene vapor in both effusive and supersonic molecular beams has been irradiated with the frequency doubled output from a tunable dye laser. Photoelectrons ejected as a result of two-step ionization have been kinetic energy analyzed by a time-of-flight method. Electron energy resolution is between 3 and 10 meV depending on beam conditions. Spectra resulting from the excitation of ten different vibronic bands of C_6H_6 and three of C_6D_6 are presented. Ions are found to be generated in their $^2E_{1g}$ ground electronic state in vibrational state distributions that are strongly wavelength dependent. Analysis of these distributions leads to an improved understanding of Jahn-Teller effects in benzene cation and observation for the first time of Jahn-Teller splitting in $C_6H_6^+$ and $C_6D_6^+$. Normal mode ν_{1g} is conclusively assigned as 39.5 meV (319 cm^{-1}) and 34.5 meV (278 cm^{-1}) in $C_6H_6^+$ and $C_6D_6^+$. ν_2 is tentatively assigned as 51.5 meV (415 cm^{-1}) and 43.5 meV (351 cm^{-1}) in these species, respectively. An explanation for the anomalously large frequency of ν_2 previously measured with conventional photoelectron spectroscopy is provided. It is also demonstrated that information contained in laser photoelectron spectra can be of assistance in assigning vibronic features in near ultraviolet molecular absorption spectra.

1. INTRODUCTION

The photoelectron spectrum of benzene has been the subject of several investigations in the last 15 years.¹⁻⁴ Most interest has focused on the electronic structure of the molecule, i.e., the energetic ordering of benzene's occupied molecular orbitals. Some information related to the normal modes of C_6H_6 has been derived from the vibrational structure of the first photoelectron band. However this has been somewhat limited by two commonly encountered problems. First, molecular photoelectron spectroscopy is an inherently low resolution technique (e.g., $\sim 15\text{ meV}$ in the references noted) and rotational contours can sometimes blend vibrational peaks together. A second and more important problem is that propensity or selection rules associated with the single photon ionization process tend to restrict the ion vibrational state distribution that is generated. In general, if a molecule and its ion have the same symmetry then only symmetric normal modes of vibration should be excited with high probability upon photoionization. (Asymmetric modes can, in fact, be excited by $\Delta v=2$ transitions, although these transitions are substantially weaker.) This is simply a manifestation of the Franck-Condon principle applied to molecules that are initially in the ground vibrational level of their ground electronic state. If the symmetry of a molecule and ion differ, then normal modes of vibration may be excited in the ion that are symmetric in the group consisting of just the symmetry elements common to the molecule and ion. Alternatively put, modes that most closely correspond to the change in equilibrium molecular geometry induced by photoionization will be excited in the ion.⁵⁻⁷ It is important to recognize that the photoionization Franck-Condon factors are simply functions of the potential energy surfaces of two electronic states. Since to a good approximation these determine

the vibrational structure of a photoelectron spectral band, the latter is essentially independent of illumination wavelength. For example, in conventional photoelectron spectroscopy Lyman α (10.2 eV) and HeI (21.2 eV) resonance lamps may yield spectra with somewhat different electron energy resolution, but the ion vibrational state distributions generated with both light sources are comparable.

The particular case of benzene is somewhat complicated by the fact that the $^2E_{1g}$ ground state of the ion is doubly degenerate. By the Jahn-Teller theorem, this degeneracy should be split by distortions along certain normal coordinates. For a molecule of D_{6h} symmetry, these are of e_{2g} symmetry. For benzene, there are four of these so called Jahn-Teller active modes ν_8 , ν_7 , ν_8 , and ν_9 ⁸ but only two totally symmetric a_{1g} normal modes ν_1 and ν_2 . The generally accepted interpretation of benzene's conventional single photon photoelectron spectrum is based on the existence of Jahn-Teller distortions in the ion. Only one of the two symmetric modes is excited upon photoionization, but three of the four Jahn-Teller active modes have been assigned in the conventional photoelectron spectrum. Because of the similarity of the potential energy surfaces of the ion and neutral molecule the peaks associated with vibrationally excited ions are small relative to the $v=0$ peak. Jahn-Teller splittings have never been detected. It is demonstrated in this paper that this was not a problem in experimental resolution but a limitation imposed by the selection rule for single photon ionization.

Considering that D_{6h} benzene has 20 normal mode frequencies (ten degenerate, ten nondegenerate) even if the a_{1g} and e_{1g} normal modes were all observable and properly assigned in the photoelectron spectrum, this would represent a rather small fraction of the vibrational spectroscopic information about benzene ion that one would like to extract. Considering the fundamental importance of a molecule such as benzene this problem is somewhat critical. Consequently there have been re-

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cent attempts to directly observe $C_6H_6^+$. In the gas phase it has been found that $C_6H_6^+$ does not fluoresce.⁹ Low lying electronic states presumably undergo rapid radiationless transitions to nonemitting states. It has been demonstrated that at least one higher electronic state which can be accessed in the near ultraviolet leads to dissociation.¹⁰ In rare gas matrices some fluorescence is observable, but only three relatively broad emission bands can be discerned.¹¹ From these no new vibrational information is derivable. Absorption experiments on $C_6H_6^+$ have also been unsuccessful.¹² In contrast with these results, considerable progress has recently been made in investigating halogenated benzene cations by absorption and fluorescence experiments in the gas phase and in rare gas matrices.¹³⁻¹⁹ Application of Jahn-Teller theory to the interpretation of relatively complex spectra has been remarkably successful. Rydberg spectra of benzene have also been recorded by single photon absorption²⁰ and multiphoton ionization techniques.^{21,22} Strong similarities are expected between this data and that involving benzene ions. This will be discussed further in Sec. IV of this paper following presentation of our results.

In order to improve our limited understanding of $C_6H_6^+$, we decided to apply the new technique of laser photoelectron spectroscopy to benzene. In this method molecules are efficiently ionized by sequential absorption of two ultraviolet photons from a tunable narrow-band frequency doubled dye laser. The ejected electrons are then energy analyzed and the data interpreted as in conventional photoelectron spectroscopy. Certain advantages accrue from employing a laser as the photon source. First, the linewidth of the light source is insignificant compared with other resolution-limiting factors. This is not the case with conventional atomic resonance lamps. Second, the spatial coherence of the laser light enables one to intercept a molecular beam with ease. Doppler broadening associated with the relative motion of molecules and ejected electrons can therefore be minimized. Furthermore, rotationally and vibrationally cooled molecules can be ionized in supersonic molecular beams. The rotational contour contribution to line shapes mentioned above is then significantly reduced. As will be seen below we are able to generate electron kinetic energy line shapes that are as narrow as 3 meV FWHM. Spectra taken with effusive and supersonic beam sources will also be compared. Finally, and most importantly, the laser can be tuned to various known vibronic levels of neutral benzene in its $^1B_{2u}$ first excited singlet state. Since the ionization process then takes place from different vibronic states, the distribution of ion vibrational levels generated changes as the laser is tuned. From any particular vibrational state of a neutral molecule ions will be preferentially formed in certain vibrational levels and not in others. The enhancement of, or discrimination against, population of different ion vibrational levels depends critically on the relationship between the potential energy surfaces of excited neutral molecules and ions and also on the vibrational angular momentum quantum numbers of the relevant $^1B_{2u}$ molecular and $^2E_{1g}$ ion vibronic levels.

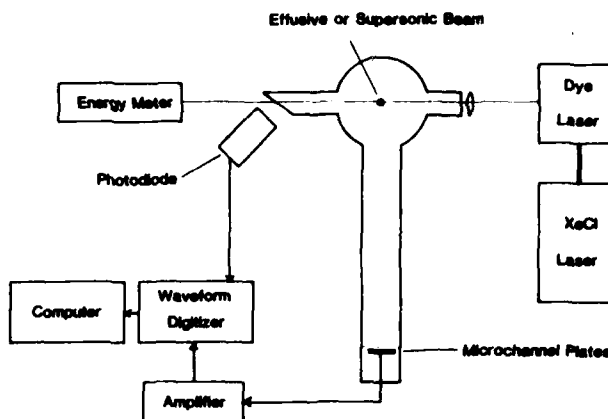


FIG. 1. Apparatus employed to record laser photoelectron spectra by time of flight electron energy analysis.

The first application of laser photoelectron spectroscopy to a molecule in fact involved benzene.²³ However, in that study we used a relatively broadband excimer laser as radiation source. More recently we reported high resolution data on toluene.²⁴ Anderson, Rider, and Zare have performed a similar study on chlorobenzene.²⁵ A $\Delta v = 0$ photoionization propensity rule seems to be followed. In other words, when a particular vibrational mode is excited in the first excited electronic state ions tend to be formed vibrationally excited in the same mode. In the present work on benzene, the situation is similar, although because of the Jahn-Teller effect it is somewhat more complicated. Due to the vast amount of high quality spectroscopic data which is available for benzene, literally hundreds of vibronic levels of the $^1B_{2u}$ state could be excited. For this reason a rich array of new ion spectroscopic data can be generated. Most importantly, the interpretation of much of this data can be simplified because we can exploit what is already known about excited states of neutral benzene. In this study C_6H_6 and C_6D_6 are ionized through ten and three of these low lying vibronic states, respectively.

As will be demonstrated, knowledge about the ultraviolet spectroscopy of a molecule is certainly crucial for interpreting a laser photoelectron spectrum, but the latter also conveys information which can be used to assign features in molecular absorption spectra.

II. EXPERIMENTAL PROCEDURE

The apparatus used to generate laser photoelectron spectra is displayed in Fig. 1. The radiation source consists of a homemade grazing incidence grating tuned dye laser pumped by a Lumonics 430 XeCl excimer laser. The temporal width of the visible laser light is about 2 ns and its frequency bandwidth is less than 0.5 cm^{-1} as measured with a Fabry-Perot interferometer. The 1 to 2 mJ visible output of the dye laser is directed through either a KDP or KPB frequency doubling crystal. The resulting 1-100 μJ ultraviolet pulse is $\sim 1 \text{ ns}$ in duration. A Corning 7-54 filter is mounted between the dye laser and the photoelectron spectrometer. It ab-

sorbs, almost all of the unconverted visible radiation and transmits 50%–75% of the ultraviolet. Although the shortest wavelength which one can generate with KDP is about 2585 Å, several of benzene's $^1B_{2u}$ vibronic states can be reached between this wavelength and 2667 Å. The KPB doubling crystal enables us to reach higher vibronic states. However, as is well known, this is not a particularly efficient frequency doubling material. Consequently between 2400 and 2600 Å less than 5 μ J of ultraviolet radiation is available and we are only able to ionize through relatively strong vibronic transitions.

As depicted in Fig. 1, the ultraviolet laser radiation passes through a 20 cm f.l. lens, enters the spectrometer through a suprasil window, and crosses either a continuous effusive molecular beam of pure benzene or a pulsed supersonic beam of benzene and argon in the center of a 15 cm diam aluminum vacuum chamber. The light then passes out of the spectrometer through another suprasil window and impinges on a Scientech power meter which monitors the average pulse energy. In effusive beam experiments the chamber is evacuated with a single CTI Cryotorr 7 which has a pumping speed of 850 l/s for Ar. For supersonic beam experiments a source chamber is added above the laser/molecule interaction chamber and is separated from it by a 500 μ m diam skimmer. It houses a pulsed gas inlet system which is modeled after the design of Otis and Johnson.²⁶ The nozzle of our pulsed valve is 350 μ m in diameter. The supersonic beam source chamber is evacuated by a CTI Cryotorr 8 which has a 1200 l/s pumping speed for Ar. The base pressure of the laser/molecule interaction region, as measured with an ionization gauge mounted on the side of the chamber, is about 3×10^{-7} Torr. During effusive beam experiments this rises to about 2×10^{-6} Torr. In supersonic beam experiments the pressure in the ionization region remains below 4×10^{-7} Torr while that in the source chamber rises to about 2×10^{-5} Torr. The pressure at the center of the molecular beam is certainly higher than we measure at the side of the chamber but we do not monitor this. Electrons generated by laser induced ionization are ejected in various directions. Some travel down a flight tube mounted on one side of the ionization chamber perpendicular to both the laser propagation direction and the molecular beam and parallel to the electric field axis of the linearly polarized ultraviolet radiation. The electron flight path to the microchannel plate detector is ~ 49 cm. In order to insure that the ejected electrons are not deflected by the earth's magnetic field the entire system is surrounded by a magnetic shield and field coils. Together these reduce the magnetic field inside the spectrometer to less than 1.5 mG as measured with an RFL Model 101 magnetometer. The output signal from the microchannel plate detector is amplified and then digitized in a Biomation 6500 waveform recorder. This provides us with information about the electrons' times of flight. Following each laser pulse the digitized information is transferred to an Apple II microcomputer and eventually stored on a floppy disk. The computer enables pulse counting and conversion of spectra from being linear in flight time

to linear in electron kinetic energy. The latter is accomplished by employing the simple relation

$$K. E._{\text{electron}} = \frac{1}{2} \frac{mL^2}{t^2},$$

where L is the 49 cm electron flight path and m the electron mass. Between 10 000 and 100 000 shots are required to generate a photoelectron spectrum with an adequate signal-to-noise ratio. The number of electrons counted per laser shot was deliberately maintained at a fairly low value (0.1 to 5) by varying sample pressure and light intensity. This was done to minimize space charge effects that can significantly deteriorate spectral quality.²⁴ The signal strength depends on both the laser intensity utilized and the oscillator strength of the vibronic band being excited.

The C_6H_6 (Fisher, Spectranalyzed grade) and C_6D_6 (Sigma, 99.5% D) employed in these experiments were vacuum degassed but not further purified.

Experiments were performed at a variety of laser wavelengths corresponding to excitation of benzene into several different vibronic states of its $^1B_{2u}$ first excited singlet state. Hundreds of vibronic transitions into this state have been assigned.^{27,28} As our guide for selecting laser wavelengths and matching them to benzene absorptions we have used the work of Atkinson and Parmenter.²⁸ Fine tuning of our laser to some specific absorption band was initially accomplished by performing simple I/I_0 absorption measurements with a 10 cm long cell containing between 1.5 and 70 Torr of benzene vapor. However, because of the rotational cooling of the benzene, in supersonic beam experiments it became necessary to record and maximize electron yield as a function of wavelength when searching for resonances. Table I contains a list of the vibronic bands of C_6H_6 and C_6D_6 that were irradiated along with the wavelengths we employed in each case. The spectra which we obtained are exhibited in the next section, along with information explaining our method of data presentation. Details of our interpretation are delayed until Sec. IV.

III. EXPERIMENTAL RESULTS

In order to facilitate comparison of spectra obtained by exciting different vibronic bands, following transformation of our time-of-flight data to a scale which is linear in energy, the spectra were lined up by overlapping $v=0$ ion peaks. This was accomplished by plotting the electron signal intensity not as a function of electron kinetic energy but as a function of ion internal energy, as given by

$$E_{\text{internal}} = 2h\nu - I. P. - K. E._{\text{electron}}$$

This effectively corrects for the dependence of electron kinetic energy on photon energy. When the frequency doubled laser radiation was tuned into resonance with benzene's 6_0^1 transition, photoelectron spectra depicted in Fig. 2(A) and 2(B) were recorded. The effusive molecular source and the supersonic source, respectively, were employed to generate these spectra. As is readily apparent, the peak line shapes are significantly different in the two cases. Rotational cooling reduces

TABLE I. Energetics of benzene vibronic transitions excited.

Transition	Frequency (cm ⁻¹)	Two photon energy (eV)	Available ion ^a energy (meV)
C₆H₆			
6 ₀ ¹	38611.3	9.574	329
6 ₀ ¹ 1 ₀ ¹	37617.1	9.328	206
6 ₀ ¹ 1 ₀ ¹	39534.6	9.803	558
6 ₁ ⁰	37481.6	9.294	125
6 ₁ ⁰ 1 ₀ ¹	38406.3	9.524	354
6 ₁ ⁰ 16 ₁ ¹	37321.1	9.255	134
6 ₁ ⁰ 16 ₁ ¹	38450.5	9.535	339
16 ₀ ²	38562.4	9.562	317
6 ₁ ² 1 ₀ ¹	38529.3	9.554	385
6 ₁ ² 1 ₀ ¹	38522.5	9.552	383
C₆D₆			
6 ₀ ¹ 1 ₀ ¹	37841.0	9.383	256
6 ₁ ⁰	37712.0	9.351	178
6 ₁ ⁰ 16 ₁ ¹	37572.2	9.317	187

^aAvailable ion energy = $2h\nu + E_{vib} - I. P.$ where E_{vib} is the vibrational energy above the zero point level from which the excitation occurs. The same ionization potential (9.245 eV) is used for both C₆H₆ and C₆D₆ in calculating these numbers.

linewidths from 6–10 meV in the effusive case to ~3–5 meV with the supersonic beam. The latter represents the highest resolution yet obtained in the field of laser photoelectron spectroscopy. This is particularly noteworthy since the subject of the investigation is a polyatomic molecule. Because of this line narrowing, the improvement in separating closely spaced vibrational levels is clearly pronounced. The peaks in Fig. 2(B) are sharper than those appearing in any other band we attempted to record. This is because 6₀¹ happened to be one of the strongest bands in the spectral region we are investigating and considerable time was spent optimizing conditions for recording this spectrum and in gathering the data. Although with considerable work most of our other spectra could have been improved, it would have been difficult to obtain equivalently high quality cooled-beam spectra with hot band transitions; the intensity of these is naturally reduced because of vibrational cooling in the supersonic expansion.

For reasons discussed earlier it is anticipated that when a molecule is ionized from some particular vibronic level using different light wavelengths, the resulting photoelectron spectra should be similar. In order to verify this we excited the 6₀¹1₀¹ transition which involves the same vibronic level in the ¹B_{2u} state as does 6₀¹. The resulting photoelectron spectrum appears in Fig. 2(C). When the 6₀¹1₀¹ transition is excited, considerably more energy is introduced into the molecule. Consequently more highly vibrationally excited ion states become accessible. Because ν_1 is a totally symmetric a_{1g} normal mode it might be expected that the distribu-

tion of ion vibrational states would resemble that generated by 6₀¹ excitation. The result of testing this hypothesis is exhibited in Fig. 2(D).

In order to investigate the effect of ionizing benzene from a vibrationless intermediate state, we excited the 6₀⁰ transition and recorded the photoelectron spectrum in Fig. 3(A). This is the longest wavelength ionizing transition investigated in our current series of experiments. It is worth noting that the energy of two photons at this wavelength barely exceeds the ionization potential of C₆H₆ (see Table I). Similarly, just a single quantum of ν_1 is excited in the ¹B_{2u} state when we irradiate at the 6₀¹1₀¹ transition wavelength. The resulting spectrum is exhibited in Fig. 3(B). Due to the existence of peaks in several of our spectra which must correspond to low frequency ion vibrations, we hypothesized that benzene's lowest frequency normal mode ν_{18} might be involved in some of our spectra. For this reason we deliberately excited only ν_{18} in the ¹B_{2u} state by irradiating at a wavelength corresponding to the 6₀¹6₁¹ transition. The resulting photoelectron spectrum appears in Fig. 3(C). We also excited a quantum of ν_{18} in conjunction with ν_8 and then two quanta of just ν_{18} . The corresponding photoelectron spectra are displayed in Figs. 4(A) and 4(B). Finally, in order to observe the effect of ionizing from a vibronic level of the ¹B_{2u} state involving two quanta of ν_8 , we excited the 6₁² transition of benzene. It has been shown that this band actually consists of two subbands spaced by 6.8 cm⁻¹.²⁸

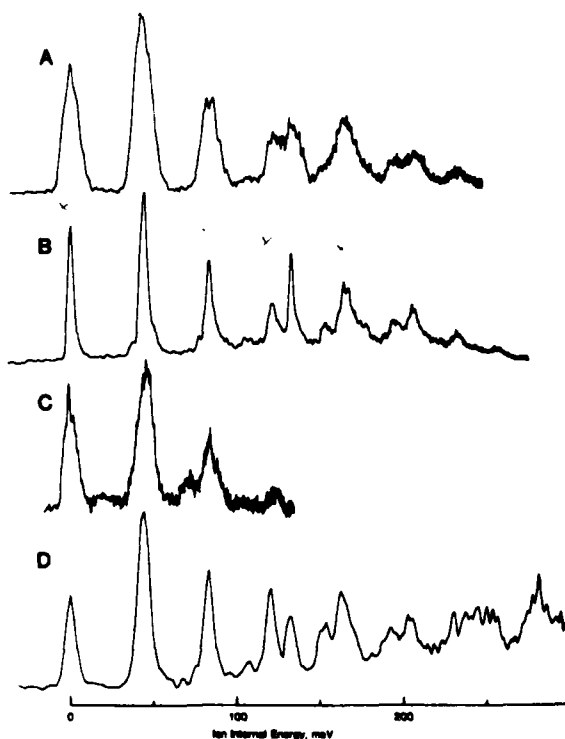


FIG. 2. Photoelectron spectra recorded by exciting the following transitions of C₆H₆: (A) and (B): 6₀¹; (C) 6₀¹1₀¹; (D) 6₀¹1₀¹. In (A) and (C) an effusive molecular beam was employed, in (B) and (D) a pulsed supersonic beam.

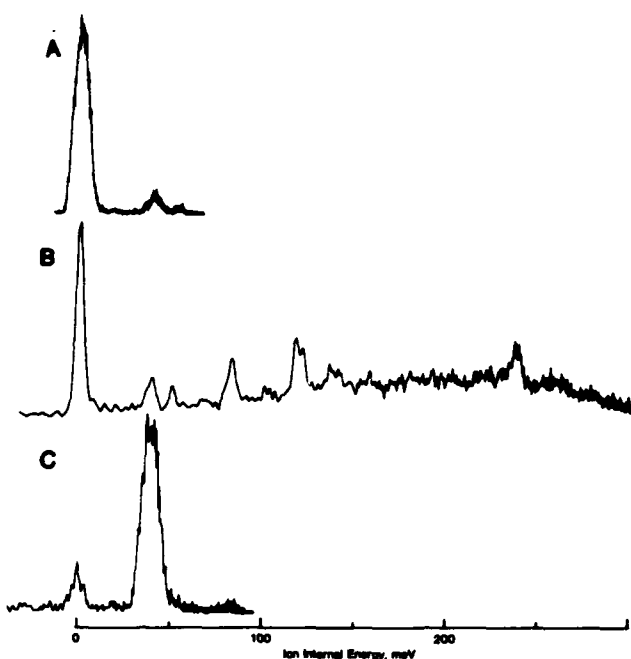


FIG. 3. Photoelectron spectra recorded by exciting the following transitions of C_6H_6 : (A) 6_1^0 ; (B) $6_1^0 1_1^0$; (C) $6_1^0 1_6^1$. In (A) and (C) an effusive molecular beam was employed, in (B) a pulsed supersonic beam.

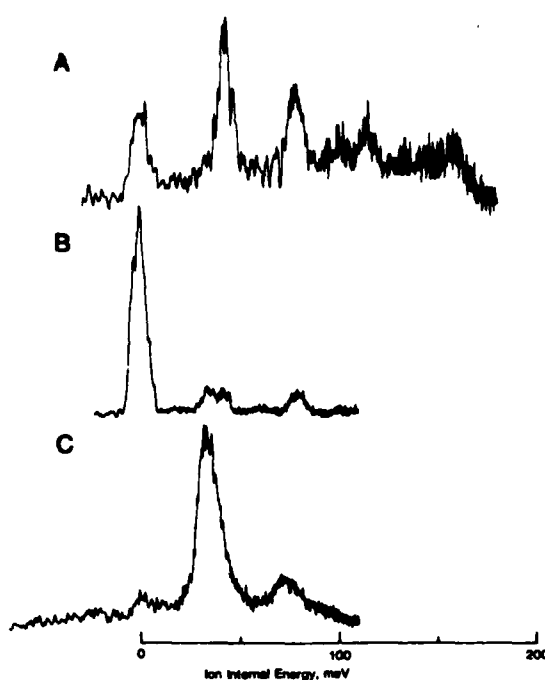


FIG. 5. Photoelectron spectra recorded by exciting the following transitions of C_6D_6 in an effusive molecular beam: (A) $6_1^0 1_1^0$; (B) 6_1^0 ; (C) $6_1^0 1_6^1$.

