Production and Unimolecular Decay Rate of Internal Energy Selected Molecular Ions in a Laser Reflectron Time-of-Flight Mass Spectrometer

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Monoenergetic, internal energy selected polyatomic ions are produced in a new two-laser pump-pump experiment. Low energetic parent ions produced with the first laser are further excited with the tunable second laser to a specified internal energy after extraction from the ion source. The metastable decay of energy-selected ions is monitored in a reflectron time-of-flight mass spectrometer, and as a first example, dissociation rates have been measured for two decay channels of $C_6H_6^+$. The result clearly demonstrates directly that C-loss as well as H-loss channels are competing and originate from the same electronic state of the benzene cation.

Introduction

During the past three decades the unimolecular decay of polyatomic ions in a mass spectrometer has been studied in great detail.[1] The results, e.g. breakdown curves, metastables, and kinetic energy release, have been suggestive of a statistical behavior in the unimolecular decay. A critical test of the assumption made in statistical theories would, however, be only really optimal if the ions are prepared in a defined internal energy level rather than with a broad energy distribution as e.g. after electron impact ionization or vacuum-UV excitation. Even though the energy of the vacuum-UV photons is well-defined, this type of excitation still produces a broad range of final ion energies associated with differing relative kinetic energies of the electron.

An alternative method to produce molecular ions is multiphoton and in particular two-photon ionization via a resonant intermediate state of the neutral molecule.[2] In this way at low light intensities soft ionization is possible[3] whereas at high light intensities strong fragmentation is observed.[4,5] In the multiphoton excitation process the original parent ions are produced with relatively little internal energy as a consequence of the "ladder-switching" process.[5] Then, during the laser pulse the parent ions begin to absorb further photons until they finally dissociate. When the two- or three-photon energy is tuned close to the ionization threshold, the parent ions are preferentially produced in their vibrationless ground state. This wavelength, however, fixes the internal energy of the ions such that further photon absorption is specified, and hence one cannot vary the internal energy as would be desirable for any study of unimolecular decay behavior. On the other hand, if the photon energy is increased, ions are produced in higher vibrational states and the final energy of the excited ions, even though variable, is no longer defined, an unknown quantity going into kinetic energy of the electron. Recent one-laser experiments yielding metastable decay rates for aniline[6] and chlorobenzene[7] cations inherently display this uncertainty.

In this work it will be shown that in a two-laser pump-pump experiment polyatomic ions can be produced with differing energy content but now internal energy selected. Dissociation rates of two decay channels of energy-selected benzene cations at different energy levels are presented as measured in a reflectron time-of-flight mass spectrometer.

Experimental Section

A scheme of the experimental setup is shown in Figure 1. The beam of laser 1 is focused into an effusive molecular beam of benzene molecules yielding a focus diameter of 300 μm. The laser intensity is adjusted to about 10^6 W/cm^2 so that efficient soft ionization without fragmentation is achieved. The frequency-doubled light of the nitrogen laser (Molectron UV 24) pumped dye laser (Molectron DL II) is tuned to $\lambda_{1\text{vac}} = 2667.9$ Å. This corresponds to the peak of the 6^0_1 hot-band transition in benzene.[8] As shown in Figure 2, after the absorption of one photon with energy $h\nu_1$ benzene molecules are excited to the vibrationless S_1 state. The absorption of a second photon with the same energy $h\nu_1$ leads to the ionization of benzene with an excess energy of only 123.8 meV above the ionization potential. Due to the small excess energy, nearly all ions are produced in their vibrationless electronic ground state. The laser photoelectron spectrum for this wavelength has been measured recently by Reilly et al.[9] Even though the excess energy is somewhat larger than the energy of the ν_1 (a_{1g}, 121 meV) and the ν_6 (e_{2g}, $j = {}^1/_2$, 83.5 meV) vibrations, it has been shown that no more than 10% of all $C_6H_6^+$ ions are produced in these spurious vibrational states.[10]

After production the benzene cations are accelerated within the acceleration field of a reflectron time-of-flight (TOF) mass spectrometer.[11] Some 200 ns later, after they have travelled more than 1 mm out of the molecular beam, a second laser is fired and the $C_6H_6^+$ ions are further excited to a defined higher energy level in a one-photon absorption step. The wavelength λ_2 has been chosen so that after one-photon absorption $C_6H_6^+$ is excited to an internal energy range of about 5.1-5.4 eV. This is more than 1 eV above the thermodynamic threshold for several dissociation channels (see eq 2-5) and leads to a slow metastable decay of $C_6H_6^+$ which can be observed in the reflectron TOF.[12] (If some benzene cations had absorbed more than one photon, they would decay rapidly and not be detected as metastable ions.) Light pulses between 2300 and 2430 Å are produced by mixing the fundamental frequency of a Nd:YAG laser (Quantel YG:481 A) with the frequency-doubled output of a dye laser (Quantel TDL IV), pumped by the same Nd:YAG laser, in a KD*P crystal. The dyes

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(1) See, for example, R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions"; Elsevier Publishing Co.: Amsterdam, 1973.