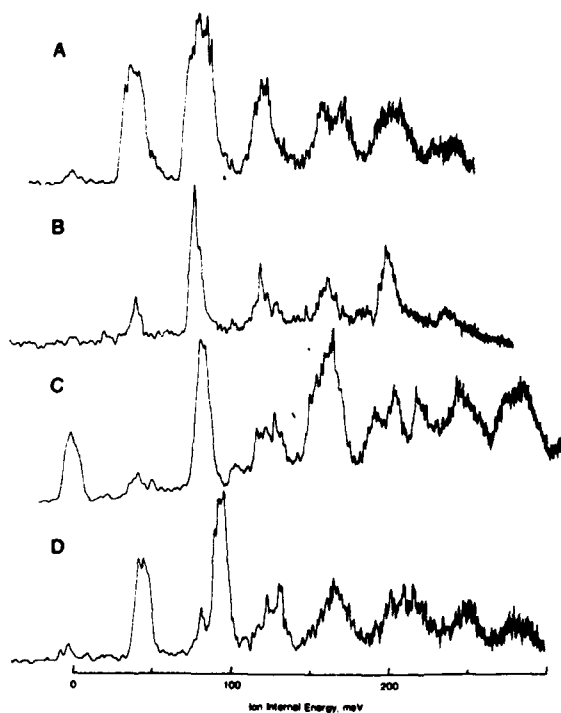


FIG. 4. Photoelectron spectra recorded by exciting the following transitions of C_6H_6 in an effusive molecular beam: (A) $6_1^0 1_6^1$; (B) 1_6^0 ; (C) $6_1^2 1_6^1$; (D) $6_1^2 1_6^2$.

They are labeled $6_1^2 \nu_6^1$ and $6_1^2 \nu_6^2$, where l is the vibrational angular momentum quantum number associated with the degenerate normal mode ν_6 . For reasons discussed in the next section we expected strikingly different photoelectron spectra when ionizing through each of these. The results are depicted in Figs. 4(C) and 4(D).

As an aid to interpreting our laser photoelectron spectra of benzene we excited three transitions of C_6D_6 analogous to those studied in C_6H_6 . These included $6_1^0 1_1^0$, 6_1^0 , and $6_1^0 1_6^1$. The resulting photoelectron spectra are displayed in Figs. 5(A), 5(B), and 5(C), respectively.

The locations of the peaks in all of the photoelectron spectra that we recorded, relative to the $v=0$ ion peaks, are summarized in Tables II and III. They should be accurate to between ± 1 and ± 3 meV depending on the peak widths and congestion in the spectra from which they are derived.

IV. DISCUSSION

Before considering our detailed assignments of various photoelectron peaks to particular ion vibrational states it is worthwhile noting two qualitative features that characterize our spectra. First, as can be seen from Fig. 2, spectra obtained from effusive and supersonic sources are virtually identical except for the line shape narrowing noted in the previous section. The relative peak intensities are apparently not affected by the rotational temperature of the molecules in the beam.

TABLE II. Observed C_6H_6 photoelectron peak locations and assignments.^a

Peak assignments	Transitions excited											Calc.
	$6_0^1(\sigma)$	$6_0^1(\pi)$	$6_0^1 1_1^0$	$6_0^1 1_1^1$	6_1^0	$6_1^0 1_1^0$	$6_1^0 16_1^1$	$6_1^1 16_1^1$	16_0^2	$6_1^2 1_1^0$	$6_1^2 1_1^1$	
16^1					41	40	39	39	40	41		
$6^1(3/2)$	43	44	45	43							44	40.3
4^1					53	51				51		
16^2									77			
$16^1 6^1(3/2)$								81				
$6^1(1/2)$	85	83	84	82		82.5	83			83		82.8
$6^2(5/2)$											93	86.3
16^3									119			
1^1	123	121	123	120		120			119	122	123	
$16^1 6^1(1/2)$								121				
$6^2(3/2)$	133	132		132							132	137
$9^1(1/2)$		153		152								
$1^1 16^1$								159	160			
$6^2(1/2)$	165	165								165		154
$1^1 6^1(3/2)$	165	165		163							167	
$16^1 6^2(3/2)$								170				
$8^1(1/2)$	195	195		192						192		
$1^1 16^2$									199			
$1^1 16^1 6^1(3/2)$								203				
$1^1 6^1(1/2)$	207	206		204						203		
$6^3(1/2)$										219		211
$1^1 6^2(5/2)$											215	
$6^3(3/2)$		232		230								228
1^2				243		238				243		
$1^1 16^1 6^1(1/2)$								244				
$1^1 6^2(3/2)$		255									250	
$1^2 6^1(3/2)$				280							283	
$1^1 6^2(1/2)$										281		
$1^3 6^1(3/2)$				401								

^aExperimental and calculated data are listed in meV units.

Second, the production of vibrationally excited ions is strongly dependent on the vibronic level of the $^1B_{2u}$ state from which ionization takes place. Depending upon which vibronic level is excited, ions may be formed with a vibrational state distribution which is quite similar or very different from that produced by single photon ionization. Examples of these two cases are spectra obtained by exciting the $6_0^0 1_1^0$ and $6_0^1 1_1^0$ transitions, respectively. This agrees with results obtained on other aromatic molecules that have been studied using laser photoelectron spectroscopy.

A thorough, quantitative analysis of our photoelectron spectra is possible if the implications of vibrational angular momentum and the Jahn-Teller effect are considered in depth. Basically, the effect of Jahn-Teller

TABLE III. Observed C_6D_6 photoelectron peak locations and assignments.

Peak assignments	Transitions excited		
	$6_0^1 1_1^0$	6_1^0	$6_1^0 16_1^1$
16^1		35	34
$6^1(3/2)$	41.5		
4^1		43.5	
16^2			70.5
$6^1(1/2)$	79	80.5	
1^1	114		
$6^2(1/2)$	158		
$1^1 6^1(3/2)$	158		

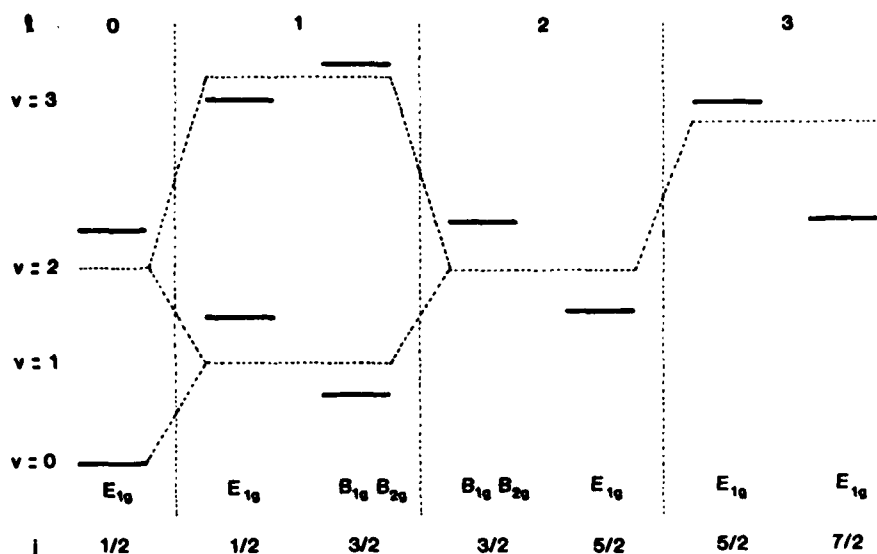


FIG. 6. The effect of weak Jahn-Teller interaction on the energy levels for a degenerate e_{2g} vibration in a D_{6h} molecule in an E_{1g} electronic state. Heavy lines represent actual levels, broken horizontal lines indicate the levels without vibronic interaction. Level splittings are depicted qualitatively. Their exact magnitudes depend on the Jahn-Teller coupling parameters.

distortion in a degenerate electronic state is to change the vibrational potential. Consequently vibrational levels associated with a certain normal mode k which would otherwise be degenerate, equally spaced, and labeled by a single vibrational quantum number v_k , become shifted and split. Solutions to the vibrational wave equation containing a Jahn-Teller distorted potential have been calculated by Longuet-Higgins *et al.*^{30,31} and discussed by Herzberg.²⁹ The energy levels derived from diagonalizing a Hamiltonian that includes the Jahn-Teller perturbation are labeled by a vibronic angular momentum quantum number j_k , which distinguishes levels of a given v_k that have different energies. The spacings between vibronic levels with the same v_k and different j_k are referred to as Jahn-Teller splittings. An energy level diagram qualitatively depicting anticipated first order splittings of an e_{2g} vibrational ladder in an E_g electronic state is presented in Fig. 6.

The selection rule for an allowed optical transition between vibronic levels of a nondegenerate electronic state characterized by vibrational angular momentum l'_k and a degenerate electronic state characterized by vibronic angular momentum j_k is^{29,30}

$$j_k - l'_k = \pm \frac{1}{2}.$$

If we apply this same selection rule to photoionization processes it follows that when ionization takes place from a level having $l'_k = 0$ (e.g., the ground vibrational level of any electronic state), then only ion levels with $j_k = \pm \frac{1}{2}$ can be populated. (Since the energy of a level depends on the absolute value of j_k , negative values of this quantum number will henceforth be suppressed.) In the conventional photoelectron spectrum peaks at 84, 160, and 197 meV have been associated with ions in their $v_g = 1$, $v_g = 1$, and $v_g = 1$ states.³² If these assignments are correct then these levels should be more precisely labeled as $6^1(1/2)$, $9^1(1/2)$, and $8^1(1/2)$, respectively. [In this notation $k^r(j_k)$ refers to an ion vibronic state in which the k th normal mode has been

excited with n quanta yielding a state with vibronic angular momentum j_k .] The fact that $j = 1/2$ for all of these states is important since it implies that no improvement in single photon photoelectron spectral resolution will enable one to measure Jahn-Teller splittings associated with these e_{2g} ion vibrational modes. The only other $C_6H_6^+$ normal mode that has been assigned from benzene's photoelectron spectrum is the totally symmetric non-degenerate v_1 , which is associated with a peak at 122 meV. This assignment is really unambiguous considering the appearance of simple harmonic progressions involving this frequency that have been observed previously and in our $6^0_1 1^1_0$ and $6^0_1 1^1_0$ spectra.

Based on the selection rule presented above, laser photoelectron spectra should exhibit a variety of peaks not found in the conventional single photon photoelectron spectrum. For example, when exciting the 6^0_1 transition of benzene the value of l'_g in the 1^1B_{2u} level populated by the laser is ± 1 . Therefore, when molecules in this state absorb a second photon ions should be generated in vibrational levels with $j_g = \frac{3}{2}$ and $\frac{1}{2}$. On the other hand, when the 6^0_1 transition is excited l'_g in the 1^1B_{2u} state is 0 so only $j_g = \frac{1}{2}$ ions are anticipated. In this case, the laser photoelectron spectrum should look similar to the conventional one. As a more complex example, completely different laser photoelectron spectra are anticipated when exciting the $6^2_1 l'_{g1}$ and $6^2_1 l'_{g1}$ transitions. From the former only $j = \frac{1}{2}$ levels should be populated. From the latter only $j = \frac{3}{2}$ and $\frac{5}{2}$ levels are expected. It should be emphasized that all of the ion vibronic levels depicted in Fig. 6 except $6^3(j = 7/2)$ should be observable by two-step ionization of benzene through 6^0_1 , 6^0_1 , and 6^0_1 transitions.

In order to assign the peaks in our laser photoelectron spectra we diagonalized the Jahn-Teller perturbed Hamiltonian matrix following the approach of Longuet-Higgins *et al.*^{30,31} The distortion parameter, which they define D , was initially assumed to be 0.5 since this is typical of the values found by Sears, Miller, and Bondybey for halogenated benzenes.^{15,19} The magnitude

of the unperturbed ν_6 quantum in $C_6H_6(^2E_{1g})$ was initially estimated as that of ν_6 in the $^1B_{2u}$ state of C_6H_6 (viz. 64.6 meV or 521.4 cm^{-1}). With these assumptions the lowest four eigenvalues corresponding to $j=\frac{1}{2}$ levels of $C_6H_6^+$ are found to be 0, 81.1, 151, and 200 meV. For the $j=\frac{3}{2}$ levels, the calculated eigenvalues are 39.5, 134, 223, and 268 meV. For the $j=\frac{5}{2}$ levels the lowest three eigenvalues are 84.4, 186, and 286 meV. [In all cases these numbers represent energy spacings from the $6^0(1/2)$ ion vibrational level.] These calculated results are in qualitative agreement with our experimental data and provide great help in interpreting it. Our laser photoelectron spectra will now be discussed individually. Subsequent to this the Jahn-Teller model will again be considered.

The spectra in Figs. 2(A) and 2(B) exhibit considerable evidence of ion vibrational excitation. In contrast with the conventional photoelectron spectrum the first peak in each, corresponding to production of $v=0$ ions, is not even the strongest one. This conforms with our previous experience that vibrational excitation in a resonant intermediate state tends to yield vibrationally excited ions upon photoionization from that state. Peaks appearing at ion internal energies of 83, 121, 153, 195, and 206 meV (670, 976, 1230, 1570, and 1660 cm^{-1}) are in good agreement with those at 84, 122, 156, 197, and 207 meV in single photon induced photoelectron spectra.^{2,3,32} As discussed above these must either be associated with ν_1 or with $j=\frac{1}{2}$ levels of Jahn-Teller active modes. Based only on the above approximate calculation the 84, 153, and 206 meV peaks might seem to correspond to ions in their $6^1(1/2)$, $6^2(1/2)$, and $6^3(1/2)$ levels. However, as will be seen our spectrum obtained by ionizing through the 6^2_1 transition conclusively identifies the $6^2(1/2)$ level with a 165 meV peak. Furthermore, the 206 meV peak is more likely associated with production of $1^6 6^1(1/2)$ ions since progressions involving ν_1 are ubiquitous in our data. We have no compelling arguments by which to assign the 153 and 195 meV peaks. Therefore, for now we retain the 9^1 and 8^1 assignments of previous workers. Several peaks appear in our spectra that have not been previously observed or assigned. These occur at 44, 132, 165, 232, and 255 meV. The first two of these agree quite well with calculated eigenvalues listed above so these must be associated with ions in their $6^1(3/2)$ and $6^2(3/2)$ vibronic levels. The 165 meV peak could be $6^2(1/2)$ mentioned above but it could also be $1^6 6^1(3/2)$. Its broadened and irregular shape suggest that it is a combination of both. The weak 232 and 255 meV peaks in this spectrum are tentatively assigned to $6^3(3/2)$ and $1^6 6^2(3/2)$ ion levels, respectively.

The photoelectron spectrum obtained by exciting the 6^0_1 benzene transition is quite similar to the 6^0_0 case, as had been expected. The three main peaks in Fig. 2(C) appear at the same locations and with similar relative intensities as in Figs. 2(A) and 2(B). The fourth peak at 121 meV is diminished in intensity. This may result because the ionizing photon energy is so small that the electrons in this peak possess less than 70 meV and our spectrometer's transmission drops somewhat

for electrons having less than about 100 meV kinetic energy. Those which are slower than this usually either cannot be seen or they appear in peaks of diminished intensity. A small peak also appears in this spectrum between the $6^1(3/2)$ and $6^1(1/2)$ ion peaks. This does not appear in any of our other spectra and has not been reproduced. We are currently ignoring it.

The photoelectron spectrum produced by exciting through the 6^0_1 vibronic transition is also quite similar to the 6^0_0 spectrum although because of the higher photon energy it contains additional peaks corresponding to more vibrationally excited ions. The first three peaks in the spectrum appear similar to their counterparts in Figs. 2(A)–2(C) although now the ground state ion peak is somewhat smaller than both peaks associated with 6^1 levels. More dramatically, the 121 meV peak 1^1 grows substantially as a result of the excitation of ν_1 in the intermediate vibronic state. The $6^2(3/2)$ peak at 132 meV is reduced somewhat while $1^6 6^1(3/2)$ at 165 meV is slightly more intense. A strong new peak appears at 280 meV and this is assigned as $1^6 6^1(3/2)$. Although not shown in this spectrum one other peak stands out at 401 meV. This is certainly $1^3 6^1(3/2)$.

The other peaks appearing in the 6^0_1 spectrum occur at 82, 120, and 243 meV. The first two were discussed above. The last peak undoubtedly corresponds to production of ions in the 1^2 vibrational state. Apparently the 1^1 and 1^2 peaks stand out well in this spectrum because of the excitation of ν_1 in the $^1B_{2u}$ intermediate state.

It is apparent from Fig. 3(A) that when benzene is ionized from a vibrationally unexcited $^1B_{2u}$ level almost all of the ions produced are vibrationally unexcited. The two small peaks which follow the $v=0$ peak may appear weaker than they should be because of the spectrometer transmission at 40 meV. Nevertheless, generation of vibrationally excited ions must be highly disfavored at this laser wavelength. The two small peaks, at about 40 and 52 meV, are more clearly seen in Fig. 3(B) which exhibits the photoelectron spectrum generated by ionizing through benzene's 6^0_1 transition. Neither of these peaks overlaps with our assigned $6^1(3/2)$ ion peak which, as discussed above, is not expected to appear in this spectrum. Noting once again that no peaks at all are observed in this region of the conventional photoelectron spectrum of benzene,¹⁻⁴ their appearance in our spectra may initially seem surprising. Only one normal mode of benzene has a vibrational frequency of this magnitude. This is ν_{16} which is 399 cm^{-1} (49.5 meV) in the ground state of C_6H_6 and 238 cm^{-1} (29.5 meV) in the $^1B_{2u}$ state.²⁸ In various excited Rydberg states ν_{16} has been reported to be between 300 and 335 cm^{-1} (37 and 41.5 meV),³⁰⁻³² in excellent agreement with our 40 meV peak. The photoelectron spectrum derived from exciting benzene's 6^0_1 transition appears in Fig. 3(C) and confirms this assignment. Here we find strong evidence for a $\Delta\nu_{16}=0$ propensity rule for ionization from an excited vibronic level of benzene. This is an impressive example of how vibrationally excited ions can be preferentially produced even with light that exceeds an ionization potential by only 0.13 eV.

Two possible assignments for the weak 52 meV peak should be considered. ν_{16} is a doubly degenerate normal mode in ground state benzene but it could possibly be split in the ion. However if this were true, we would expect to see the 52 meV peak in our $6_0^1 16_1^1$ spectrum [Fig. 3(C)] and we do not. The ν_{16} normal mode of vibration corresponds to an out-of-plane skeletal bending. While several of benzene's normal modes involve out of plane motion, the only other one classified by Varsanyi as a skeletal vibration is ν_4 .³³ In the $^1A_{1g}$ and $^1B_{2u}$ states this has frequencies of 707 cm^{-1} (87.6 meV) and 365 cm^{-1} (45.2 meV), respectively.²⁸ Our 52 meV peak may well be associated with this normal mode. Further evidence supporting this assignment comes from our isotope substitution data which is presented below.

It is worthwhile to consider why out-of-plane normal modes of vibration should be excited when benzene is ionized from a vibrationless or symmetrically vibrating $^1B_{2u}$ intermediate state. Since out of plane modes are neither symmetric nor Jahn-Teller active for a D_{6h} molecule their excitation is not anticipated and, in fact, is not observed in the conventional photoelectron spectrum of benzene. The simplest explanation for their appearance in our spectra is that the equilibrium geometry of benzene in its $^1B_{2u}$ state must not be exactly planar. We emphasize that the nonplanar distortion must be slight because our peaks at 40 and 52 meV are certainly very small. This interpretation agrees perfectly with the recent results of Riedle, Neusser, and Schlag who have demonstrated through rotational analysis of a very high resolution two photon absorption spectrum that $^1B_{2u}$ benzene is indeed slightly nonplanar.³⁴

The photoelectron spectrum generated by ionizing through the $6_0^1 16_1^1$ transition is depicted in Fig. 4(A). The separation between the first two peaks agrees with that measured from the $6_0^1 16_1^1$ spectrum. Furthermore, it overlaps almost perfectly with the 6_0^1 spectrum of Fig. 2(A), if the $\nu=0$ peak of the 6_0^1 spectrum is lined up with the 39 meV peak of the $6_0^1 16_1^1$ spectrum. In other words, all peaks in the $6_0^1 16_1^1$ spectrum except the first one correspond to levels in which ν_{16} is excited in conjunction with those modes excited in the 6_0^1 spectrum. This spectrum provides further confirmation of the assignment of ν_{16} as 39.5 meV. Exciting ν_{16} by way of the 16_0^2 transition leads to the rather unusual photoelectron spectrum depicted in Fig. 4(B). The $\nu=0$ ion peak is really not discernable from the noise. This leads to some ambiguity in measuring peak spacings, since we normally measure these from a well defined $\nu=0$ peak. Nevertheless, based on our best estimate of the $\nu=0$ peak location we observe very strong peaks at 77 and 199 meV, that are attributable to ions in their 16^2 and $1^1 16^2$ levels. Smaller peaks at 40 and 160 meV probably correspond to ions in their 16^1 and $1^1 16^1$ levels. A relatively complex peak near 119 meV probably consists of overlapping contributions from 16^3 and 1^1 ions. Similarly, a small peak at 236 meV probably results from ions in both 1^2 and $1^1 16^3$ levels. It is interesting to note a general trend in Figs. 3(B), 3(C), 4(A), and 4(B). Although for ν_{16} a $\Delta\nu=1$ process is not completely forbidden, probably because of the reason discussed

above, nevertheless a $\Delta\nu=0$ process is much more strongly favored. The effect of vibrational excitation is apparently greater than the effect of a small change in molecular geometry in leading to excitation of ions in this nonsymmetric mode of vibration.

The photoelectron spectra obtained by ionizing benzene through its $6_1^2 7_{+1}^0$ and $6_1^2 7_{+1}^{+2}$ transitions certainly provide the most striking demonstration of wavelength and selection rule dependence thus far uncovered by laser photoelectron spectroscopy. These transitions are just 6.8 cm^{-1} apart in the near ultraviolet. Yet one expects only $j_6 = \frac{1}{2}$ ion levels in one case and $j_6 = \frac{3}{2}, \frac{5}{2}$ ion levels in the other. As evidenced in Figs. 4(C) and 4(D) the experimental results confirm these predictions. In Fig. 4(C) we detect substantial peaks at 0, 83, and 165 meV of ion internal energy. The first two of these are certainly $j_6 = \frac{1}{2}$ levels. The fact that the 165 meV peak is the most intense one in the spectrum strongly argues for its assignment as $6^2(1/2)$, a conclusion that was briefly mentioned above. Other substantial peaks that we have only observed in this one spectrum include $6^3(1/2)$ and $1^1 6^2(1/2)$ at 219 and 281 meV, respectively. [The latter actually overlaps with the expected $6^4(1/2)$ peak location. However, we suspect that the intensity of $6^4(1/2)$ would be substantially weaker than that of $1^1 6^2(1/2)$.] Two very weak peaks at 41 and 51 meV are undoubtedly the same pair that we have observed in some other spectra [e.g., Figs. 3(A) and 3(B)]. We did not anticipate or observe a peak at 44 meV in this spectrum. However an unexpected rather complex peak between 120 and 130 meV appears. Its assignment is uncertain.

In Fig. 4(D) we see a striking reversal of the spectral pattern depicted in Fig. 4(C). The vibrationless ion peak is now insignificantly small as is the one at 83 meV. (The fact that they are detectable at all could either be a consequence of a breakdown of the selection rule presented earlier or it could simply be from slight overlapping of the rotational contours of the two 6_1^2 vibrational angular momentum components.) This spectrum is dominated by peaks at 44 and 93 meV. These correspond to $6^1(3/2)$ and $6^2(5/2)$ levels according to our rough calculation above. Naturally one then expects to see $1^1 6^1(3/2)$ and $1^1 6^2(5/2)$ peaks and finds these at 167 and 215 meV. The $6^2(3/2)$ level at 132 meV also appears along with $1^1 6^2(3/2)$ and $1^2 6^1(3/2)$ at 250 and 283 meV, respectively.

A discussion of the two photoelectron spectra derived by exciting 6_1^2 transitions would not be complete without establishing the final assignment of these two vibrational angular momentum components. Atkinson and Parmenter²⁸ clearly showed that from their ultraviolet absorption spectra alone one could not determine which component accounts for the observed bandhead at $38\,529.3\text{ cm}^{-1}$ and which accounts for the one at $38\,522.5\text{ cm}^{-1}$. Our photoelectron spectrum in Fig. 4(C) was obtained by ionizing benzene at the former frequency and that in Fig. 4(D) resulted from employing the latter. From the preceding discussion we conclude that the higher frequency transition must be $6_1^2 7_{+1}^0$ and the lower frequency transition $6_1^2 7_{+1}^{+2}$.

TABLE IV. Final normal mode assignments and isotope ratios.

	$^1A_{1g}$ ^a			$^1B_{2u}$ ^a			$^2E_{1g}$ ^b		
	H	D	Ratio	H	D	Ratio	H	D	Ratio
ν_1	995.4	945.6	1.053	923	879	1.050	121	115	1.052
ν_4	707	599	1.180	365	...	...	51.5	43.5	1.184
ν_6	608.3	580.2	1.048	522.4	498.0	1.049	83.5	79	1.057 ($j=\frac{1}{2}$)
							44	42.5	1.035 ($j=\frac{3}{2}$)
ν_{16}	398.6	347.7	1.146	237.3	207.1	1.146	39.5	34.5	1.145

^aEnergy levels in cm⁻¹ for $^1A_{1g}$ and $^1B_{2u}$ levels taken from Refs. 27, 28, and 40.^bOur measured energy levels in meV.

Laser photoelectron spectra of C_6D_6 generated by exciting the $6_0^11_0^0$, 6_0^1 , and $6_1^016_1^1$ vibronic transitions are presented in Figs. 5(A), 5(B), and 5(C), and should be compared with their C_6H_6 analogs in Figs. 2(C), 3(A), and 3(C), respectively. The data are tabulated in Table III. The first vibrationally excited ion peak in Fig. 5(A) is separated by 41.5 meV from the $v=0$ peak. This spacing is associated with the $6^1(3/2)$ mode of $C_6D_6^+$. The second peak, at 79 meV, should correspond to ions in their $6^1(1/2)$ level. The third peak, at 114 meV, results from production of ions excited with one quantum of ν_1 . This agrees with the observation and interpretation of Potts *et al.*³ The final peak, at 158 meV, could be assigned to ions in either their $1^16^1(3/2)$ or $6^2(1/2)$ levels. Analogous to the 6_1^0 spectrum of $C_6H_6^+$, when exciting this transition of C_6D_6 most of the ions are produced vibrationally unexcited. However, three small peaks appear at energies of 35, 43.5, and 80.5 meV. They are assigned to $C_6D_6^+$ ions in their 16^1 , 4^1 , and $6^1(1/2)$ levels. The 4^1 assignment, which is the least certain, is further discussed in the next paragraph. When C_6D_6 is irradiated at the wavelength of its $6_1^016_1^1$ transition most of the ions generated are vibrationally excited in their 16^1 level. This is in complete agreement with the analogous C_6H_6 spectrum. A noteworthy feature in this spectrum is that for C_6D_6 a significant additional peak appears at 70.5 meV. We conclude that this corresponds to ions generated in their 16^2 vibrational level. Therefore, once again we see evidence of a propensity for $\Delta v_{16}=0$ but a small probability for a $\Delta v_{16}=1$ transition.

In order to quantitatively exploit isotope substitution data the Teller-Redlich product rules should be employed.³⁵ Unfortunately to apply these, information about all of the normal modes belonging to a certain irreducible representation must be available. Since our data on $C_6H_6^+$, and especially $C_6D_6^+$, is still sketchy we can only employ the approximate, empirical isotope substitution rule that the ratio of a normal mode frequency in a molecule to that in an isotopically substituted molecule is independent of the molecular electronic state. Based on this we compared the frequencies of ν_1 , ν_4 , ν_6 , and ν_{16} for C_6H_6 and C_6D_6 in the $^1A_{1g}$ ground electronic state, the $^1B_{2u}$ state, and the $^2E_{1g}$ ion ground state. It is evident from the results listed in Table IV that agreement based on our assignments of these modes is quite reasonable. This is particularly helpful

in the case of ν_4 since its assignment was based on such little hard evidence. Calloman, Dunn, and Mills²⁷ list vibrational frequencies for C_6H_6 and C_6D_6 in their $^1A_{1g}$ ground electronic states. Our experimentally observed isotope ratio for the peaks that we assigned to ν_4 is closer to the ν_4 ratio that they list than it is to the isotope ratio of any of benzene's other 19 normal mode frequencies. Hopefully, final confirmation of this assignment will be derived in future experiments when we will ionize benzene from vibronic levels in which ν_4 is known to be excited.

Since the density of accessible ion vibronic levels increases with ion internal energy, unambiguous assignment of our laser photoelectron peaks requires better than semiquantitative agreement between our model's predictions and the experimental data. Some of our peaks could be assigned to two or more indistinguishable ion levels, for example. While the limited electron energy resolution certainly exacerbates this problem our model for the Jahn-Teller distorted vibrational frequencies certainly requires optimization. The approach employed by Sears *et al.*^{15,16} has been to fit their experimental halogenated benzene cation fluorescence data by varying the value of the Jahn-Teller distortion parameter and the unperturbed ion vibrational frequency until agreement between the observed and calculated data results. When our D parameter is varied between 0.30 and 0.70 in steps of 0.01, best agreement is obtained for $D=0.50$ with an unperturbed vibrational frequency equal to 66 meV (532 cm⁻¹). This value of D implies that the electronic stabilization induced by Jahn-Teller distortion along the ν_6 normal coordinate is only one-half of the energy of the ν_6 vibrational quantum. Therefore, benzene cation cannot be pictured as having just D_{6h} or Jahn-Teller distorted D_{2h} symmetry. Rather, in the course of its vibrational motion its geometry changes and it spends some time in the symmetric configuration and some time distorted.

The calculated energy level spacings for $C_6H_6^+$ are included in Table II along with the experimental data. Figure 7 presents this information pictorially. Agreement between the model and the experimental data must still be viewed as semiquantitative. Sears *et al.* obtained significantly better agreement between theory and their experimental data by including additional off-diagonal matrix elements in their Jahn-Teller perturbed

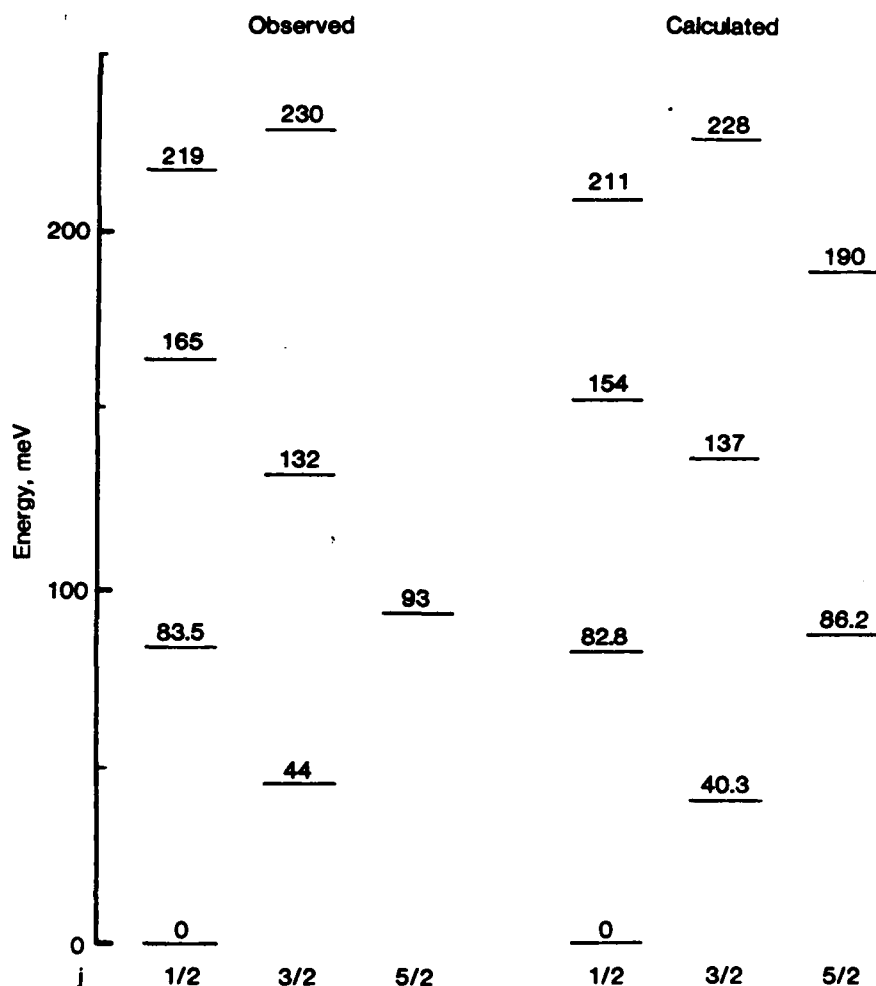


FIG. 7. Observed and calculated vibronic level structure in the ${}^2E_{1g}$ ground electronic state of $C_6H_6^+$.

Hamiltonian. These derived from nonlinear contributions to the molecular potential and coupling between three or four of the Jahn-Teller active e_{2g} modes. Their model required the diagonalization of up to 7000×7000 matrices, in contrast with the 16×16 matrices which we employ in our single mode model. In the future when more experimental data on ν_6 and ν_9 becomes available the additional effort to perform such a sophisticated calculation on benzene cation will probably be justified. The fact that a simple single mode model seems to be more adequate to explain data on $C_6H_6^+$ than on $C_6F_6^+$ may not be fortuitous. In conventional photoelectron spectra $C_6F_6^+$ ions are generated with considerably more vibrational excitation than are $C_6H_6^+$ ions.³ Furthermore, $C_6F_6^+$ normal modes tend to be lower in frequency and therefore more closely spaced than those of $C_6H_6^+$. One might therefore expect to observe more coupling between the modes of $C_6F_6^+$, thus explaining the greater need for a multimode model to interpret this ion's spectroscopic data. Several groups have calculated the total Jahn-Teller stabilization energy of benzene from first principles. The results, summarized by Sears *et al.*¹⁵ are comparable to what we have observed for ν_6 alone. Further comparison awaits experimental data on other Jahn-Teller active modes.

The values that we have obtained for ν_6 and ν_{16} are justifiable and appealing to a chemist's intuition. As mentioned above, our optimized value for the unperturbed ν_6 vibrational frequency is 532 cm^{-1} . This is in between the values of ν_6 in benzene's ${}^1A_{1g}$ ground state (608.3 cm^{-1}) and ${}^1B_{2u}$ first excited singlet state (521.4 cm^{-1}). An e_{1g} π electron is promoted to an antibonding e_{2u} π^* orbital to generate the ${}^1B_{2u}$ excited state. This same π electron is then removed to form an ion in its ground electronic state. It is qualitatively reasonable not only that the bonding capability of benzene's π electron system is weakened upon photoionization (leading to a lower ion vibrational frequency) but also that the bonding is further weakened when the π electron is retained in an antibonding π^* orbital. Although this observation may now seem rather obvious, 85 meV (680 cm^{-1}) has been the accepted value for ν_6 in $C_6H_6^+$, even though this implies that the ν_6 frequency is higher in the ion than in the ground state of the neutral molecule. To rationalize this it has sometimes been argued that benzene's π electrons are basically nonbonding—a suggestion which is clearly incorrect. An equivalently simple and understandable situation now exists for ν_{16} and ν_4 . Our ion frequency of 39.5 meV (319 cm^{-1}) is in between the ${}^1A_{1g}$ and ${}^1B_{2u}$ values for ν_{16} of 398.8 and

237.5 cm^{-1} . Likewise, our 51.5 meV (415 cm^{-1}) ion assignment for ν_4 is between the ${}^1A_{1g}$ and ${}^1B_{2u}$ values of 707 and 365 cm^{-1} , respectively.

Implicit in this paper has been a model of the C_6H_6 ionization as a two-step process. Initially, an e_{1g} π electron is promoted to an e_{2u} molecular orbital leaving benzene in some vibronic level of its ${}^1B_{2u}$ first excited electronic state. Subsequently, a second photon is absorbed by the excited benzene, generating an ion in some vibrational level of its ground electronic state. However, we cannot rule out the possibility that benzene in its excited ${}^1B_{2u}$ state absorbs a photon promoting a second e_{1g} electron to an e_{2u} molecular orbital. The resulting state could autoionize to ground state ions. Alternatively, if it were sufficiently long lived this two-electron excited benzene could absorb another photon yielding an electronically excited ion. While we cannot rule out the rapid autoionization mechanism, absorption of a third photon seems unlikely for two reasons. First, the additional available energy would be expected to dramatically affect the observed photoelectron distribution. Our spectra are interpretable based on absorption of two photons. Second, the laser ionization mass spectrum of benzene taken with either dye laser or KrF excimer laser radiation indicates that at the low light intensities employed in these experiments only C_6H_6^+ ions are generated.^{36,37} Absorption of a third photon most likely would lead to ion fragmentation since the input energy would in this case exceed the known appearance potential for C_6H_5^+ and C_3H_3^+ formation from benzene. Photodissociation of C_6H_6^+ using ultraviolet light has in fact already been demonstrated.¹⁰ The rate of stimulated transitions is comparatively slow at the light intensities that we employ in these experiments. (Approximately $2 \times 10^8 \text{ s}^{-1}$ assuming a cross section of 10^{-17} cm^2 .) It would be surprising if any autoionization that might be occurring were not considerably faster than this. In fact if autoionization were involved and its rate were much slower than this our TOF electron peak line shapes would be affected. Experiments with higher intensity light pulses might be revealing since stimulated transitions could then compete with autoionization even if the latter took place on a more reasonable subpicosecond timescale. In that case, new, intensity dependent peaks should appear in the observed photoelectron spectra corresponding to production of a new electronic state of benzene. This would indeed be interesting since such an ion state would be the result of a two-electron excitation process. This is generally not observed in conventional single photon photoelectron spectroscopy and certainly has not been for the particular case of benzene. Aside from this fascinating possibility this technique is presently limited to deriving spectroscopic information about the ground electronic states of ions in contrast with HeI resonance lamp ionization which can access higher electronic states. Therefore, no new information has been obtained relating to the controversial energetic ordering of benzene's occupied molecular orbitals.

The present results are in excellent agreement with the recent study of benzene's E_g Rydberg states by Whetten, Fu, and Grant.²² Their spectra are dominated

by transitions to excited states having vibronic angular momenta $j_g = \frac{1}{2}$. This is exactly analogous to what is observed in the single photon photoelectron spectrum of benzene. By means of hot bands they were even able to assign a few $j_g = \frac{3}{2}$ levels. In all comparable cases our benzene ion vibrational frequencies are found to be very similar to the Rydberg state values.

This work has considerable relevance to other studies involving laser induced ionization of benzene. For example, it has been suggested that because the laser photon energy barely exceeds the ionization potential ions must be generated with only a small amount of internal energy, and furthermore that molecular ions can be excited to definite energy levels with visible or UV light.³⁸ As can be seen from the complex collection of spectra in Fig. 2, the real situation is considerably more complicated than this. The particular vibronic state excited in the course of the two-step ionization plays the greatest role in determining the vibrational state distribution of the resulting ions. Smalley and co-workers have performed two color ionization experiments with benzene.³⁹ Using one wavelength in resonance with the 6_0^1 transition and a second tuned from 2800 Å to shorter wavelengths they measured the threshold ionization spectrum of benzene. One of their important observations was a sharp rise in ion yield at about 335 cm^{-1} (41 meV) and a slower rise at about 860 cm^{-1} (107 meV) above ionization threshold. The latter was attributed to excitation of ν_6 in C_6H_6^+ , but the first feature was not assigned to a vibrational spacing due to its failure to appear in benzene's conventional photoelectron spectrum. However, now that we have observed ions in their $6^1(3/2)$ vibrational state following laser excitation through 6_0^1 , the assignment of this feature in their spectra to this same vibrational spacing appears justified. It is unnecessary to invoke an autoionization mechanism to explain their observed threshold ionization spectra.

V. SUMMARY AND CONCLUSIONS

It has been demonstrated that laser induced photoelectron spectra of benzene can be generated that are rich in vibrational structure. The enhanced vibrational information content results because ionization occurs from vibrationally excited levels of electronically excited states. In addition to accessing previously unobserved ion vibrational states, laser photoelectron spectroscopy expedites the interpretation of spectral peaks because ionization proceeds through known, previously assigned vibronic levels. Spectroscopic information about excited molecular electronic states which has been gathered over the past several decades can therefore be fully exploited. This method of deriving or confirming ion vibrational spectroscopic assignments can be used in conjunction with classical methods involving molecular isotope substitution. The combination of these approaches was useful in interpreting photoelectron bands involving ν_6 and ν_{16} . Conclusive assignments for these normal mode frequencies have been derived. A tentative assignment for ν_4 in benzene ion has also been proposed. The necessary data to measure and interpret the Jahn-Teller splitting of vibronic states in-

volving ν_6 was derivable for the first time as a consequence of the two-step nature of the photoionization process employed in laser photoelectron spectroscopy. Our new value for the "unperturbed" ν_6 frequency is in much better agreement with the expectations of chemical intuition than was the ion frequency derived for ν_6 from the conventional photoelectron spectrum.

A $\Delta v = 0$ propensity rule for photoionization from an excited state has once again been demonstrated, although its application to benzene's ν_6 normal mode is complicated by the existence of Jahn-Teller distortion. It seems that this $\Delta v = 0$ rule will generally hold for cases in which a ground electronic state, an excited state, and a molecular ion are of similar symmetry. We have also demonstrated that a vibronic angular momentum selection rule that is normally applied to transitions between bound electronic states can also be usefully applied to photoionization processes in molecules. This is particularly helpful in identifying and assigning Jahn-Teller splittings.

Remarkably different spectra can be derived by ionizing benzene at slightly different wavelengths. In the most striking example of this, the wavelengths employed to excite the $6^2_{11}0$ and $6^2_{11}2$ transitions differ by only 0.5 Å (6.8 cm⁻¹) yet the photoelectron spectra recorded were quite dissimilar. This particular example also represents the first case where laser photoelectron spectroscopy has been applied to determine an assignment in an ultraviolet absorption spectrum which had not been established by optical techniques alone. It has also been demonstrated that qualitative information about the relative geometries of excited state molecules and ions is derivable with this technique. This can complement the results of very high resolution optical spectroscopy experiments.

Since the ion vibrational state distributions that we observe depend so critically on details of the potential energy surfaces of the molecule and ion they should be a sensitive test of the quality of calculated potential energy surfaces. While the 3–5 meV (24–40 cm⁻¹) resolution of the technique is still inferior to that of most optical methods, it is excellent by electron spectroscopy standards. Furthermore some ions, such as C₆H₆⁺, have thus far not been amenable to study by fluorescence or absorption methods, and it is important to develop general techniques that can handle important cases such as these. Considering the rapid development of laser photoelectron spectroscopy from very low, to moderate and now to a fairly high resolution technique, it seems likely that further substantial advances will be made, and resolution may soon approach the single cm⁻¹ realm. This is important since the density of ion vibrational states certainly increases with energy. It is clearly evident in our spectra that peak overlap and congestion develop in the region corresponding to high ion vibrational energy. This leads to problems and ambiguities in assigning ion combination modes. Higher electron kinetic energy resolution would help to alleviate this problem.

In this work we have derived just a fraction of the vibrational spectroscopic information on benzene cation

which should be extractable. By means of allowed single photon and two photon processes, vibronic levels involving 16 of benzene's 20 different normal modes can be reached in the $^1B_{2u}$ first excited singlet state. Assuming that excitation through these levels will lead to C₆H₆⁺ ion modes vibrating similarly we expect to be able to experimentally observe most of benzene ion's normal mode frequencies using laser photoelectron spectroscopy.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Army Research Office under contract number DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0.

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Multiphoton Ionization Photoelectron Spectroscopy

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(Received 2 December 1983; revised 12 February 1984)

Abstract. Recent research involving the monitoring of photoelectrons generated in the course of molecular multiphoton ionization is reviewed. Information about the order of the multiphoton ionization process, the identity and ionization potential of the species ionized, and spectroscopic data about excited states of neutral molecules and the ground states of ions can all be extracted using this new technique.

INTRODUCTION

Research involving the ionization of gaseous samples commenced soon after the initial development of powerful pulsed lasers.¹⁻³ Following the successful demonstration of laser induced ionization it was once again just a short time before attempts were made to monitor the kinetic energy distribution of the electrons ejected in the photoionization process.⁴⁻⁶ Unfortunately these early studies were not particularly encouraging. Using laser photons with energies of 1-2 eV researchers detected electrons ejected from the focal regions with kinetic energies ranging from 0 to 160 eV! The acceleration of electrons to such energies has been rationalized by invoking electromagnetic field gradient forces (a classical effect involving time averaged acceleration of a charged particle out from the center of a focussed laser beam). Nevertheless the lack of resolvable or interpretable structure within the observed photoelectron energy distributions evoked little interest in the technique among chemical spectroscopists. This was in marked contrast with the very successful concurrent blossoming of the field of conventional (resonance radiation induced) ultraviolet photoelectron spectroscopy. Laser ionization did not become chemically relevant until the development of molecular multiphoton ionization spectroscopy by Johnson and coworkers.^{7,8} This technique was quickly adopted by others.⁹ Several research groups then became interested in the fact that fragmentation, in addition to ionization, can occur when an intense UV laser beam irradiates isolated gas phase molecules. To investigate this phenomenon laser ionization sources were interfaced with mass spectrometers.¹⁰⁻¹² While the latter are successful at identifying exactly which ions are generated (and this is crucial in studies of van der Waals complexes and isotopically substituted species), they do not provide mechanistic information about how ion fragments are actually created. Our initial motivation for monitoring the ejected photoelectrons was to try to extract information of this kind.

The first low resolution but clearly interpretable laser photoelectron experiments involved Xe atoms and C₆H₆ molecules.¹³⁻¹⁵ (For the present discussion we explicitly exclude discussion of laser induced photodetachment of electrons from negative ions. Considering that research of this kind involves single photon processes and nontunable laser sources it is really quite similar to conventional photoelectron spectroscopy. Only studies involving the production of electrons from the laser induced ionization

of neutral species will be considered herein.) Following the successful Xe and C₆H₆ experiments considerable effort has gone into improving the resolution of the photoelectron energy analyses. As will be discussed below resolution comparable to or even better than that of conventional resonance lamp photoelectron spectrometers has been attained and it is improving all the time. Samples of current interest to researchers can be broadly classified into three types:

- (1) diatomic molecules,
- (2) polyatomic molecules,
- (3) transient species.

The purpose of the present paper is to briefly review how laser photoelectron experiments are performed, what has been learned about molecules and ions, and what might be investigated with this technique in the future.

EXPERIMENTAL

Because fast pulsed (< 10 nanosecond duration) lasers are used for generating ions the time of flight (TOF) method is the obvious choice for electron kinetic energy analysis. Photoelectrons are produced in a short well-defined time interval and the laser light pulse provides a convenient start signal for timing electronics. In addition, the TOF method usually does not require electron optics. This eliminates optical aberration problems that tend to degrade energy resolution in conventional PES electrostatic instruments.

The nonrelativistic kinetic energy of an electron is

$$E = \frac{mv^2}{2} = \frac{mL^2}{2t^2}$$

where m is the electron mass, L is the flight path length and t is the time required for the electron to traverse the distance L . Evaluation of an electron's kinetic energy is thus simply a matter of measuring its flight time to an electron multiplier over a known distance. One apparatus that accomplishes this task is displayed in Fig. 1. While a pulsed, skimmed supersonic beam of molecules is depicted therein, we often use a simple unskimmed effusive source. 1 to 10 μ J pulses of ultraviolet radiation emanating from either an excimer laser or a frequency doubled dye laser are focussed with a 20 cm f.l. lens and intercept the molecular beam. The ejected electrons fly off in various directions. A small fraction of them reach a microchannel plate detector 49 cm away that has a gain of over one million. Following amplification the signal is digitized by a waveform recorder or a time-to-digital converter. Electron energy resolution is determined by the narrowness of the incident laser pulse

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in space, frequency, and time, by the bandwidth of the timing electronics, and by the electric and magnetic fields that influence electrons in the course of their flight toward the electron multiplier. There is a complex interplay between these factors. Their relative importance depends on the sample being studied and particularly on the kinetic energies of the electrons being analyzed. In our earliest study of the photoelectrons ejected from the ionization of benzene vapor we employed KrF and ArF excimer lasers as photon sources.¹⁶ Their poor frequency and temporal resolution prevented us from resolving vibrational structure in the resultant photoelectron band. One spectrum that we recorded is depicted in Fig. 2. Note that the FWHM of

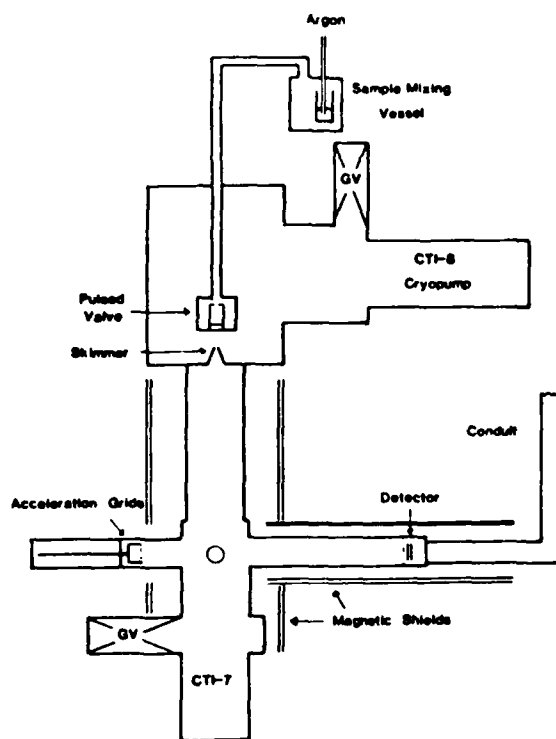


Fig. 1. Apparatus for recording laser induced photoelectron kinetic energy distributions by time of flight. Our pulsed supersonic molecular beam equipment is depicted.

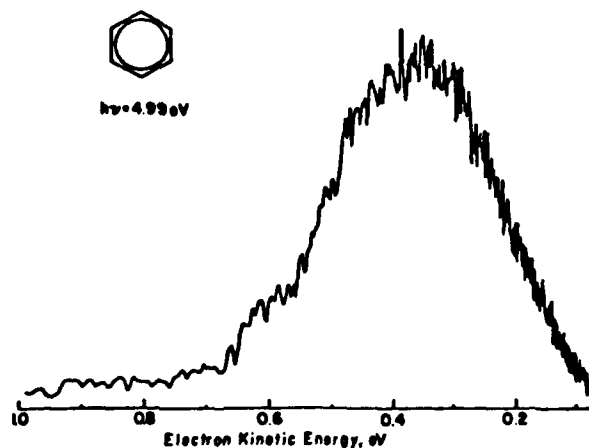


Fig. 2. Kinetic energy distribution of the photoelectrons ejected from benzene ionized by radiation from a KrF excimer laser.

the unresolved photoelectron band is on the order of 0.5 to 1.0 eV; this is comparable to those obtained in conventional photoelectron spectroscopy. Replacement of the excimer light source by a narrowband, tunable, frequency doubled dye laser has led to an enormous improvement in resolution with our best case now being about 3 meV. Due to the small solid acceptance angle of a TOF instrument such as that depicted in Fig. 1 a very small fraction of the electrons ejected from the focal volume of the laser are detected. One then has the choice of either generating an enormous cloud of charge to obtain a reasonable signal at the detector or else averaging a very weak electron signal over a very large number of laser pulses. Since we have found that the former approach leads to deterioration of electron energy resolution¹⁶ we typically add up the signals produced by about 10⁵ laser shots to record high quality photoelectron spectra. Count rates are usually about one electron per laser pulse. The low energy UV laser pulses employed in this work are obtainable from many nitrogen or excimer pumped dye lasers even after frequency doubling in nonoptimal crystals such as potassium pentaborate (KPB) or lithium formate monohydrate (LFM). Vacuum pumping requirements depend on the type of molecular beam source (effusive, supersonic, pulsed, etc.) being utilized. In order to minimize collisions between ejected electrons and background gas we usually maintain an operating pressure of less than 10⁻⁸ torr in the electron flight tube.

RESULTS AND DISCUSSION

A. Diatomic Molecules

The molecule most thoroughly studied to date has been NO.^{17, 20} This is not surprising since its relatively low lying electronic states and small ionization potential make it a convenient prototype molecule for any spectroscopic work. In most of the studies performed thus far the NO A²Σ and C²Π intermediate electronic states have been excited by two or three photon transitions using visible or near-UV dye lasers. One or two additional photons are then needed to ionize the molecule. Photoelectron data indicate that some ions are generated in the same vibrational level as was excited in the resonant intermediate state, but substantial numbers are generated in highly vibrationally excited levels. Considering that the A and C states of NO are both Rydberg states and are known to have equilibrium internuclear distances quite comparable to that of NO⁺ this is at first sight somewhat surprising. Franck-Condon arguments would suggest that NO⁺ ions should be created predominantly in the same vibrational level as is populated in the resonant intermediate state. Similar results have recently been reported with CO,²¹ although at least in this case the fact that the A¹Π intermediate electronic state excited has a different equilibrium internuclear distance compared to that of the ion warns us not to expect solely Δv = 0 transitions upon photoionization. Apparently something more than a simple two-step excitation/ionization process must be occurring in these molecules. Complications that could lead to unusual ion vibrational state distributions include:

- (1) vibrational autoionization,
- (2) electronic autoionization,
- (3) production of electronically excited ions,
- (4) excitation of another electronic state between the initially populated intermediate state and the ion.

Arguments associated with the contributions of these mechanisms have been presented.^{17, 19} The last of these mechanisms has received recent support.²² We have ionized NO by directly exciting the v = 0 vibrational level of the A electronic state using single UV photons near 2160 Å.²⁰ Virtually no photoelectrons were observed that could be associated with production of ions in

any level other than $v = 0$. Since the energy of two of our photons exactly equals that of four of the photons used by earlier workers, we should be able to reach the same autoionizing levels that they reached, if they really were exciting autoionizing levels. At the wavelength we used only the lowest electronic state of NO^+ ions can be populated. Our data therefore suggest that in the previous multiphoton ionization experiments electronic states in between the $A^2\Sigma$ excited state of neutral NO and the $X^2\Sigma$ ion ground state probably have been populated.

The major goal of our NO work had, in fact, not been to elucidate the four-photon ionization mechanism, but rather to obtain rotationally resolved photoelectron spectra so as to experimentally uncover rotational selection rules associated with photoionization processes. Rotationally resolved molecular photoelectron spectra have only been previously recorded in studies with H_2 which has an unusually large rotational constant.^{21,22} These studies were somewhat limited by the fact that ionization takes place from a distribution of rotational levels in a single vibrational and electronic state. This led to ions being generated in a distribution of rotational levels, independent of the photoionization rotational selection rule. Bonham and Lively have recently predicted that the rotational selection rule should depend on the symmetry of the state from which photoionization occurs.²³ Clearly this cannot be investigated by ionizing molecules only from their ground states. In a major step forward Pratt et al. recently photoionized H_2 from selected rotational levels of its $B^1\Sigma_u^+$ excited electronic state and recorded photoelectron spectra that were partially rotationally resolved.²⁴ More recently we have photoionized NO from high rotational levels of its $A^2\Sigma$ ($v = 0$) state and obtained rotationally resolved spectra.²⁵ An example of one of our distributions is depicted in Fig. 3. This was obtained by exciting the $J = 21.5$ level of

$v = 0$ of the $A^2\Sigma$ electronic state. (Actually due to a slight wavelength uncertainty the assignment of the J level is only certain to ± 1 . However when various rotational levels in this wavelength region are excited, all yield simple spectra similar to that depicted in Fig. 3.) The separation between the center peak and each of the small side peaks corresponds to two rotational quanta in the ion according to data listed by Huber and Herzberg.²⁶ We conclude that the rotational selection rule for photoionization from the $A^2\Sigma^+$ electronic state is $\Delta N = 0$ with $\Delta N = \pm 2$ being slightly allowed. These results agree with the predictions of Bonham and Lively. We are currently obtaining rotationally resolved photoelectron spectra by multiphoton ionizing NO from its $C^2\Pi$ and $D^2\Sigma^+$ electronic states in a further attempt to compare experiment with theory.

A second type of diatomic photoelectron study has been performed by Hepburn et al.²⁷ They simultaneously photolyzed and ionized CCl_3F and CCl_2F_2 and obtained CCl^+ and CF^+ ions. This work is significant in two respects. First it demonstrates that when ion fragments are observed in the multiphoton ionization mass spectra of polyatomic molecules, they may arise from dissociation of neutral species first followed by ionization of the fragments. This contrasts with the more commonly observed process whereby parent ions are formed and then photodissociated. Secondly and more significantly this demonstrates that photoelectron spectra of transient free radicals can be easily recorded by laser photoelectron spectroscopy. Due to the difficulty of obtaining such spectra with conventional techniques laser ionization could have a real impact in this area, both for diatomic and polyatomic samples. At present we are attempting to record the laser photoelectron spectrum of photolytically generated CH_2 radicals. If successful this will enable us to directly measure the controversial singlet-triplet electronic state splitting of this radical.

B. Polyatomic Molecules

The most popular subjects for laser photoelectron experiments among polyatomic species have been aromatic molecules. Our work has focussed on benzene, toluene and aniline^{10,11,28} while Anderson, Rider and Zare have investigated chlorobenzene,²⁹ and Kimura and coworkers³⁰ and Compton and coworkers³¹ have studied benzene and H_2S . Most of these experiments have involved just two step ionization. It is particularly gratifying that high resolution photoelectron spectra can be recorded by laser ionization because of two severe limitations of conventional PES. First, most photoelectron bands of large molecules exhibit barely resolved vibrational structure.³² Second, even when such structure is seen the number of peaks that appear is small relative to the number of vibrational modes of the molecule.³³ Thus an extremely limited amount of ion vibrational spectroscopic information can be extracted. Some ions, such as those of halogenated benzenes, can be probed by infrared absorption or laser induced fluorescence.^{40,41} But others, like C_6H_5^+ itself, have not been amenable to study by these methods. Thus, photoelectron measurements represent our primary hope for unravelling the ion vibrational spectroscopy of many of these species.

Considering that ions are an important class of molecules that commonly possess degenerate ground electronic states, they represent an important proving ground for testing our understanding of Jahn-Teller effects in isolated molecules. This is significant because

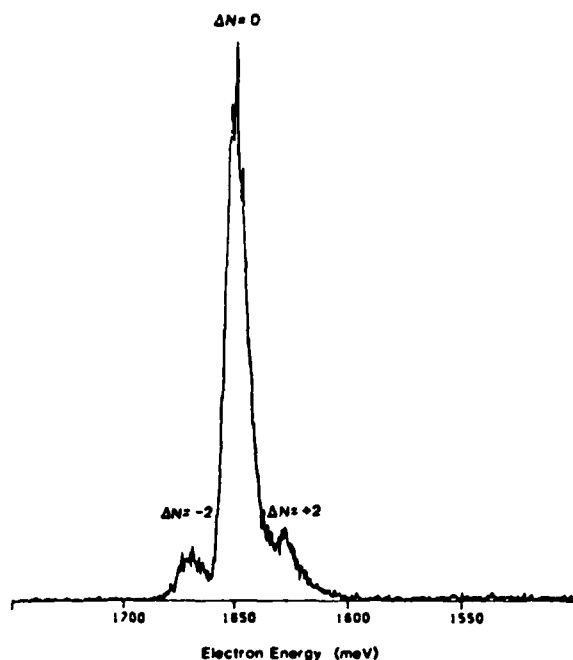


Fig. 3. Photoelectron spectrum of NO obtained by resonant one-photon excitation of a single rotational line in the O-O band of the $A \leftarrow X$ system. The rotational assignment of the excitation line is tentative and is most likely $R(21.5)$.

Jahn-Teller effects have so often been discussed in the inorganic spectroscopy literature, but inorganic compounds can rarely be investigated as isolated gas phase species. Crystal field effects can complicate the spectra of inorganic solids. C_6H_6 has always been one of the primary examples of a species that should exhibit Jahn-Teller splitting, yet until it was investigated by laser photoelectron spectroscopy its secrets had not been revealed.

The first low resolution study of benzene, as mentioned above, employed KrF and ArF excimer lasers as light sources.¹⁹ The purpose of this study was to learn whether the ejected photoelectrons could all be interpreted in terms of two photon ionization or whether some are ejected with energies corresponding to three, four or more photon absorption. The data in Fig. 2 indicate that the fastest photoelectrons possess about 0.75 eV of kinetic energy. Since the ionization potential of benzene is 9.25 eV and we were employing 4.99 photons this threshold is in excellent agreement with a simple two photon ionization mechanism. Since the photoelectron spectrum was unchanged when excimer laser pulse energies capable of creating fragment ions were employed,² we concluded that the generation of ion fragments probably occurs after parent ion formation rather than simultaneous with it. Note that our crude electron energy resolution might well have hidden from detection such processes as benzene photofragmentation followed by ionization of the photofragments. There is still no evidence suggesting that the latter occurs, but

there is also no reason why at high light intensities it could not. In fact the halomethane study of Hephurn et al.²⁰ suggests that this type of mechanism must in some cases be important.

The first high resolution (i.e., comparable to that generally obtainable with conventional single photon techniques) laser photoelectron spectrum reported was that of toluene.¹⁹ As depicted in Fig. 4, we demonstrated that when ionization occurs from vibrationally unexcited levels of toluene's first excited singlet state, vibrationally unexcited ions are preferentially produced. When normal modes ν_{10} and ν_{12} are excited in the resonant intermediate state ions are preferentially formed vibrationally excited with one quantum of excitation in each of these modes. This was significant as it pointed directly toward the immense potential of laser photoelectron spectroscopy for extracting information about ion vibrational levels that are not normally observable when a molecule is ionized from a vibrationless level of some electronic state. This potential has recently been exploited in much more thorough investigations of benzene and aniline.

The UV absorption spectrum of benzene has often been studied and is quite well understood.^{21,22} One can easily tune a frequency doubled dye laser to hundreds of different vibronic absorption bands in benzene's ${}^1B_{2u} \leftarrow {}^1A_{1g}$ 2600 Å system. A substantial fraction of these transitions have been assigned, and we have recorded photoelectron spectra by exciting several of them.²⁰ In all cases numerous peaks are observable that have not been detected in the conventional C_6H_6 photoelectron spectrum. Some are displayed in Fig. 5. The spectrum in Fig. 5A results from exciting the 6_0^0 transition of benzene. At first this spectrum was difficult to inter-

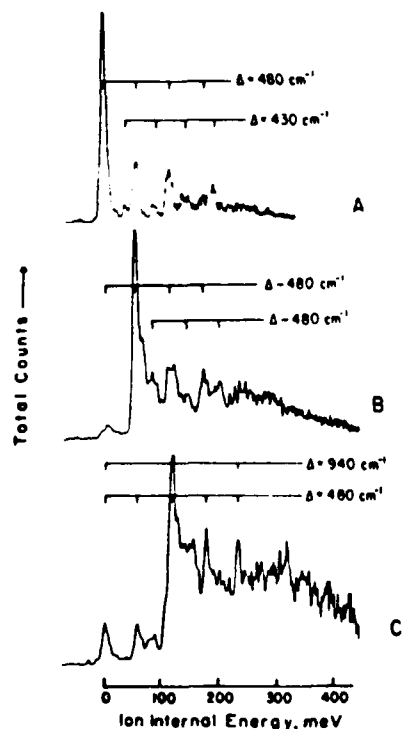


Fig. 4. Photoelectron spectra generated by two-photon ionization of gas phase toluene. Laser is resonant with the $S_1 \leftarrow S_0$ origin (Fig. 4A), $6h_0^0$ (Fig. 4B) and 12_0^0 (Fig. 2C) transitions. The abscissa, ion internal energy, is the quantity $2h\nu - IP - KE$ where $h\nu$ is the laser photon energy and KE is the photoelectron kinetic energy.

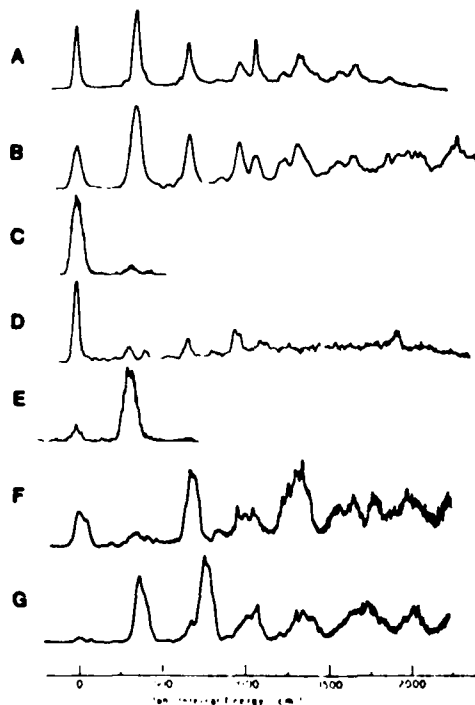


Fig. 5. Laser photoelectron spectra obtained by exciting the following vibronic levels of benzene's ${}^1B_{2u}$ electronic state: (A) 6_0^0 , (B) 6_1^0 , (C) 6_2^0 , (D) 6_3^0 , (E) 6_4^0 , (F) 6_5^0 , (G) 6_6^0 .

pret since the strongest peak in it, at 355 cm^{-1} , had never appeared in a C_6H_6 photoelectron spectrum before; the one at 680 cm^{-1} had previously been assigned to the 6_1^1 ion vibrational level. However, by calculating the vibronic energy levels allowed for C_6H_6 based on evaluating the coupling between electronic and vibrational angular momenta in a Jahn-Teller distorted electronic state we demonstrated that *both* of these peaks can be associated with $v = 1$ of ν_2 . The first represents the $j = \frac{1}{2}$ vibronic component, the second is the $j = \frac{3}{2}$ component. The spacing between these is the Jahn-Teller splitting for normal mode ν_2 . Remarkably enough this splitting of 325 cm^{-1} had never been observed in conventional photoelectron spectra of benzene. This was not because of a deficiency in resolution; rather, it was a selection rule effect. The following selection rule is found to be applicable to a photoionization process:

$$j_k' = l_k' \pm \frac{1}{2}$$

where j_k' is a vibronic angular momentum quantum number for mode k in the ion, and l_k' is the vibrational angular momentum quantum number for the level from which ionization takes place. From this expression one can see that *only* $j_k' = \pm \frac{1}{2}$ levels can be reached by ionizing a molecule from a vibrationless level, since l_k' is zero in that case. This is why the $6_1^1(\frac{1}{2})$ peak at 355 cm^{-1} had never before been seen. Assignments for other peaks in this 6_1^1 spectrum were obtained by this same method of analysis. For details see Ref. 30. In Fig. 5B the photoelectron spectrum obtained by ionizing through the $6_1^1 1_1^1$ band of benzene is observed. While qualitatively similar to the spectrum of Fig. 5A, two small differences are evident. First, the ion vibrational progression appears longer because the higher photon energy enables more ion vibrational energy levels to be accessed. Second, the peak at 976 cm^{-1} is somewhat larger now. This peak corresponds to production of ions in level 1_1^1 ; it makes perfect sense that this becomes more probable when ionization is induced from a vibrational level of the $1B_{2u}$ state in which ν_1 is excited. Figure 5C depicts the photoelectron spectrum recorded by ionizing C_6H_6 from a vibrationless level of the $1B_{2u}$ state. In contrast, when one quantum of ν_1 but no other normal mode is excited the spectrum appearing in Fig. 5D results. Every peak in this spectrum has been assigned. As an example of how definitive assignments can be made, we hypothesized that the peak at 320 cm^{-1} corresponds to ions vibrationally excited in mode ν_{10} . To confirm this we excited benzene's $6_1^1 16_1^1$ transition and recorded the spectrum appearing in Fig. 5E. This peak is now *clearly* enhanced, indicating that our proposed assignment was correct. Probably the most spectacular examples of the success of our Jahn-Teller distortion model of C_6H_6 are displayed in Figs. 5F and 5G. Different vibrational angular momentum components of benzene's 6_1^1 transition are excited in these two spectra. The UV wavelengths used to generate these spectra differ by less than $0.5\text{ \AA}$, yet the resulting photoelectron spectra are dramatically different. This is because in one case (Fig. 5F) ionization is occurring from an $l_k = 0$ level whereas in the other case (Fig. 5G) it is occurring from an $l_k = \pm 2$ level. The appearance, or lack of appearance, of every peak in the first 1600 cm^{-1} of ion internal energy in both spectra turns out to be clearly understandable!

We have recently completed a similar rather comprehensive study of aniline's laser photoelectron spectrum. Aniline is a molecule of considerably lower sym-

metry than benzene. Due to the increased number of atoms and the reduction in molecular symmetry it possesses more normal mode frequencies and, in particular, many more totally symmetric vibrational modes. Consequently its laser photoelectron spectrum contains even more vibrational information than does that of benzene. While the first band in the conventional photoelectron spectrum of aniline is barely resolvable,⁴⁵ and assignments based on it are entirely speculative, the laser photoelectron spectrum is *rather* clearly interpretable. Figure 6 depicts laser photoelectron spectra recorded by exciting the origin and two hot bands. As one would expect by the Franck-Condon principle these spectra are virtually identical. The center spectrum is particularly significant since the I_1^0 transition in the UV absorption spectrum of aniline (at 33990 cm^{-1}) had not been previously assigned before. It has been labelled "origin-40" by Scheps et al.⁴⁶ who assumed that it was a sequence transition. However, the $v = 1$ level of the inversion mode of aniline is only 40 cm^{-1} above the $v = 0$ level and we hypothesized that the band at 33990 cm^{-1} might be a simple hot band involving the inversion mode. Two observations have confirmed our hypothesis: (1) The first peak of the laser photoelectron spectrum recorded by ionizing aniline at this wavelength appears at exactly the correct electron kinetic energy if the two-step ionization process is assumed to initiate from a vibrational level 40 cm^{-1} above the $v = 0$ level of the ground electronic state. (2) The general similarity of the spectra in Fig. 6 indicates that all arise from ionization of aniline from the same ($\nu_k = 0$ for all k) vibronic level of its excited electronic

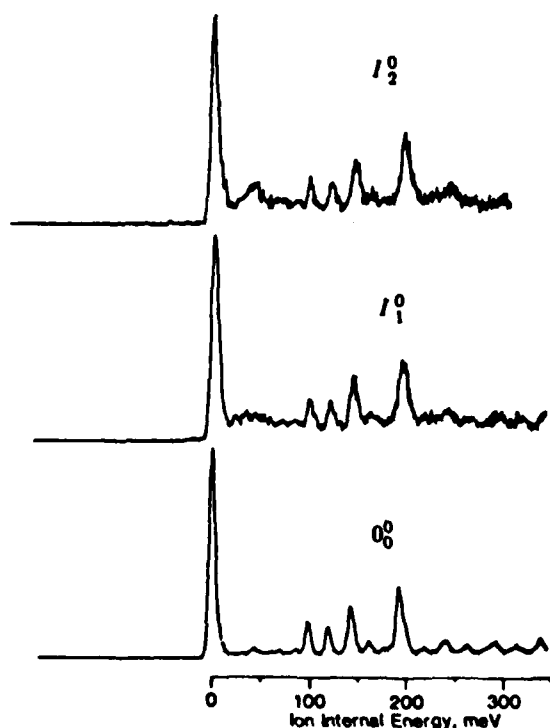


Fig. 6. Laser photoelectron spectra obtained by exciting the $v = 0$ level of the first excited singlet state of aniline from various vibrational levels of its ground electronic state.

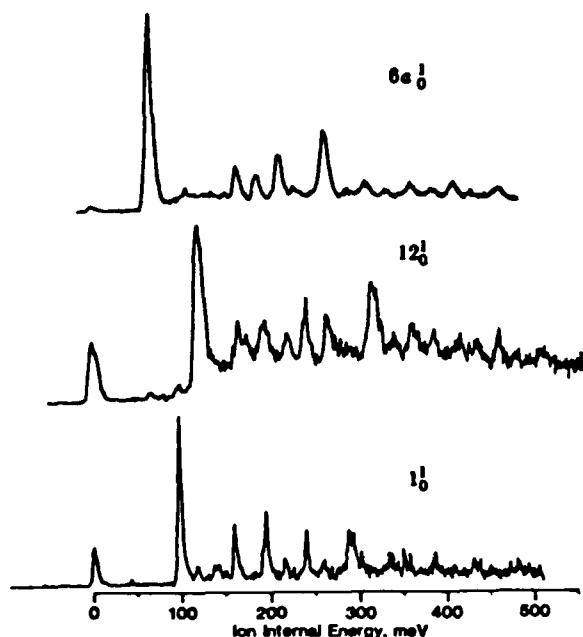


Fig. 7. Laser photoelectron spectra of aniline involving three different intermediate vibronic states. Transitions excited in each case are noted.

state. By contrast, when aniline is ionized from a vibrationally excited level of any normal mode, vibrationally excited ions are preferentially generated. This is adequately displayed in Fig. 7. Assignments for virtually all of the ion vibrational peaks appearing in Figs. 6 and 7 have been worked out and will soon be published.³¹

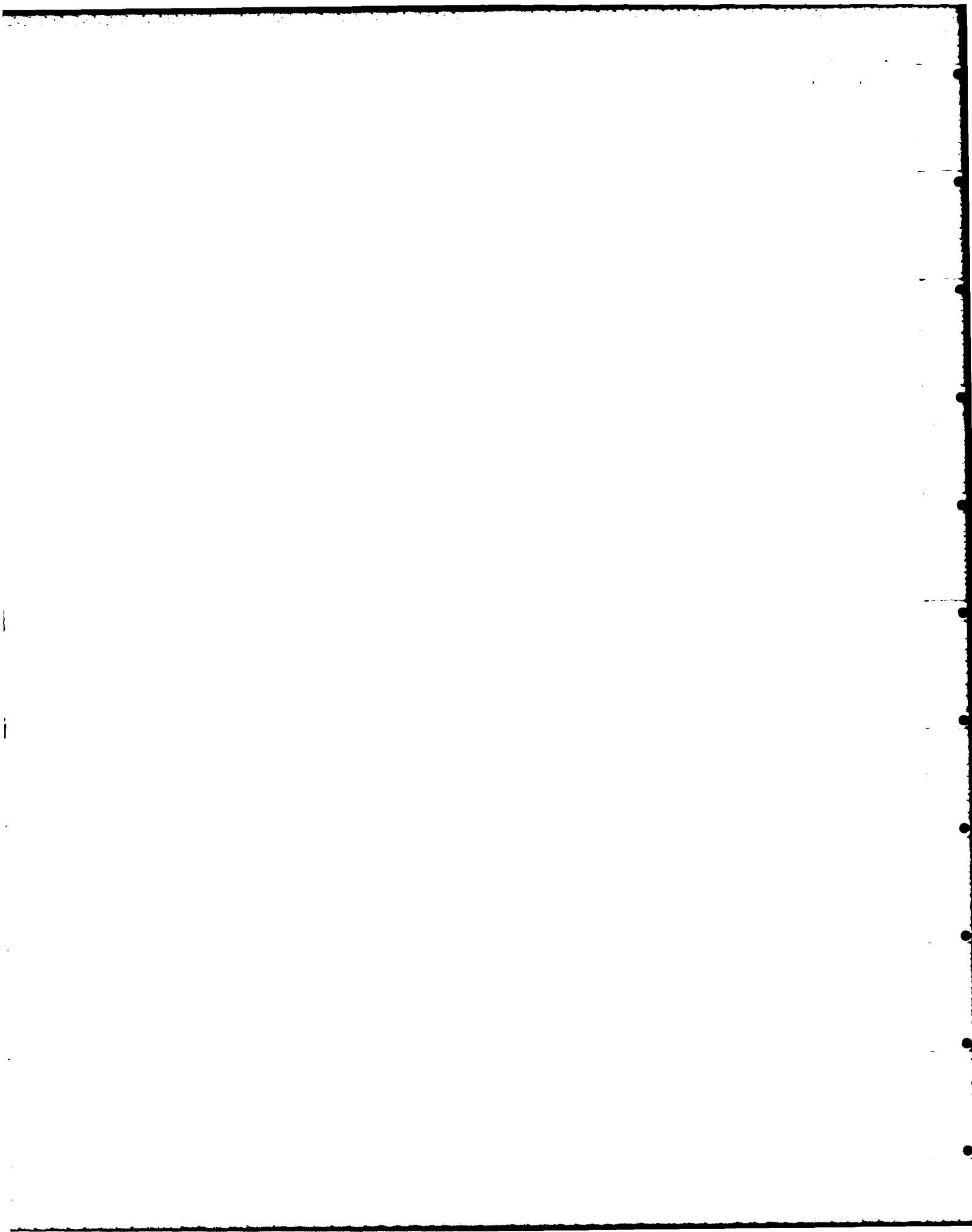
In conclusion, laser photoelectron spectroscopy is demonstrating a remarkable capability for generating ion vibrational spectroscopic information that should contribute significantly to our understanding of free radical and polyatomic ions. Detailed information about the spectroscopy of neutral molecules can also be extracted with this method. This has been demonstrated in the cases of aniline and benzene and is a primary goal of multiphoton ionization investigations of diatomic molecules. While spectroscopic studies of innumerable species can be and certainly will be performed equivalent to those described herein, future research in this area will probably also involve the investigation of the angular distributions of the ejected photoelectrons. Dynamical processes may also be probed by intensity dependence or ultrashort-pulse experiments. Achiba et al.³⁴ already have argued that fast intramolecular vibrational relaxation in the excited ${}^1E_u$ electronic state of benzene affects their four photon ionization photoelectron spectra. Future experiments of this type should be both revealing and exciting.

Acknowledgments. We gratefully acknowledge the Camille and Henry Dreyfus Foundation for a Teacher Scholar Award and the Research Corporation for a Cottrell Research Grant. This work has been supported by the U.S. Army Research Office under contract number DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R810896-01-0.

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Benzaldehyde photochemistry studied with laser ionization mass and photoelectron spectroscopy

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Multiphoton ionization has been successfully employed for several years as a molecular spectroscopic tool.¹⁻³ More recently, it has been utilized to generate molecular ions in the source regions of mass⁴⁻⁸ and photoelectron⁹⁻¹⁵ spectrometers. The low operating pressures employed in these instruments make them ideally suited for studies of isolated molecule photochemical processes. In two-step ionization, a molecule is first promoted to an excited electronic state from which it is subsequently ionized. If it dissociates or rearranges following the first step but before the second, the observed mass and photoelectron spectra can be affected. In the course of ionizing benzaldehyde unanticipated spectra are generated, and their description and interpretation provide the subject of this correspondence.

The laser ionization mass⁶ and photoelectron^{13,15} spectrometers employed in this work are described in detail elsewhere. Briefly, an effusive beam of benzaldehyde (chamber pressure 1×10^{-6} Torr) is irradiated with the focused output of a tunable narrowband frequency-doubled dye laser pumped by a Lumonics TE-430 XeCl excimer laser. Photoelectrons are energy analyzed by time-of-flight with resolution of about 10 meV. Ion mass spectra are recorded by utilizing a TOF mass spectrometer with the same molecular beam and vacuum chamber. Extensive signal averaging is performed in both experiments with a small computer. Less than 15 μ J of ultraviolet radiation per laser pulse were employed in these ionization experiments. Since high light fluxes generally yield extensive ion fragmentation in laser induced mass spectra, these low pulse energies were expected to minimize this effect.

Earlier mass spectral experiments by Antonov *et al.*¹⁶ revealed that even at relatively low KrF laser intensities irradiation of benzaldehyde produces substantially more $C_6H_5^+$ than $C_6H_5CHO^+$. Benzene ions could be produced

either by absorption of several photons to produce a highly excited benzaldehyde ion which rearranges and fragments to form $C_6H_5^+$ or by decomposition of single-photon excited C_6H_5CHO to C_6H_5 and CO followed by ionization of C_6H_5 . Berger *et al.*¹⁷ have shown that C_6H_5 molecules appear with high quantum yield in the course of benzaldehyde photolysis at 2760 and 2840 Å in a low-pressure bulb.

Our experiments employ laser wavelengths at 2587 and 2589 Å. While the S_2-S_0 absorption of benzaldehyde¹⁷ is continuous from 2900 to about 2450 Å, bands appear in the benzene absorption spectrum near 2600 Å. Benzene exhibits a strong S_1-S_0 , 6_0^1 band head at 2589 Å but does not absorb at 2587 Å.¹⁸ Two 2589 Å photons ($2h\nu \approx 77\,222\text{ cm}^{-1}$, 9.57 eV) are sufficiently energetic to ionize both benzaldehyde (I. P. = 9.52 eV) and benzene (I. P. = 9.245 eV).

Figure 1 displays the mass spectrum observed when (a) benzene is irradiated at 2589 Å, and when benzaldehyde is irradiated at the two wavelengths, (b) 2589 Å, and (c) 2587 Å. For 2589 Å irradiation of either molecule, the strongest peak, by two orders of magnitude, is at mass 78. When benzaldehyde is irradiated at 2587 Å, the mass 78 peak intensity is 100 times smaller than it is when the laser is resonant with the 6_0^1 transition of benzene while the mass 106 peak is very weak but of comparable magnitude at the two wavelengths. To investigate if the mass 78 peak obtained when irradiating benzaldehyde is the result of benzene impurity, we employed our gas chromatographic inlet⁶ to separate benzene (which we found present in the benzaldehyde at a level of one part in 860 by conventional GC analysis) from the benzaldehyde before irradiating it in our spectrometer. The benzaldehyde mass spectrum was unaffected by this separation.

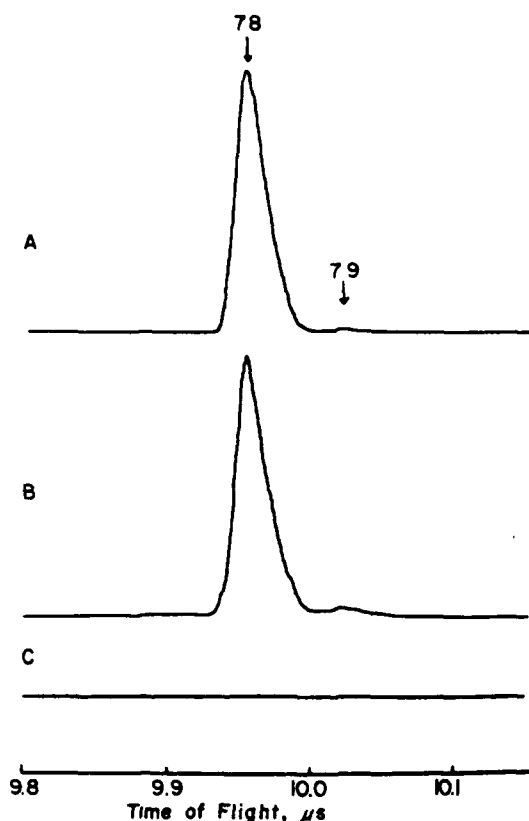


FIG. 1. The mass 78 region in the laser ionization mass spectra of benzaldehyde and benzene. Trace A: benzene irradiated at 2589 Å ($S_1 \rightarrow S_0$ 6_0^1 band head). Trace B: benzaldehyde irradiated at 2589 Å. Trace C: benzaldehyde irradiated at 2587 Å. Approximately 6 μ J is used in all cases. Masses 78 and 79 are designated by arrows.

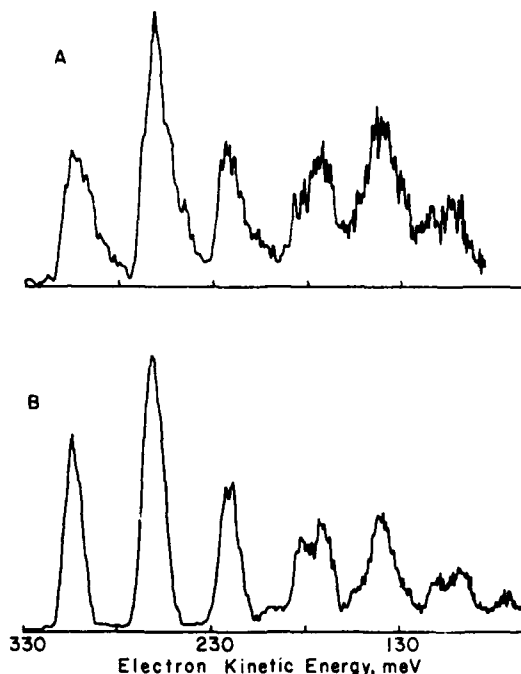


FIG. 2. Laser photoelectron spectra of (A) benzaldehyde and (B) benzene with irradiation at 2589 Å.

The implications of our benzaldehyde study for the field of photochemistry are clear. This method provides a new means of identifying transient as well as stable products of photochemical processes. Transients whose ionization potentials and ionic vibrational frequencies are unknown may be conveniently studied with laser photoelectron spectroscopy. Furthermore, the rates of fast photochemical reactions occurring in isolated gas phase molecules are measurable if two laser pulses with a variable time delay can be employed to induce the two-step ionization process.

We gratefully acknowledge the Camille and Henry Dreyfus Foundation for a Young Faculty Award and the Research Corporation for a Cottrell Research Grant. This work has been supported by the U. S. Army Research Office under contract number DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0.

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Figure 2 depicts photoelectron spectra recorded during 2589 Å irradiation of (a) benzaldehyde and (b) benzene. The two are apparently identical. A detailed interpretation of the benzene spectrum is being published elsewhere.¹⁵ No photoelectron spectrum is obtained with 2587 Å irradiation of either molecule. These data demonstrate conclusively that the $C_6H_6^+$ generated in the two-step ionization of benzaldehyde results in fact from ionization of neutral C_6H_6 . Furthermore, the photochemical decomposition of S_2 benzaldehyde into C_6H_6 and CO must occur on a ns timescale. This process appears to be faster than the rate of photoionization of S_2 excited-state benzaldehyde. If the photoionization cross section of benzaldehyde in this state is estimated to be 10^{-17} cm², the latter rate would be approximately 1 to 15×10^8 s⁻¹ at the light intensities employed in these experiments. In the analysis of their kinetic data on benzaldehyde photolysis, Berger *et al.*¹⁷ concluded that intersystem crossing populates two triplet states which then decompose with lifetimes of ~ 20 ns and ~ 2.5 μ s.¹⁷ Our observations indicate that substantial benzene formation occurs within the 2 ns laser pulse. Unfortunately, we cannot be more quantitative than this because of differences in the gas pressures and light intensities used in studying the two molecules.

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ULTRAVIOLET LASER INDUCED IONIZATION OF MOLECULES NEAR SURFACES

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Received 15 April 1983; in final form 9 June 1983

Aromatic molecules are multiphoton ionized in the source region of a time-of-flight mass spectrometer using the output from a KrF excimer laser. Under certain operating conditions unusually sharp mass spectral peaks are observed. It is demonstrated that these result from ionization of molecules initially adsorbed to a metal surface. The implications of this phenomenon are briefly discussed.

Mass analysis in laser ionization mass spectrometry is often done by time of flight [1-5]. With the exception of a recently developed reflection instrument [6], the resolution of most spectrometers of this type is mediocre. $M/\Delta M$, which is typically ≈ 250 , depends upon:

- (1) The spatial spread of the region over which ionization occurs.
- (2) The velocity distribution of molecules being ionized.
- (3) The time resolution of the laser and TOF electronics.

The possibility of eliminating the first and second factors by ionizing molecules which are not in the gas phase but which are actually adsorbed to a flat surface is intriguing. If spectrometer resolution were determined by the third factor alone, the use of ultrashort laser pulses and low jitter picosecond timing electronics would lead to excellent mass resolution. Furthermore, ionization of molecules adsorbed to surfaces could be a practical and sensitive method of surface spectroscopy. Finally it may be advantageous to use low-intensity pulses of ultraviolet radiation for ionizing involatile, thermally labile samples instead of high-power infrared radiation which is usually employed in laser desorption mass spectrometry [7-11]. Motivated by these considerations we have investigated the UV laser induced ionization of small aromatic molecules

adsorbed to metal surfaces.

Our homemade TOF mass spectrometer has been described recently [12]. The ion drawout region consists of four parallel nickel grids as depicted in fig. 1. The potentials on each of these can be set independently. When gaseous benzene is introduced and 0.1-1.0 mJ pulses of KrF excimer laser radiation illuminate the region between the first two grids, $C_6H_6^+$ ions are generated and easily detected [1,2]. In order to distinguish ionization occurring at or near the surface of a grid from that taking place in the bulk gas phase, grids 0-3 are maintained at relatively high potentials of +2000, -2000, -2000 and -2000 V. Under these high drawout electric field (6350 V/cm) conditions, ions formed at slightly different locations within the region between grids 0 and 1 are imparted significantly different kinetic energies and therefore have significantly different flight times. Due mainly to the spatial spread caused by the finite width of the laser beam which produced them, the $C_6H_6^+$ ions yield

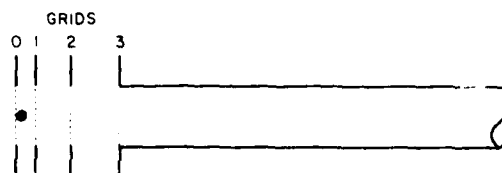


Fig. 1. The ionization region and acceleration grids in our laser TOF mass spectrometer.

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a TOF peak which is relatively broad as seen in fig. 2A. Its fwhm is ≈ 195 ns. Note that this is definitely broader than a $C_6H_6^+$ ion peak would normally be in a conventional laser mass spectrum. If recorded in our mass spectrometer under normal low-voltage ion draw-out conditions such a peak would have a fwhm of only 24 ns. The temporal resolution of our waveform recorder and ion time-of-flight electronics is sufficient for accurate measurement of the fig. 2A peak width. A simple computer program which calculates an ion's flight time as a function of its initial position enables us to estimate the spatial fwhm of the laser focal spot to be 0.36 mm. (This actually assumes a linear relation between light intensity and ion production which has been found for moderate laser intensities [2]. The spot size estimate should be construed as rough.)

The precise location of the laser beam in the ionization region could be shifted using a lens mounted in a translation stage. As the light was moved toward the

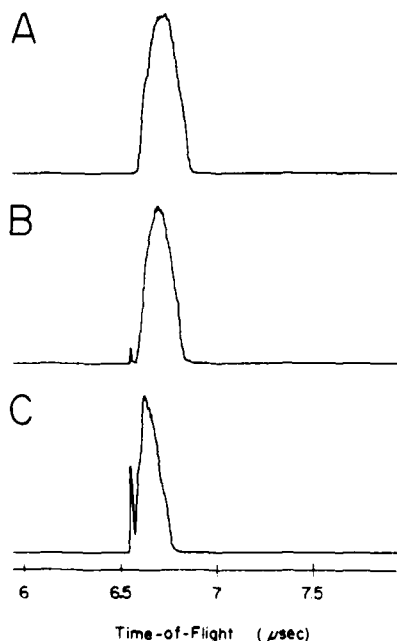


Fig. 2. TOF mass spectra of benzene ionized with KrF laser radiation. Only the parent ion mass region is displayed. In (A) the laser irradiates gas phase molecules between the first two ion drawout grids. In (B) and (C) the laser focal spot is progressively moved toward the first grid.

first grid, mass spectra displayed in figs. 2B and 2C were recorded. The sharp peak, whose fwhm is ≈ 18 ns, is identified as $C_6H_6^+$ ionized at or very near to the grid surface. This interpretation follows not only because of the mass spectral dependence on lens position but also because the temporal location of the sharp peak agrees with our calculated TOF only if we assume that it corresponds to $C_6H_6^+$ originating at the surface. Furthermore whenever the sharp peak is detected, it always appears at the same flight time. The broad peak, in contrast, shifts when the focusing lens is translated. Finally, application of high positive voltages to the third grid of our mass spectrometer reduces the intensity of the broad peak relative to that of the sharp one. This is because ions produced further from the first grid approach the third one with lower kinetic energy and are therefore discriminated against by a high decelerating electric field. The width of the surface ionization peak is determined by the three factors listed at the beginning of this paper. Its narrowness in comparison with the gas phase peak observed under these same high drawout field conditions indicates that the region over which surface ionization occurs must be substantially narrower. The 12 ns temporal width of our KrF laser pulse contributes significantly to the surface ionization peak width. However, if this contribution is ignored upper limits on the width of the region over which ionization occurs and on the kinetic energies of the initially generated $C_6H_6^+$ ions can be calculated using our ion flight time analysis program. The conclusions are that the ions must be generated within $36 \mu\text{m}$ of grid 0 and with kinetic energies less than 14 eV. Once again we emphasize that these are upper limits.

It is interesting to note that the sharp, surface peak in figs. 2B and 2C appears at an earlier time than the broad gas phase peak even though in our picture ions generated at the surface must travel a greater distance to the electron multiplier. This is a consequence of their receiving more kinetic energy by starting their flight at a higher positive potential. The temporal relationship between these two peaks depends critically on the voltages applied to the ion drawout grids and on the distance of the laser focal spot from the surface of grid 0. Our ion flight time program enables us to estimate the distances between the center of the laser spot and the metal surface for generating the spectra of figs. 2B and 2C to be 310 and $140 \mu\text{m}$ re-

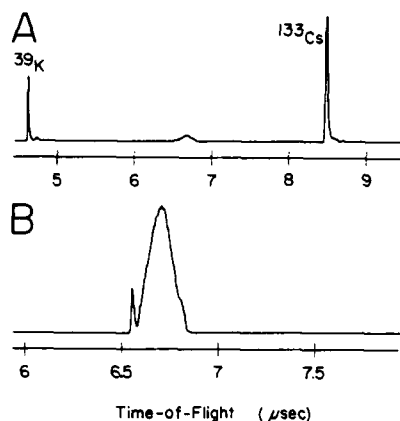


Fig. 3. (A) TOF mass spectrum resulting from KrF grazing incidence illumination of the first ion drawout grid. $\approx 100 \mu\text{J}$ of energy per laser pulse. Gas phase benzene is simultaneously being introduced, while potassium and cesium has been evaporated onto the grid beforehand. (B) Expanded view of the central portion of (A).

spectively. When the laser is moved even closer to the surface than in fig. 2C the surface and gas phase peaks overlap yielding a triangular-shaped peak with a 5 ns rising edge and a 300 ns tail. When lower voltages are employed the surface peak can actually appear at later times than the gas phase peak. The two are experimentally most easily distinguished under high electric field conditions.

When potassium and cesium were evaporated onto the first grid and irradiated by the laser, mass spectra depicted in fig. 3 were recorded. The alkali-metal peaks provided a convenient mass spectrometer calibration. Note that the naturally occurring isotopes of potassium with masses of 39 and 41 are both detected. The benzene surface and gas phase peaks are barely discernable in fig. 3A but stand out on the expanded scale of fig. 3B.

The relative areas of the surface and gas phase peaks strongly depend on the precise location and angular orientation of the laser beam with respect to the metal surface. While in fig. 3 the surface peak appears small relative to the gas phase peak, under some operating conditions we have observed it to be substantially taller than the latter (although its area is generally smaller). The absolute areas of the two peaks depend upon the benzene pressure and the laser intensity

used. We observe the same peak profiles independent of whether we are collecting our data in an ion counting mode (i.e. one ion or fewer per laser pulse) or in a current recording mode (e.g. on the order of 100 ions per laser pulse). Because most of the laser beam irradiates gas phase molecules and only a fraction of it skids across the metal surface we cannot draw any firm conclusions regarding the relative efficiencies of the processes which yield our broad and sharp ion peaks.

The narrowest surface ionization peaks which we have obtained thus far, with a ns frequency doubled dye laser as light source, are approximately 6 ns fwhm. While our Biomation 6500 waveform recorder has a 500 MHz digitizing rate, its jitter is specified as 3 channels so it is unlikely that a signal-averaged peak narrower than 6 ns could have been recorded with our instrumentation. Since the temporal spacing between a mass 78 and a mass 79 ion under the high-voltage conditions which we utilized is 42 ns we can currently claim surface ionization mass spectral resolution of only ≈ 500 . If the time resolution of the laser and electronics is our limiting factor, then the attainment of higher mass resolution will require lower accelerating voltages and correspondingly longer ion flight times. Under these conditions the velocity distribution of the ions in the surface peak will contribute more to its width because any kinetic energy spread will be more comparable to the ion acceleration energy. How serious this velocity distribution effect will be remains to be seen.

The mechanism of the UV laser induced surface ionization of benzene is not yet clear although the possibilities include:

- (1) Single-photon excitation of adsorbed molecules followed by electron transfer to the nickel substrate.
- (2) Two-photon ionization of molecules which are actually adsorbed to the surface.
- (3) Laser induced desorption followed by gas phase two-photon ionization of molecules very near to the surface (e.g. a benzene neutral molecule with 10 eV of kinetic energy only travels $60 \mu\text{m}$ during a 12 ns laser pulse).

However the ions are generated, the high electric field draws them away from their place of origin toward the second drawout grid.

In contrast with infrared laser desorption mass spectrometry which involves a non-selective, thermal

processes [7-11], the $C_6H_6^+$ surface ionization yield exhibits a sharp wavelength dependence when a tunable frequency doubled dye laser is employed as the radiation source [13]. By this we mean that when the UV wavelength is tuned over a benzene vibronic band, such as 6_0^1 , the wavelength dependence of the surface ionization signal is similar to that of benzene's gas phase absorption spectrum. We have not yet determined whether the two are exactly identical because when our wavelength is tuned our frequency doubling crystal must be rotated to maintain phase matching. Consequently the laser beam position shifts slightly. The surface ionization signal is sensitive to these shifts, so we really need an improved method to record accurate surface ionization wavelength dependences. As further evidence of selectivity, when an excess of air or helium is introduced along with the benzene vapor, the observed mass spectrum is unaffected and appears to be that of C_6H_6 alone. This indicates that the mechanism of surface ionization is *not* laser ionization of gas phase benzene, acceleration of the emitted electrons toward grid 0 followed by electron impact ionization of benzene on the surface. Selective ionization of benzene in the presence of other species like air and helium is commonly observed in gas phase multiphoton ionization [1-5, 14]. Toluene and several polyaromatic hydrocarbons also yield strong surface ionization signals. Further details about these experiments will be provided in a future publication [13].

In summary, we have demonstrated a new method of molecular ionization which can occur in the source region of a laser mass spectrometer. Its ultimate significance and range of applications depend on details of the surface ionization mechanism which are yet to be resolved. Experiments to measure the ion velocity distribution, and the dependence of the surface ionization signal on the substrate material, the applied elec-

tric field and the laser intensity and wavelength are now underway.

We gratefully acknowledge the Camille and Henry Dreyfus Foundation for a Young Faculty Award and the Research Corporation for a Cottrell Research Grant. This work has been supported by the US Army Research Office under contract number DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0.

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MULTIPLE PEAK FORMATION IN LASER IONIZATION MASS SPECTROMETRY

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Received 14 November 1983

Molecules in the source region of a time of flight mass spectrometer are ionized by ultraviolet laser radiation. Under certain conditions mass spectra consisting of a remarkably periodic set of ion peaks are generated. It is demonstrated that these result from spatially periodic ionization within the mass spectrometer which is a consequence of the development of standing electromagnetic waves.

While numerous studies of laser induced ionization of gas phase molecules in mass spectrometers have been performed in recent years, selective, non-thermal ionization of species adsorbed to surfaces has only recently been reported [1,2]. It has been demonstrated that when unfocused excimer laser radiation impinges on one of the accelerating grids in a TOF laser mass spectrometer (see fig. 1) two types of mass spectral

peaks appear: broad ones which result from sample ionization in the bulk gas phase and narrow ones corresponding to ionization at or near to the grid surface. The appearance of these peaks has previously been discussed [2]. When a single substance like benzene is introduced into the mass spectrometer and the excimer laser intensity is low enough (under 1 mJ per pulse) no ion fragmentation occurs and only $C_6H_6^+$ ions are formed. Under these conditions one broad and one narrow peak appear in our TOF mass spectrum.

Recently we have been performing similar experiments with 1–50 μ J pulses of narrowband frequency doubled dye laser radiation. In one study the laser was tuned to the 6_0 transition of benzene (259 nm) and

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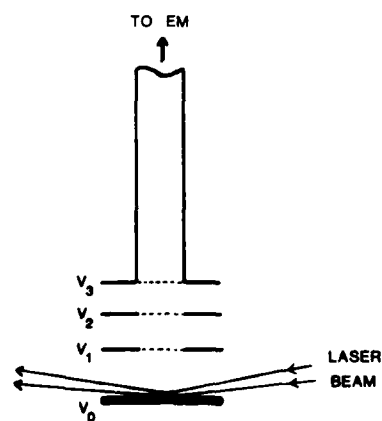


Fig. 1. Ion drawout region of TOF laser ionization mass spectrometer exhibiting irradiated plate and accelerating grids. Applied voltages, V_0 – V_3 are noted.

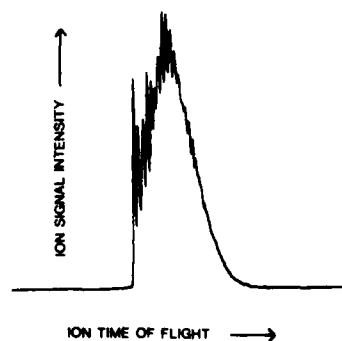


Fig. 2. TOF mass spectrum (in the region near mass 78) resulting from irradiation of benzene vapor and a Ni foil ion repelling plate. The first sharp peak appears at 6488 ns. The FWHM of the distribution is approximately 200 ns.

was allowed to impinge on a sheet of Ni foil which serves as the initial acceleration grid of the mass spectrometer depicted in fig. 1. The remarkable TOF mass spectrum displayed in fig. 2 was then generated. Under these conditions a series of rather sharp, equally spaced peaks appear. The first of these peaks, although it no longer appears unique, occurs at exactly the same flight time as our previously observed narrow surface ionization peak. In order to investigate the mechanism by which these "multiple peak" spectra are produced several experiments were performed and these will now be discussed.

(1) A few different organic compounds, such as toluene, aniline and benzaldehyde, were introduced into the mass spectrometer. Results similar to those with benzene were obtained. In each case the observed mass spectrum consisted of a series of sharp peaks, the first of which appeared at a flight time corresponding to molecular ion production at the first mass spectrometer grid. At higher laser intensities fragment ions were generated. To each fragment there corresponded a series of multiple ion peaks. Cs was also vapor deposited onto our mass spectrometer grid. Mass spectra recorded by irradiating such a coated grid with dye laser light yielded only one single sharp surface ion peak whose flight time corresponded to that of Cs^+ . This result was thus identical to that previously obtained with a KrF laser.

(2) Different metals were employed as the first "target" grid. In place of the Ni foil mentioned above we employed a glass plate onto which we had deposited a coating of Al metal. Multiple peak mass spectra again resulted. The observed patterns were even smoother and more regular than those obtained with Ni foil. (Examples will be presented below.) Identical patterns were obtained when the Al coating on the glass was replaced by an evaporated Ag coating.

(3) Most of our dye laser induced surface ionization mass spectra were obtained with S-polarized UV radiation (i.e., the electric field of the radiation was perpendicular to the plane of incidence). With P-polarized radiation the observed mass spectra were virtually unchanged, indicating that light polarization does not play an important role in the phenomenon.

(4) The voltages normally applied to the ion drawout grids in our mass spectrometer during these experiments, V_0 , V_1 , V_2 , and V_3 in fig. 1 were +2000, 2000, 2000 and -2000 respectively. In order to

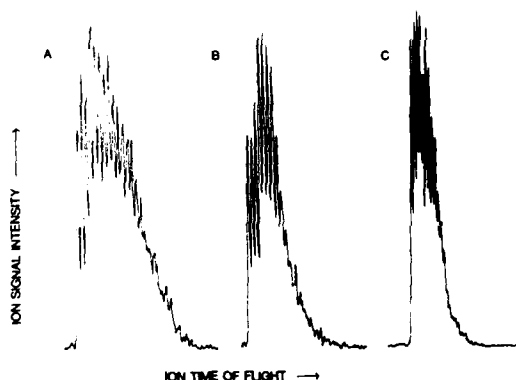


Fig. 3. Multiple peak mass spectra of benzene exhibiting the effect of drawout field variation. Voltages applied to initial drawout grids and temporal locations of the first sharp peak were (a) ± 2000 V, 6488 ns (b) ± 1500 V, 6944 ns (c) ± 750 V, 7866 ns.

probe the effect of drawout field variation we reduced the voltages applied to the first two grids from ± 2000 to ± 1500 , ± 1000 and finally to ± 750 . The effect of this on our multiple peak mass spectra was profound, as can be seen in fig. 3. Its significance is discussed below.

(5) In order to probe whether the laser beam might possess some reproducible spatial intensity structure we scanned across our 3 mm diameter unfocused UV laser beam with a $10\ \mu\text{m}$ wide spectroscopic slit, monitoring light transmission as a function of slit position. The result was a rather smooth curve in fig. 4 which



Fig. 4. Variation of UV laser light intensity across an approximately 3 mm diameter unfocused frequency doubled dye laser beam.

exhibits no evidence of intensity periodicity.

(6) The angle between the incident laser beam and the target plate was varied over a range from 0.1° to 2° . It could be accurately measured in the following way. Two spots would appear on a card located 30 cm from the mass spectrometer's laser output window. One was from the undeflected incident UV beam, the second resulted from the beam reflected at grazing incidence off the target plate. The angle of the laser beam with respect to the plate, in radians, is just one half of the spacing between the spots divided by 30 cm. Fig. 5 shows the results of ionizing benzene by illuminating an Al-coated glass plate with dye laser radiation incident at three different angles.

In order to interpret the results of experiments (4) and (6) we employed a computer program which calculates ion flight times as a function of their precise points of origin and the mass spectrometer's operating parameters. It was definitely shown from this analysis that as the drawout field was reduced the observed mass spectral pattern changed exactly as would be expected if the ions were formed only at a certain set of unchanging discrete positions within the drawout region. These results are displayed in table 1. The strong effect of incident angle suggested that this set of discrete ionizing locations might be the result of electromagnetic standing waves. Considering that the temporal spacings between successive peaks depicted in fig. 5 would imply physical spacings on the order of 5 to 30 μm and that the laser wavelength utilized was only

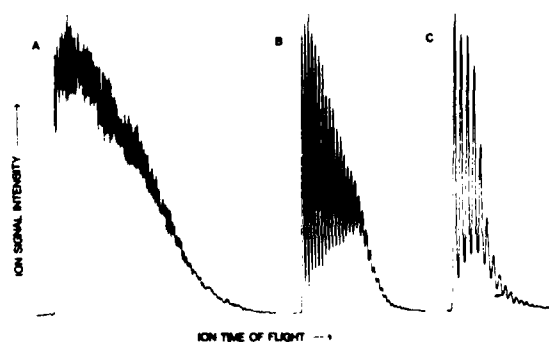


Fig. 5. Multiple peak mass spectra of benzene exhibiting the effect of varying the laser beam angle of incidence, θ . In all cases the first sharp peak appears at 6488 ns. Angles of incidence and approximate observed peak spacings were (a) $\theta = 1.1^\circ$, 8 ns (b) $\theta = 0.6^\circ$, 15 ns (c) $\theta = 0.3^\circ$, 28 ns.

Table 1

Effect of ion drawout voltage on temporal spacings of multiple peaks

Target material	Potentials ^{a)} (V)	Peak separation ^{b)} (ns)		Implied ^{c)} spacings (μm)	
		1 $\rightarrow$ 6	1 $\rightarrow$ 11	1 $\rightarrow$ 6	1 $\rightarrow$ 11
Al coated glass	± 2000	75	153	59.2	119
	± 1500	70	144	60.5	123
	± 1000	58	116	60.0	119
	± 750	50	100	61.0	120
Ni plate	± 2000	72	146	57	114
	± 1000	56	146	58	114

- a) Voltages applied to first two acceleration grids, with -2000 V applied to each of the next two grids.
 b) Experimentally measured temporal spacings between the first and sixth, and first and eleventh of the multiple peaks in benzene mass spectra for a constant incident illumination angle.
 c) Implied distances, in μm , to be associated with temporal spacings between first and sixth and first and eleventh of the multiple peaks, for constant incident illumination angle. These were calculated with ion flight time computer program by assuming that different peaks result from ionization at different places within the drawout region.

0.259 μm this initially seemed somewhat remarkable. Nevertheless the following derivation is quite conclusive. A model of an incident plane wave striking a surface at a grazing incidence angle is depicted in fig. 6. It is assumed that rays 1 and 2 are initially parallel and in phase and that they meet at point P. Geometrical parameters x , y , α and s are defined in the figure. A condition on parameter h , the distance between point P and the target surface, is sought. From simple geometry,

$$h = x \sin \theta, \quad \alpha = 2\theta, \quad y = x \cos \alpha = x \cos 2\theta.$$

Assuming that the phase of ray 2 is unaffected by reflection at grazing incidence [3] the condition for rays 1 and 2 to be in phase at point P is:

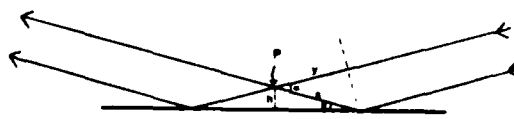


Fig. 6. Model to explain standing wave formation when a plane wave strikes a reflective metal surface at grazing incidence.

$$x - y = n\lambda.$$

Substituting in the above equations it follows that

$$x = n\lambda / (1 - \cos 2\theta)$$

and

$$h = \frac{n\lambda \sin \theta}{1 - \cos 2\theta} \approx \frac{n\lambda}{2\theta}.$$

The last approximation is quite accurate because of the smallness of θ .

When the data of fig. 5 is compared with the expectations of this formula by using measured values of θ , exact agreement results.

In summary we have demonstrated that when a monochromatic UV laser beam is incident upon a flat reflecting plate electromagnetic standing wave patterns develop the wavelengths of which can be much larger than that of the incident light. When the light intensity is sufficiently intense to induce gas phase multiphoton ionization, a spatially periodic distribution of ions is generated. This periodicity is an undesirable

complication in laser induced surface ionization studies. However such periodic ion distributions might be useful for some other type of scientific experiment and the method described herein is straightforward and simple to set-up and provides patterns which are highly reproducible as long as the angle of laser incidence is carefully fixed.

This work has been supported by the U.S. Army Research Office under contract number DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under grant number R808790-01-0.

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Analysis of Polyaromatic Hydrocarbon Mixtures with Laser Ionization Gas Chromatography/Mass Spectrometry

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Excimer laser induced multiphoton ionization has been utilized for ion generation in capillary gas chromatography/mass spectrometry and the technique applied to the separation and detection of polyaromatic hydrocarbons. Detection limits as low as 200 fg and linearity over a range of 5×10^{-4} were obtained for the polyaromatic hydrocarbons examined. Multiphoton ionization mass spectra were dominated by parent ions. Selective ionization based upon small differences in ionization potentials has been demonstrated for coeluting chrysene and triphenylene. Instrumental parameters have been investigated to assess possible improvements in sensitivity.

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Laser-induced multiphoton ionization of polyatomic molecules has been an area of recent active analytical interest due to the appealing possibility of sensitive and selective detection of certain molecular species (1-8). The availability of high intensity ultraviolet laser sources, which permit one photon resonant excitation of intermediate states and two photon ionization of many polyatomic molecules, has resulted in the manifestation of the analytical advantages of multiphoton ionization: enhanced sensitivity, spectral selectivity, and convenience compared to conventional single photon photoionization (9, 10) and other analytical molecular detection methods.

Following the conceptual fundamentals employed in atomic resonance ionization (11) and molecular multiphoton ioniza-

tion spectroscopy (12-15), Wessel and co-workers have clearly demonstrated the possibility of ambient pressure ultrasensitive and, in some cases, spectrally selective molecular detection, applied to both molecular vapors (5, 6) and gas chromatographic effluents (7, 8) utilizing laser ionization coupled with a proportional counter. Their results appear applicable to a wide variety of molecular species. Multiphoton ionization is also being applied in the development of a highly sensitive and spectrally selective ion source for mass spectrometry in which the extent of fragmentation may be controlled (12-14) by a simple adjustment of laser intensity. It is capable, at low laser intensities, of being a highly efficient soft ionization method, while at higher laser intensities, considerable fragmentation generally occurs. The possibility of spectral selectivity has resulted in discussions concerning the feasibility of two-dimensional mass-optical spectrometry (1-3). Since the initial recognition of the potential of laser ionization in mass spectrometry (1, 2) numerous experimental investigations have been reported. Several investigations of the mechanistic aspects of laser multiphoton ionization have appeared, resulting in considerable progress in describing the dynamics and energetics of the process (3, 12-19). One study compared the mass spectral fragmentation patterns of 27 organic compounds obtained by ArF laser ionization, with electron impact mass spectra obtained at 14- and 70-eV electron energy (19). More recently, multiphoton ionization of about 20 aromatic molecules induced by 2660 Å radiation has been demonstrated in a supersonic beam (20). Increased selectivity due to vibrational and rotational cooling was demonstrated although the analytical practicality of these results was not fully addressed. The potential of laser multiphoton ionization in analytical mass spectrometry for both sensitive and selective detection remains to be thoroughly explored.

In this paper, we report the application of laser multiphoton ionization, at a fixed wavelength, for ion generation in the combined technique of capillary gas chromatography/mass spectrometry (GC/MS). The analytical power of conventional capillary GC/MS for the qualitative and quantitative analysis of complex mixtures is well-recognized. Nevertheless, improvements in sensitivity and selectivity are continually sought to meet such challenges in modern trace analysis as the determination of environmental pollutants, pesticides, etc. Polyaromatic hydrocarbons represent a challenging trace analytical problem with important environmental and health considerations; many are documented or suspected carcinogens. In addition, numerous molecular detection methods have been applied to these compounds thus facilitating comparison with the results reported here. Since capillary gas chromatography itself provides a very high degree of selectivity based on a physical separation of mixture components, this paper examines the potential of laser multiphoton ionization to increase the sensitivity and selectivity of capillary GC/MS. The capillary gas chromatograph multiphoton ionization time-of-flight (TOF) mass spectrometer utilized in this work will be described in detail. The application of this instrument to the analysis of polyaromatic hydrocarbon mixtures will be demonstrated, the advantages of ionization potential selectivity with coeluting isomers will be illustrated, and the pertinent instrumental and experimental parameters will be discussed.

EXPERIMENTAL SECTION

Figure 1 depicts the multiphoton ionization gas chromatograph/time-of-flight mass spectrometer (MPI GC/MS) utilized in the experiments reported here. A description of the instrumental components follows.

Laser and Optics. A Lumonics TE861 excimer laser, operated with either KrF or XeCl as lasing media ($\lambda = 2485$ and 3080 Å, respectively) was utilized as the photon source. The excimer laser provided pulses of roughly 10 ns duration, with a maximum

available energy per pulse of 200 mJ. A fraction of the laser beam passed through a rectangular aperture (6 mm $\times$ 1 cm) and was focused into the ionization region of the mass spectrometer with a Suprasil cylindrical lens having a focal length of 20 cm. This yielded a rectangular ionization volume 6 mm in height (y axis), approximately 1 mm wide (z axis) and 10 mm long, centered about the mass spectrometer's time-of-flight axis (also z axis). This arrangement permitted irradiation of as large a proportion of analyte molecules as possible, without totally sacrificing mass spectral resolution. The focused laser beam passed through the mass spectrometer ionization region and exited from the spectrometer through another Suprasil window on the opposite side of the vacuum manifold. The average laser pulse energy was monitored with a Scientech Model 362 power meter. In the experiments reported here, this typically ranged from 1.35 to 1.80 mJ, and the laser was operated at a repetition rate of 20 Hz. It should be noted that reproducible mass spectra of a variety of molecules have been recorded with an excimer laser on a single shot basis (13, 14). However, high repetition rates are naturally more desirable for studying low concentrations of molecules or those which ionize inefficiently and particularly for monitoring gas chromatographic effluent.

Time-of-Flight Mass Spectrometry and Detection Electronics. The time-of-flight mass spectrometer in Figure 1 was constructed in-house and is similar in design to previous conventional spectrometers (21). The instrument consists of an ion source and acceleration region containing four grids constructed of 90% transmission nickel mesh. The grid spacings were 1.1, 1.0, and 1.2 cm, respectively, and the applied voltages were +105.2, -105.2, -400, and -2000 V dc, respectively. The flight tube was constructed of aluminum with a total drift length of 61 cm. The entire chamber was evacuated by a liquid nitrogen baffled NRC HS-6 diffusion pump backed by a Welch 1397 mechanical pump. Estimated pumping speed for helium is 500 L/s. While chromatograms were being recorded, the pressure in the spectrometer remained below 3×10^{-6} torr.

Ion detection was accomplished utilizing Varian microchannel plates (tandem configuration—VUW 8900). The signal from the microchannel plates was preamplified (LeCroy Model VV101), delayed for 190 ns and then processed by a Biomation Model 6500 transient wave form recorder. Each laser shot provided the start acquisition signal for the transient recorder via a fiber optic/photodiode (Hamamatsu S1223) trigger signal. Output from the transient recorder was displayed on an oscilloscope for immediate spectral viewing and stored in an Apple II microcomputer programmed for mass spectral data acquisition. This electronic arrangement provided a full mass spectrum following each laser pulse and also exploited the signal averaging capabilities of the computer.

A delay period, after the initial trigger, could be adjusted on the transient recorder to control the range of the mass spectrometer. Mass spectral resolution could be adjusted by varying the sampling period (2-50 ns) of the transient recorder and the ion source grid voltages. The mass spectral resolution available under the operating conditions employed (10 ns sampling period) was approximately 110 and was limited by both the sampling period and the modest focusing of our excimer laser in the spectrometer.

Gas Chromatography and GC/MS Interface. The gas chromatograph utilized in the experiments reported here was a Hewlett-Packard Model 5750 modified with a splitless injection system for use with capillary GC columns. A borosilicate glass capillary column (18 m $\times$ 0.25 mm i.d.) coated with 0.4% SE-52 as stationary phase was utilized. It was prepared by drawing borosilicate glass (Kimble 9970) to 0.25 mm i.d. using a Shimadzu Model GDM-1B glass drawing apparatus. The drawn capillary was then thoroughly rinsed, leached, and persilylated, according to Lee and Grob (22, 23), and coated statically with a solution of SE-52 stationary phase (0.4% in methylene chloride).

All chromatographic analyses were performed at a helium carrier gas flow rate of 2 mL/min, and temperature programmed from 80 °C to the upper temperature limit indicated in Figures 2 and 3 at 6 °C/min. A cryogenic molecular sieve trap (Linde 13X) was inserted in the carrier gas flow line for purification purposes. All chromatographic injections were splitless, involving volumes between 0.05 and 0.20 μ L of solution. The gas chro-

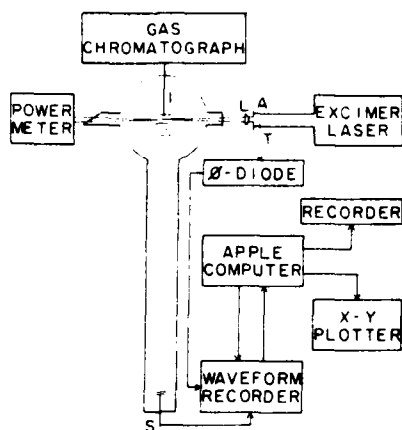


Figure 1. Block diagram of the multiphoton ionization GC/MS apparatus.

matographic column was directly interfaced to the ion source of the TOF mass spectrometer through a heated all-glass interface. Sample transfer through the interface was accomplished utilizing a fused silica capillary column connected to the glass capillary analytical column via an in-house constructed low dead volume $1/16$ in. union.

Acquisition of Mass Spectra and Total Ion Current Chromatograms. The Apple II computer generated a total ion current chromatogram (TIC) by integrating the signal over all transient recorder channels for 20 laser shots, thus generating one total ion current data point each second. Each digital total ion current value was converted to an analog voltage, via an internal digital to analog converter, and this was displayed on a strip chart recorder. This sampling rate was sufficient to accurately reproduce a capillary gas chromatogram. Additionally, by averaging 20 shots per total ion data point, base line fluctuations due to laser pulse-to-pulse intensity variations were drastically reduced.

Mass spectra were recorded only during the elution of a component (evidenced by the TIC chromatogram). This was accomplished by manually throwing a switch, which resulted in the Apple II computer storing not only the integrated ion yield but also mass resolved spectra following each laser pulse. On switch command, the Apple II computer would cease acquiring mass spectral data, and the computer would then transfer the respective mass spectrum (i.e., the total ion intensity data in each channel) to floppy disk for later retrieval. This procedure was independent of, and in no way interfered with, the acquisition of the total ion current chromatogram.

At low detection levels, multiple ion monitoring was employed to reduce the contribution of background ions to the integrated ion yield. The background results from ionization of impurities either residing in the mass spectrometer or bleeding off of the chromatographic column. With this operating procedure the computer monitored only certain preselected transient recorder channels. These preselected channels were used to generate multiple ion chromatograms. As before one data point was generated each second, by summing the voltages in all preselected channels for 20 laser shots.

Reagents and Standards. The polyaromatic hydrocarbons utilized in this report were reagent grade, with no further purification performed. Several PAH solutions of various concentrations were prepared by dilution of standard stock solutions of naphthalene, biphenyl, acenaphthene, fluorene, anthracene, phenanthrene, and pyrene (2 g/L of each component), in spectra grade methylene chloride. Individual solutions of naphthalene were prepared analogously from a stock solution (1 g/L in methylene chloride).

A Varian 3700 gas chromatograph modified for capillary gas chromatography and equipped with a flame ionization detector was utilized to check the integrity of all solutions.

RESULTS

The gas chromatography multiphoton ionization mass spectrometry apparatus depicted in Figure 1 was applied to

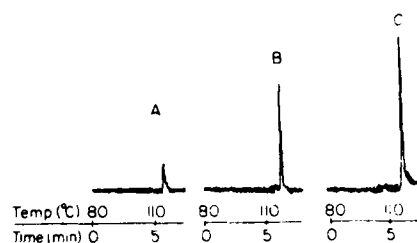


Figure 2. Selected ion chromatograms demonstrating detection sensitivity for naphthalene: A = 500 fg, B = 2.5 pg, C = 5 pg.

Table I. Dependence of Ion Yield on Quantity of Naphthalene Injected

sample size, pg	ion yield, arbitrary units	sample size, pg	ion yield, arbitrary units
0.5	1.3×10^{-4}	100	1.1×10^{-2}
2.5	6.4×10^{-4}	250	4.9×10^{-2}
10	2.0×10^{-3}	500	1.0×10^{-1}
25	4.8×10^{-3}	1000	1.9×10^{-1}
50	8.5×10^{-3}	10000	1.7

the detection and identification of selected polyaromatic hydrocarbons in order to assess its overall potential. Initial experiments were directed toward ascertaining the detection limits and the response of the multiphoton ionization GC/MS instrument for naphthalene. Toward that end, 0.1- μ L injections of naphthalene solutions of various concentrations were performed. Amounts of naphthalene injected ranged from 500 fg to 100 ng. Each injection was performed at an initial chromatographic column temperature of 80 °C, followed by temperature programmed analysis as indicated in Figure 2. KrF excimer laser pulses (4.98 eV/photon) were employed at a repetition rate of 20 Hz, with pulse energies ranging from 1.3 to 1.8 mJ. For these experiments only the ion signal in those preselected transient recorder channels corresponding to the parent ion of naphthalene ($m/z = 128$) was recorded. This selected ion monitoring was necessary for very high sensitivity measurements. The level of the background ion signal increased as the temperature of the column was raised during a chromatographic run, leveling off to a constant value when the upper column temperature limit was reached.

Figure 2 provides examples of the sensitivity observed. Selected ion chromatograms are displayed for 5 pg, 2.5 pg, and 500 fg of injected naphthalene. The chromatographic peak height obtained for 500 fg of naphthalene is five times that of the base line noise. The minimum detectable amount of naphthalene, at a signal to noise ratio of 2, is thus 200 fg by extrapolation. In all cases, appropriate blank injections were performed to verify the authenticity of observed signals and the absence of memory or carry-over effects. The quantity of naphthalene injected into the GC/MS system was varied over several orders of magnitude and the integrated ion signal measured as a function of sample size. The results are displayed in Table I. Due to the wide range of sample sizes examined, the data were obtained at two different microchannel plate gain settings in order to avoid saturating the detection electronics. The numbers listed in Table I have been normalized to a single microchannel plate gain. A log-log plot of the mass integrated ion yield as a function of naphthalene injected is linear over a range of 5×10^4 . Deviations from linearity were observed above 10 ng. This is most likely due to space charge effects in the ionization region of the mass spectrometer and it contributes to a loss of mass spectral resolution.

Figure 3 displays a direct comparison of conventional flame ionization GC with laser multiphoton ionization GC/MS in

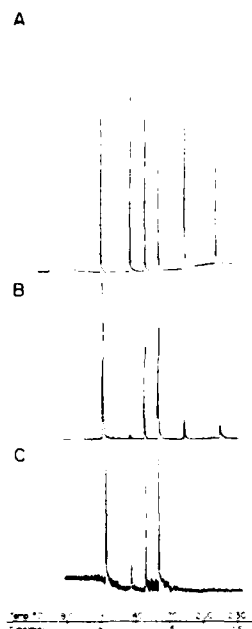


Figure 3. Chromatograms of a polyaromatic hydrocarbon mixture: (A) 30 ng each of naphthalene, biphenyl, acenaphthene, fluorene, anthracene and pyrene with a flame ionization detector; (B) 500 pg of same compounds with laser ionization detector, monitoring total mass-integrated ion yield; (C) 20 pg of same compounds with laser ionization detector selectively monitoring masses 128, 154, and 166 only.

Table II. Detection Limits for Selected Polyaromatic Hydrocarbons Utilizing KrF Excimer Laser Ionization GC/MS

PAH	LOD, ^a pg (S/N = 2)	PAH	LOD, ^a pg (S/N = 2)
naphthalene	0.20	anthracene	0.92
biphenyl	5.0	phenanthrene	0.30
acenaphthene	0.55	pyrene	1.10
fluorene	0.23		

^a LOD, limit of detection.

analyzing a mixture of polyaromatic hydrocarbons. Figure 3A displays the capillary gas chromatogram of a mixture of naphthalene, biphenyl, acenaphthene, fluorene, anthracene, and pyrene (30 ng of each component) with flame ionization detection. Figure 3B depicts the total ion current chromatogram of the same mixture taken with the same GC column but with only 500 pg of each compound injected and with KrF laser ionization MS detection. The TOF mass spectrometer electronics were adjusted to cover a mass range from 31 to 205 amu on each laser shot. The total ion current chromatogram and individual mass spectra for each chromatographic peak were generated simultaneously. Figure 3C is a multiple ion chromatogram of the same polyaromatic hydrocarbon mixture (20 pg of each component) in which the TOF mass spectrometer detection electronics monitored only the parent ions of naphthalene, biphenyl, acenaphthene, and fluorene: m/z 128, 154, 154, and 166, respectively. In all three cases, the polyaromatic hydrocarbon mixture was injected at an initial column temperature of 80 °C, followed by temperature programmed analysis as indicated in Figure 3. Immediately apparent from the chromatograms in Figure 3B,C is the variation in responsivity, at the fixed laser wavelength utilized, for different polyaromatic hydrocarbons.

Table II lists the minimum detectable levels, at a signal to

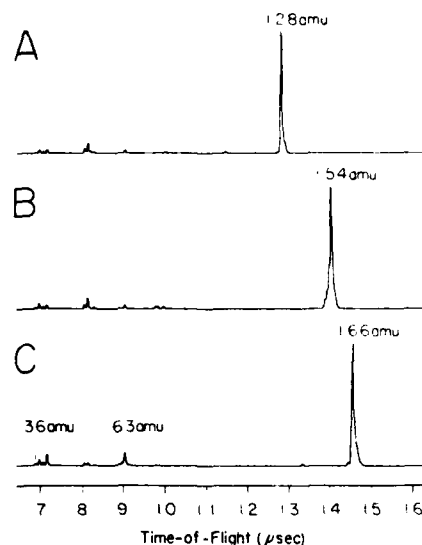


Figure 4. Multiphoton ionization mass spectra obtained with KrF excimer laser irradiation of (A) naphthalene, (B) acenaphthene, and (C) fluorene.



Figure 5. Total ion current chromatograms for 75 ng of triphenylene (left) and chrysene (right), obtained with XeCl excimer laser radiation.

noise ratio of 2, for the polyaromatic hydrocarbons examined in this study. These values were determined from the relative peak areas of the polyaromatic hydrocarbons, referenced to naphthalene, and the measured detection limit for naphthalene. As demonstrated in Table II, the sensitivity obtained with multiphoton ionization GC/MS in its present configuration is excellent. Nevertheless, as will be discussed shortly, several possible instrumental improvements could lower the detection limits considerably.

Representative multiphoton ionization mass spectra of the polyaromatic hydrocarbons examined are shown in Figure 4, which displays data for naphthalene, acenaphthene, and fluorene. Under the laser ionization conditions utilized in these experiments (i.e., 1.3–1.8 mJ energy), the mass spectra of the polyaromatic hydrocarbons examined were dominated by the parent ion. Lower mass fragment ions appeared consistently, but at a very low relative abundance (9% maximum). As is also true with electron impact ionization, multiphoton ionization mass spectra could not readily distinguish isomeric polyaromatic hydrocarbons, such as anthracene and phenanthrene. The time-of-flight mass spectrometer available for these studies does not provide sufficient resolution above mass 110 to fully separate adjacent ions at unit resolution. Work

is presently under way to improve the mass spectral resolution considerably.

Useful ionization selectivity can be attained for molecules which coelute chromatographically but differ somewhat in ionization potential. Figure 5 displays just such a case for the polyaromatic hydrocarbons chrysene and triphenylene, which have identical retention times on an SE-52 capillary column. With KrF excimer laser radiation (4.98 eV/photon), absorption of two photons results in the ionization of both chrysene and triphenylene (ionization potentials of 7.8 and 8.1 eV, respectively). Absorption of two photons of XeCl excimer laser radiation (4.0 eV/photon), on the other hand, results in the ionization of chrysene only at moderate light intensities. The two total ion chromatograms in Figure 5 display separate 75 ng GC/MS injections of triphenylene (left) and chrysene (right) and irradiation with XeCl excimer laser light (600 μ J of energy/pulse). No ion current is detected for triphenylene. Selective ionization and detection of chrysene in the presence of coeluting triphenylene are therefore clearly possible. Subtraction of the signal obtained by XeCl ionization from that obtained with KrF ionization would then also permit the quantitation of triphenylene. Similar selectivity is available for the chromatographic solvent, if it is appropriately chosen. For instance the chromatographic solvent utilized here, methylene chloride (ionization potential of 11.35 eV), did not produce any detectable ion current under any of the conditions utilized in these experiments. The absence of a chromatographic solvent peak could prove useful in the quantitation of coeluting analyte molecules. As expected the gas chromatographic carrier gas, helium, also exhibited no tendency to ionize under our operating conditions.

DISCUSSION

The experiments reported here have been designed to explore the potential sensitivity advantages available by utilizing laser multiphoton ionization for detection in capillary gas chromatography/mass spectrometry of polyaromatic hydrocarbons. Although the results reported here have demonstrated some limited selectivity based on small differences in ionization potential, no attention has been focused on the spectral selectivity possible via resonant enhanced multiphoton ionization through real intermediate states, since this has been amply demonstrated in numerous spectroscopic studies with tunable dye laser radiation. Spectral ionization selectivity requires differences in the one photon absorption spectra and/or the ionization potentials of the species of interest. Since UV absorption bands are often broad and featureless at room or elevated temperatures, spectral ionization selectivity is a useful supplement but not a replacement for the selectivity achievable with capillary gas chromatography. In other words the laser light, the gas chromatography, and the mass spectrometry each contribute their unique advantages and capabilities to this analytical detection system. The addition of a tunable dye laser would further improve the system's flexibility and effectiveness.

Even with a low duty cycle in which ions were generated for only 0.2 μ s per second of analysis time, excellent sensitivity was obtained in the analysis of the polyaromatic hydrocarbons examined utilizing multiphoton ionization GC/MS. The low duty cycle of pulsed laser multiphoton ionization makes time-of-flight the optimal choice for ion mass analysis. The ability to record a full mass spectrum and thus collect all ions generated during each laser shot coupled with the relatively high ion transmission of a time-of-flight mass spectrometer and the high efficiency of UV laser multiphoton ionization offset, to some extent, the duty cycle limitations. The sensitivity obtained here for multiphoton ionization GC/MS analysis of the polyaromatic hydrocarbons is clearly comparable to other conventional techniques with or without mass

spectrometric analysis. It should be noted that repetition rates for commercial excimer and pulsed dye lasers are continually being increased, so the duty cycle problem will certainly become less significant as time goes on.

The low sensitivity for detecting biphenyl in comparison with naphthalene deserves comment. The former absorbs approximately 10 times more strongly than the latter at 2485 Å. The ionization potentials of both molecules are less than 8.3 eV so a pair of KrF laser photons should, in principle, provide enough energy to easily ionize either. Fluorescence and phosphorescence quantum yield measurements with room temperature solutions or frozen alcohol-ether glasses indicate that intersystem crossing is substantially faster in biphenyl than in naphthalene (24). If this were also true in the gas phase at the wavelength employed in this experiment, ionization yields for the two molecules would probably be expected to differ. For example, if a biphenyl molecule quickly relaxes to a triplet state following excitation of its singlet, ionization from that lower lying triplet state may be substantially less efficient than from the singlet state as a result of reductions in either the electronic or vibrational parts of the transition integral. This kind of effect has been observed in the ionization of benzene with KrF and ArF lasers (13, 14). While benzene absorbs the shorter wavelength ArF light much more strongly, at the light intensities used in these experiments more ions are generated by using the longer wavelength KrF radiation. The significance of these observations is that photochemical processes occurring in the gas phase under isolated collision-free conditions must be investigated and understood in detail before the ionization efficiencies of different types of molecules in a laser ionization mass spectrometer can be reliably interpreted or predicted.

Although excellent sensitivity has been obtained, the instrument described herein was far from optimized. The excimer laser utilized has a maximum repetition rate of 100 Hz. However, the mass spectral data acquisition speed of the Apple II computer limited the experimental repetition rate to 20 Hz. Furthermore the gas chromatographic effluent exits the GC/MS interface 2.5 cm above the multiphoton ionization volume, allowing considerable sample beam expansion. Combined with the low duty cycle, this results in the irradiation of only a small proportion of the available analyte molecules.

Another problem encountered in these experiments was high ion background levels which limited our ability to obtain accurate full mass spectra at very high sensitivity levels. In addition, the current mass spectrometer has no provision for heating the acceleration grids to prevent or reduce ion source contamination. Most of the background ion signal was due to sensitive detection of chromatographic bleed, with the level increasing at elevated column temperatures.

Clearly, the time-of-flight mass spectrometer utilized in these studies is not entirely adequate for the GC/MS analysis of larger molecules due to the limited mass spectral resolution. Nevertheless, this instrument has demonstrated the obvious advantages of time-of-flight mass analysis in laser multiphoton ionization, in agreement with previous experiments (13, 14, 25). For improved mass spectral resolution, an ion reflecting time-of-flight mass spectrometer is under construction which should provide a resolution of up to 3000 (26, 27). Such a design would preserve at least moderate mass resolution when relatively large focal volumes are illuminated, as in high sensitivity experiments. Further, an improved ion source design is included, which will permit multiphoton ionization of molecules only millimeters away from the exit of the GC/MS interface. Planned improvements in detection electronics and data acquisition speed should allow the laser to be operated at considerably higher repetition rates.

Chromatographic improvements will include the use of on-column injection and bonded stationary phase fused silica columns to decrease, substantially, the background ionization observed and also allow for quantitative delivery and analysis of larger polyaromatic hydrocarbons.

Further sensitivity improvements are possible utilizing a high intensity tunable laser source to effect multiphoton ionization at the optimum wavelength for each particular molecule studied. Additional laser power is clearly attainable with a frequency doubled Nd:YAG pumped dye laser and, coupled with tunability, this would provide enhanced sensitivity for detecting molecules. (Note that there was little advantage to be gained by using a larger fraction of our excimer laser output in the present experiments since the background ionization level increased with light intensity as much as the analyte signal did. If the background, which may be wavelength dependent, is reduced, lower detection limits should be attainable with higher light intensities as long as the resulting increased fragmentation does not obliterate the identities of parent molecules.)

With the improvements discussed above, we anticipate sensitivity for polyaromatic hydrocarbons at least in the low femtogram range. If background problems can be suppressed full multiphoton ionization mass spectra can be acquired at roughly the same level.

Although we feel the limited spectral selectivity of multiphoton ionization at elevated temperatures necessitates a high-resolution chromatographic separation and the mass analysis of generated ions, other approaches to achieving additional molecular selectivity in multiphoton ionization are possible. It is well-known that supersonic beams can be utilized to increase the spectral selectivity of laser multiphoton ionization by cooling molecules rotationally and vibrationally. Under such circumstances, spectral selectivity is quite high. However while vibronic absorption bands sharpen enormously under these conditions, the locations of these sharp bands may not be so useful in distinguishing a series of different but related molecules. For example the alkylbenzenes studied by Smalley and co-workers (28) have cooled beam absorption spectra which are largely independent of the alkyl group attached to the aromatic ring. The small differences in their spectra would certainly be exploitable in analytical experiments, but it would be much simpler to rely on gas chromatographic selectivity to analyze a mixture of these molecules. Some of the problems associated with supersonic beams for gas-phase analysis have recently been discussed (29, 30), with regard to laser-induced gas-phase fluorescence. The results of these experiments have indicated the limitations in quantitation, precision, and practicality for mixture analysis in supersonic beams. They have led to the development of the technique of rotationally cooled laser-induced fluorescence/gas chromatography, in which a low-resolution gas chromatographic column is coupled to the supersonic beam to serve, primarily, as a quantitative inlet system.

Due to the ability of laser multiphoton ionization to serve as a highly efficient soft ionization method, its potential use for ion generation in the technique of tandem mass spectrometry (MS/MS) (29, 30) is appealing (31, 32). In this mode, the function of laser multiphoton ionization would be, primarily, to generate parent ions of mixture components in high yield. The MS/MS instrument would then accomplish mixture analysis or functional group screening in any of several reported scanning modes. The highly advantageous features of the MS/MS technique are the speed of analysis and, in many cases, the minimal sample preparation required. However, since present MS/MS instruments are dynamic scanning mass spectrometers, the present low duty cycle of laser multiphoton ionization would impose sensitivity limi-

tations in coupling the two methods. However, if pulsed laser duty cycles are improved considerably, this limitation may be overcome.

The analytical system described in this paper combines the proven quantitative ability of high-resolution capillary gas chromatography/mass spectrometry in mixture analysis of polyaromatic hydrocarbons with the high sensitivity attainable through multiphoton ionization with high-power UV lasers. With the addition of a tunable laser source, spectral selectivity should improve the analytical flexibility of the system. A disadvantage, of course, is the lengthy time of analysis often required with gas chromatography/mass spectrometry.

The general applicability of multiphoton ionization GC/MS to nonaromatic compounds is not yet clear. While numerous other molecules have been investigated since the development of multiphoton ionization as a spectroscopic technique (33, 34), quantitative ionization efficiencies for these molecules as a function of various laser parameters have generally not been measured, optimized, or reported. Further studies will be required to assess overall sensitivity and the usefulness of multiphoton ionization fragmentation patterns for qualitative identification of molecules. Aside from the instrumental improvements under way, studies are planned to improve our understanding of the photochemical processes which affect ionization sensitivity, and to investigate the application of this technique to nitrogen- and sulfur-containing polyaromatic hydrocarbons.

ACKNOWLEDGMENT

We gratefully acknowledge Milos Novotny for allowing us to use his equipment for preparation of glass capillary chromatographic columns. We wish to thank Donald Fowler, John Dorsett, and the Chemistry Department machine shop for expert craftsmanship in the construction of the GC/MS apparatus.

Registry No. Chrysene, 218-01-9; triphenylene, 217-59-4; naphthalene, 91-20-3; biphenyl, 92-52-4; acenaphthene, 83-32-9; fluorene, 86-73-7; anthracene, 120-12-7; phenanthrene, 85-01-8; pyrene, 129-00-0.

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RECEIVED for review August 30, 1982. Accepted November 1, 1982. We wish to thank the Camille and Henry Dreyfus Foundation for a Young Faculty Award and the Research Corporation for a Cottrell Research Grant. This work has been supported by the Office of Research and Development, Environmental Protection Agency, under Grant No. R808790-01-0, and by the U.S. Army Research Office under Contract No. DAAG 29-81-K-0097.

Observation of Polyatomic Ion Vibrational State Distribution by Laser Photoelectron Spectroscopy

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Vibrationally resolved photoelectron spectra of a polyatomic molecule resulting from laser two-photon ionization are observed for the first time. Ion vibrational state distributions generated by exciting three different vibronic states of gas-phase toluene clearly demonstrate a propensity for $\Delta v = 0$ transitions in the ionization of the excited singlet state. Progressions in the photoelectron spectra are tentatively assigned to vibrational modes of the toluene cation.

Introduction

The primary emphasis in studies of multiphoton ionization of molecules to date has been on detecting total ion yields so as to derive spectroscopic information about neutral intermediate states.¹⁻³ Studies applying the MPI technique to mass spectrometry and the generation of intensity-dependent fragmentation patterns have more recently appeared.⁴⁻⁷ Spectroscopic examinations of the photoions themselves have until now not been conducted with this technique, although laser-induced fluorescence and photodissociation studies on ions produced in other ways are now being performed. We report here an ion spectroscopic study based on monitoring photoelectron kinetic energy distributions by the time-of-flight method. In an earlier investigation we obtained a low-resolution UV laser ionization photoelectron spectrum of benzene, which was interpreted as being the result of a two-photon ionization process.⁸ No vibrational structure was observed in that work. As a result of apparatus improvements, we have been able to record for the first time the vibrationally resolved laser photoelectron spectrum of a similar molecule. Very recently, Hepburn et al. reported observing the resolved photoelectron spectra of diatomics (CF, CCl) by multiphoton ionization.²⁰

Experimental Section

Time-of-flight photoelectron spectra were generated by crossing an effusive molecular beam of toluene with the frequency-doubled output of a pulsed dye laser. Coumarin 6 (Eastman Kodak) dye pumped with a XeCl excimer laser and frequency doubled with a KDP crystal provided continuously tunable radiation from 2600 to 2700 Å. Laser pulse widths were about 6 ns (fwhm) and spectral bandwidths were on the order of 0.4 cm⁻¹. Ultraviolet pulse energies employed in this work were generally 20 μJ or less. The laser light was focused into the toluene beam with a 20-cm focal length suprasil lens. The electron spectrometer

consists of a vacuum chamber (base pressure 3×10^{-7} torr) and a flight tube, both surrounded by magnetic shielding. Toluene flow through a 0.35-mm orifice was such that the pressure in the vacuum chamber was typically 3×10^{-6} torr during an experiment as measured with an ionization gauge. Photoelectrons travel 49 cm from the laser focal region to a microchannel plate detector, the output of which is amplified and digitized in a Biomation 6500 waveform recorder. Its output is stored and processed in an Apple II computer. With count rates typically less than one per laser shot, more than 30 000 shots are required for the development of a spectrum.

Results and Discussion

The spectroscopy of the $S_1 \leftarrow S_0$ transition of toluene has been thoroughly studied.⁹⁻¹² In our experiment the dye laser was tuned to three particular vibronic bands in the S_1 state: the 0-0 origin band at 2667.5 Å (37 477 cm⁻¹, 4.65 eV); the 6b₀ band at 2630.2 Å (38 008 cm⁻¹, 4.71 eV); and the 12₀ band at 2602.7 Å (38 410 cm⁻¹, 4.76 eV). Vibrational energies at these levels are, respectively, 0 cm⁻¹, $\nu_{6b} = 528$ cm⁻¹, and $\nu_{12} = 932$ cm⁻¹. Absorption of two photons at these wavelengths is sufficient to exceed the ionization potential of toluene, which has been reported to be in the range 8.72-9.0 eV.¹³

Vibrationally resolved laser photoelectron spectra of toluene were successfully recorded only at low electron counting rates. To emphasize this point, Figure 1 displays time-of-flight photoelectron spectra obtained by irradiating toluene at the $S_1 \leftarrow S_0$ origin with UV pulse energies of 12 μJ/pulse and less than 1 μJ/pulse. The count rate at the higher pulse energy was about two electrons per laser shot, while that at the lower energy was 0.1 per shot. In the former case the spectrum is devoid of reproducible structure. In the latter it consists of a series of peaks with widths (fwhm) of 10-20 meV. This intensity dependence is typical for every laser wavelength used in this study. This behavior may result from perturbations on the outgoing electrons induced by the tiny cloud of ions and electrons generated in the focal volume of the laser. (Only about one electron in 10⁴ produced is detected because of

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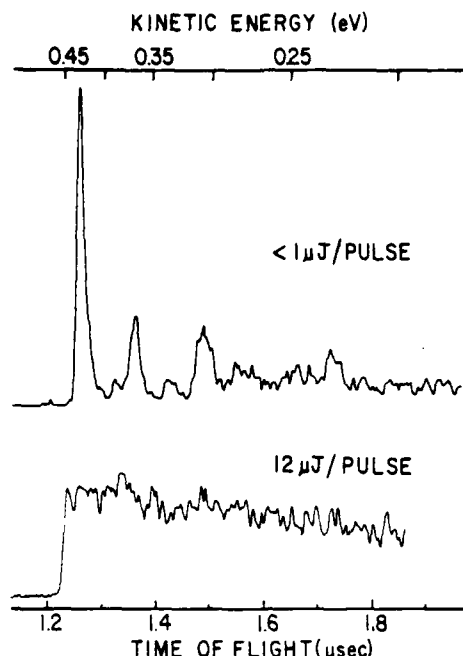


Figure 1. Raw time-of-flight photoelectron spectra of toluene at laser pulse energies of 12 and $<1 \mu\text{J}$. The laser wavelength was tuned to the $S_1 \leftarrow S_0$ origin at 2667.5 Å. Electron kinetic energy is also given along the top scale.

our detection geometry, so thousands of charged particles are produced in each pulse under our operating conditions.) In our better resolved experiments we have maintained low charge densities by using low laser intensities. This could also be accomplished by reducing the molecular flux but we have not yet attempted this. An alternative broadening mechanism which would be laser intensity dependent involves fragmentation of neutral toluene, followed by ionization of fragments whose photoelectron spectra differ from that of the parent molecule. If this were the dominant source of broadening, the spectrum would be independent of molecular beam flux. A final complication may be electromagnetic field gradient forces,¹⁴ although at the intensities and frequencies employed in these experiments, one can estimate that their effects should be negligible. Any of these mechanisms could also account for the slight shift, of $\sim 14 \text{ meV}$ to higher energy, in the threshold of the $12 \mu\text{J}/\text{pulse}$ spectrum relative to the $<1 \mu\text{J}/\text{pulse}$ spectrum. Systematic studies to discriminate between these possible mechanisms will be reported in a future publication. For the present we note that complementary TOF mass spectra of toluene which we have generated by laser ionization at the same wavelengths and in the same apparatus we use here, indicate that very little, if any, fragmentation occurs at the low energies ($<1 \mu\text{J}/\text{pulse}$) employed in our higher resolution experiments.¹⁵

Observed photoelectron spectra, which as raw data are linear in flight time, are converted to plots linear in electron kinetic energy by computer and are displayed in parts A (2667.5 Å), B (2630.5 Å), and C (2602.7 Å) of Figure 2. Since these three result from different photolysis energies (wavelengths), the kinetic energy of an electron associated with production of an ion in any particular vibrational state differs in the three cases. To facilitate visual comparison of the three traces by taking this into account, we shifted

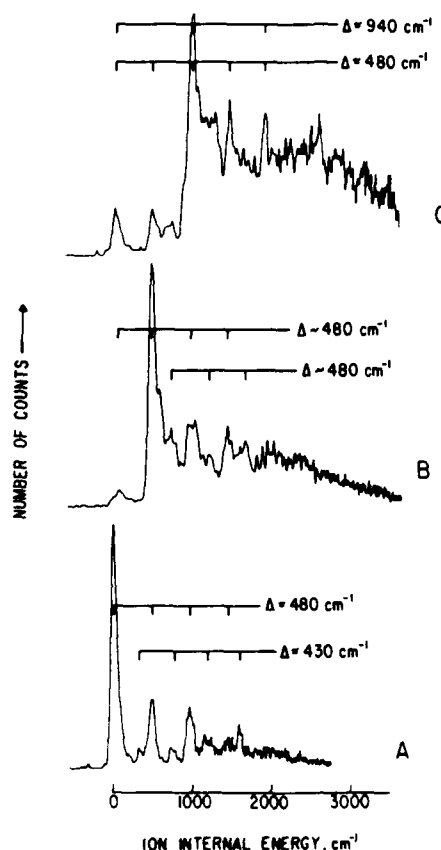


Figure 2. Photoelectron spectra generated by two-photon ionization of gas-phase toluene. Laser is resonant with the $S_1 \leftarrow S_0$ origin (Figure 2A), $6b_1^1$ (Figure 2B), and 12_1^1 (Figure 2C) transitions. The abscissa, ion internal energy, is the quantity $2h\nu - \text{IP} - \text{KE}$ where $h\nu$ is the laser photon energy and KE is the photoelectron kinetic energy.

spectra B and C of Figure 2 relative to that of spectrum A. The appropriate shift is calculated to be $2(h\nu - E_{00})$, where $h\nu$ is the laser photon energy and E_{00} is the energy of the $S_1 \leftarrow S_0$ origin. The threshold of the photoelectron kinetic energy distribution must correspond to formation of the ion in its ground vibrational state. The highest energy (shortest TOF) peaks in the three Figure 2 spectra correlate perfectly, confirming their assignment to ground vibrational state ions. Furthermore, use of the thresholds of these "origin" features to calculate the toluene ionization potential leads to $\text{IP} = 8.856 \pm 0.003 \text{ eV}$, which is at the center of the range of reported values. Precise energy scale calibration of our apparatus is better done by laser ionization of an atom; after this has been accomplished, very accurate ionization potentials will be extractable with this technique.

The positions of the most intense features in the photoelectron spectra are readily interpretable. With the laser tuned to the $S_1 \leftarrow S_0$ vibronic origin, electrons appear preferentially in the first peak, indicating that production of vibrationally unexcited ions is dominant. When the laser is in resonance with the $6b_1^1$ transition (Figure 2B), the strongest peak has its threshold approximately 60 meV (480 cm^{-1}) to lower electron energy than the much weaker "origin" peak; it correlates well with the second peak of the Figure 2A progression. Detailed spectroscopic studies of a number of halogenated benzenes indicate that frequencies of vibrational modes in the ground-state ions differ typically by no more than a few tens of wavenumbers from those of the same modes in the neutral parent ground

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and excited electronic states.¹⁶ The 60-meV, 480-cm⁻¹, spacing corresponds well with $\nu_{6b} = 528$ cm⁻¹ of the S₁ neutral. Accordingly, the most intense peak of Figure 2B is reasonably attributed to ions formed with one quantum in the 6b mode of the ion. Similarly with the laser resonant in the 12₀¹ transition 932 cm⁻¹ above the S₁ ← S₀ origin (Figure 2C), the most intense peak lies about 110 meV (960 cm⁻¹) lower in electron energy than the first peak and is ascribed to ions produced with one quantum in vibrational mode 12 of the ion.

This behavior represents unambiguous evidence for a preference of $\Delta v = 0$ ionization transitions from excited vibronic states of toluene, as suggested in previous work by Smalley et al.,¹⁷ on naphthalene and benzene. A propensity for $\Delta v = 0$ transitions is expected in accordance with the Franck-Condon principle when the excited neutral and ground ionic states are described by similar potential curves.¹⁸

Additional peaks in our electron spectra can be ordered into progressions which include the most intense features, as indicated in Figure 2. Aside from the persistent ~60-meV spacing and the short ~117-meV progression of Figure 2C, one with 53-meV (430-cm⁻¹) spacing appears in Figure 2A and is tentatively assigned to the 6a mode of the ion. This has a 456-cm⁻¹ frequency in the neutral S₁ electronic state. The structure of Figure 2B appears more complicated. The 60-meV progression has somewhat irregular spacings and may involve short progressions and combinations in other modes. In the Figure 2 spectra, structure is less distinct at electron energies corresponding to production of ions with 1000 cm⁻¹ or more internal energy. The most probable cause of this feature is spectral congestion involving excitation of various high frequency or combination modes of the ion. Apparatus distortion of electron kinetic energy distribution at low kinetic energy seems unlikely if one notes that well-resolved structure in Figure 2A is observed at the same kinetic energies at which broadening begins to appear in Figure 2C. In future experiments, we hope to resolve structure in these congested regions and establish more firmly our tentative vibrational assignments under higher resolution conditions.

Our two-photon ionization photoelectron spectra may be contrasted with the conventional (He I, 584 Å, 21.22

eV) photoelectron spectrum of toluene reported by Debries and Rabalais.¹³ Vibrational structure is just resolved in the latter case, yielding short progressions with spacings of 584 and 1694 cm⁻¹. The resolution of our apparatus is about 7 meV (the narrowest line width we measure in our spectra). This is somewhat better than the ~14-meV resolution of the spectrometer used by Rabalais,¹⁹ but not sufficiently different to account for the significantly enhanced detail of our spectra. With the low backing pressure used in our effusive beam source (a few torr), substantial rotational and vibrational cooling in the molecular expansion is unexpected. The primary cause of the nearly indistinct structure in the one-photon photoelectron spectrum seems likely to be congestion due to the activity of many ion vibrational modes in the spectrum. Laser two-photon ionization in principle selects a single S₁ vibronic state in the neutral and apparently excites few other ion vibrational modes in the ionization transition. Sequence bands may still be introducing unwanted vibrational congestion into our spectra, and we hope to eliminate this possibility in future experiments with a cooled supersonic molecular beam source.

This technique of laser photoelectron spectroscopy certainly has considerable potential because of its high resolution (and further improvements are expected). Just as importantly, if the electronic spectroscopy of the neutral parent molecule has been analyzed and understood, resonant ionization through previously assigned vibronic levels which leads to enhanced production of particular ion vibrational states provides strong supporting evidence for the assignment of these states. Furthermore laser ionization may also enable one to study the vibrational state dependence of ion reactivity. By combining a laser ionization source with, for example, an ion cyclotron resonance spectrometer, the reaction rates of ions preferentially produced in different vibrational states can be measured.

Acknowledgment. We gratefully acknowledge the Camille and Henry Dreyfus Foundation for a Young Faculty Award and the Research Corporation for a Cottrell Research Grant. This work has been supported by the U.S. Army Research Office under Contract No. DAAG 29-81-K-0097 and by the Office of Research and Development, Environmental Protection Agency, under Grant No. R808790-01-0.

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Rotationally Resolved Laser Photoelectron Spectrum of Gas-Phase NO

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The first rotationally resolved photoelectron spectrum of a molecule other than H_2 is reported. NO is ionized from selected quantum levels of its $A(^2\Sigma^+)$ excited electronic state. One strong peak and two weaker peaks, corresponding to $\Delta N = 0$ and $\Delta N = \pm 2$ rotational transitions, respectively, are observed. This rotational selection rule is the same as that observed when hydrogen is ionized from its $X^1\Sigma_g^+$ ground electronic state but differs from that observed when it is ionized from its $B^1\Sigma_u^+$ state.

Laser-induced photoionization has great promise as a tool for understanding ionization processes and for obtaining spectroscopic information about neutral molecules and ions.¹⁻⁵ In contrast with conventional photoelectron spectroscopy, the laser-induced method is demonstrating somewhat better resolution and considerably more experimental design flexibility. The latter follows because with tunable lasers one can excite individual vibronic bands and then, with one or more additional photons, ionize molecules from selected vibrational levels. A greater region of the potential energy surface of the ion can thus be studied compared with conventional photoelectron spectroscopy where ionization occurs only from thermally populated levels. While assignment of the resonant first step in a two-step ionization scheme is usually based on previous UV absorption measurements, the photoelectron experiment can also provide complementary checks on these spectroscopic assignments.^{5,6}

The resolution that we have recently attained (3 meV at best) enables us to realistically consider the possibility of resolving rotational structure in some photoelectron bands, particularly those of lighter diatomic molecules. Experiments of this kind would enable detailed studies of the rotational selection rules appropriate for photoionization processes. The only diatomic whose photoelectron spectrum has been rotationally resolved is H_2 . It has been investigated by Asbrink,⁷ Morioka et al.,⁸ and Pollard et al.⁹ They studied the transition $^2\Sigma_g^+ \leftarrow ^1\Sigma_g^+$ and observed the selection rule $\Delta N = 0, \pm 2$, as predicted by Sichel.¹⁰ However, the dependence of this selection rule on the state from which photoionization occurs could not be investigated since these experiments involved ionization from the $v = 0$ level of hydrogen's ground electronic state only. Furthermore, in conventional photoelectron experiments such as these, photoionization proceeds from a number of thermally populated rotational levels, each producing rotational lines conforming to the selection rules. The resulting spectrum, which is somewhat complex, has to be deconvoluted to obtain the contributions due to individual transitions. In laser experiments photoionization can be induced from single rotational levels, leading to simpler and easier to interpret spectra. An attempt to laser ionize H_2 from a particular rotational state has recently been reported, but the rotational structure of the photoelectron spectrum was only partially resolved.¹¹

Bonham and Lively have theoretically analyzed the rotational selection rules for Hund's case b transitions¹² and found that they depend on the intermediate electronic state from which the molecule is ionized. Our goal then is to ionize NO from different intermediate electronic states in an attempt to test these selection rule predictions. In this letter we present the results of ionizing NO from individual rotational states within the $v = 0$ vibrational level of the $A(^2\Sigma^+)$ excited electronic state. NO was chosen for this work because many of its electronic states have been well studied¹³⁻¹⁵ and are easily accessible by laser excitation.^{1,16-18} A few groups have recently measured the photoelectron kinetic

energy distribution following laser ionization of NO, but in all of these cases only the vibrational structure of the photoelectron bands was extracted.¹⁹⁻²¹

The time-of-flight photoelectron spectrometer used in our experiments has been described elsewhere.⁵ A Coumarin 450 grazing incidence dye laser pumped by a Lumonics TE 430 XeCl excimer laser was our primary light source. Its bandwidth was approximately 0.4 cm^{-1} . UV pulses of 1–20 μJ were obtained by frequency doubling the blue radiation in a KB5 crystal. An effusive beam of NO (Matheson grade CP) streamed through a 30- μm nozzle into the ionization chamber where a pressure of 1×10^{-5} torr was maintained. Photoelectrons generated by the two-step ionization were detected with two Varian VUW-8900 micro-channel plates in tandem. The resulting signal was amplified and digitized with a Biomation 6500 waveform recorder and a LeCroy 2228A time to digital converter (TDC). Their time resolutions were 2 ns/channel and 50 ps/channel, respectively.

Monitoring the total photoelectron yield as a function of wavelength (tuning the dye laser from 4490 to 4540 Å which on frequency doubling scanned the 0–0 band of the $A \leftarrow X$ system) yielded a spectrum similar to that obtained with single-photon absorption. Individual rovibronic transitions were well resolved except near the band heads.

The laser was then tuned to a specific rotational transition in the 0–0 band of the $A \leftarrow X$ spectrum. We chose to excite lines away from the band head for two reasons: First, the rotational structure of the $A \leftarrow X$ band was less congested; second, the ion

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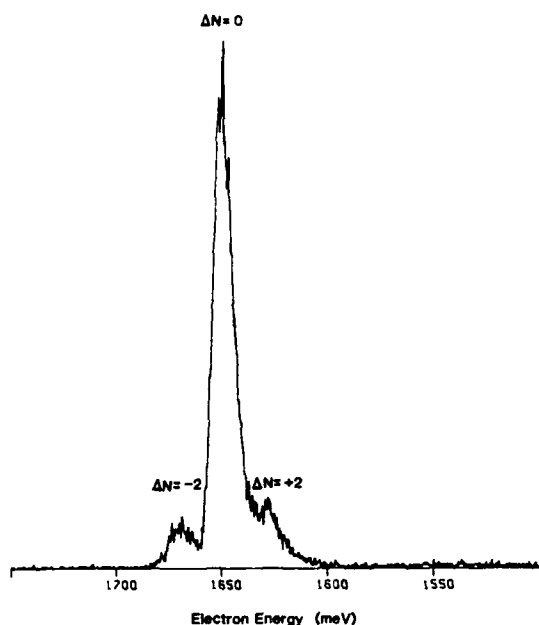


Figure 1. Photoelectron spectrum of NO obtained by resonant one-photon excitation of a single rotational line in the 0-0 band of the $A \leftarrow X$ system. The rotational assignment of the excitation line is tentative and is most likely R(21.5).

rotational levels become more widely spaced with increasing rotational quantum number. Figure 1 displays the photoelectron spectrum obtained by a resonant excitation of a single rotational line which we have tentatively assigned as R(21.5) in the 0-0 band. Work is in progress to confirm the assignment of the excitation lines.

The qualitative appearance of the spectrum, with a single strong peak and two weaker peaks on either side, indicates that $\Delta N = 0$ is the dominant selection rule. (Here N is the total angular momentum quantum number apart from spin, using currently accepted notation for case b .) A $\Delta N = \pm 1$ selection rule would predict that two strong peaks should appear. More quantitatively, one can calculate that the spacing between adjacent ion rotational levels near $N = 21$ is about 10 meV using the NO^+ rotational constants summarized by Huber and Herzberg.²³ The spacing between the central peak and each of the small side peaks in Figure 1 is 20 ± 1 meV, indicating that this separation corresponds to two NO^+ rotational quanta. These results are in keeping with theoretical predictions.¹² It is worth noting that this is the first study where rotational resolution in a photoelectron spectrum has been obtained with a molecule other than H_2 .

Photoelectron spectra have also been recorded by exciting several other rovibronic transitions in the $\text{NO } A \leftarrow X$ 0-0 band. All were similar to the spectrum appearing in Figure 1. In future experiments we will excite rovibronic levels in the C and D states of NO. Unfortunately these cannot be reached with single photons from our frequency doubled dye laser; they must be excited by two-photon transitions. The intensities of the photoelectron signals will therefore be substantially reduced. Hopefully these experiments will help us to improve our understanding of the rotational selection rules in photoionization and verify the theoretical predictions of Bonham and Lively.

Acknowledgment. This work has been supported by the U.S. Army Research Office under Contact DAAG 29-81-K-0097 and by the office of Research and Development, Environmental Protection Agency, under Grant R810896.

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