(2) E. W. Schlag and H. J. Neusser, *Acc. Chem. Res.*, **16**, 355 (1983).

(3) U. Boesl, H. J. Neusser, and E. W. Schlag, *Z. Naturforsch., A*, **33A**, 1546 (1978).

(4) L. Zandee and R. B. Bernstein, *J. Chem. Phys.*, **70**, 2574 (1979).

(5) U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, **72**, 4327 (1980).

(6) D. Proch, D. M. Rider, and R. N. Zare, *Chem. Phys. Lett.*, **81**, 430 (1981).

(7) J. L. Durant, D. M. Rider, S. L. Anderson, F. D. Proch, and R. N. Zare, *J. Chem. Phys.*, **80**, 1817 (1984).

(8) J. H. Callomon, T. M. Dunn, and I. M. Mills, *Philos. Trans. R. Soc. London, Ser. A*, **259**, 99 (1965).

(9) S. R. Long, J. T. Meek, and J. P. Reilly, *J. Chem. Phys.*, **79**, 3206 (1983).

(10) J. P. Reilly, private communication.

(11) U. Boesl, H. J. Neusser, R. Weinkauf, and E. W. Schlag, *J. Phys. Chem.*, **86**, 4857 (1982).

(12) H. Kühlewind, H. J. Neusser, and E. W. Schlag, *Int. J. Mass Spectrom. Ion Phys.*, **51**, 255 (1983).

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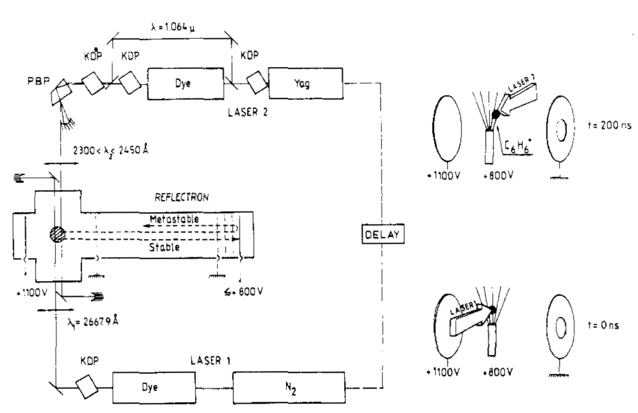

Figure 1. Experimental setup for a two-laser pump–pump experiment in a reflectron time-of-flight mass spectrometer. t = 0 ns: laser 1 produces molecular ions in a two-photon ionization process via a resonant intermediate state. t = 200 ns: excitation of $C_6H_6^+$ ions with laser 2 after spatial separation from the remaining neutral molecules within the molecular beam.

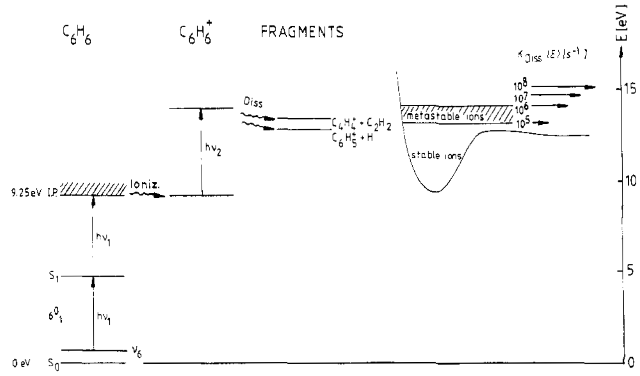

Figure 2. Schematic energy diagram for the excitation process obtained with the two-laser experiment shown in Figure 1. Benzene ions with low internal energy are produced after two-photon ionization via the hot-band transition $6^0{}_1$. These $C_6H_6^+$ ions are then further excited beyond the respective thermodynamic thresholds of the first four dissociation channels and dissociate in a slow metastable decay process.

used are Rhodamine 610 and Rhodamine 640. The UV light of wavelength λ_2 is separated from the various other light beams in a Pellin-Broca prism (PBP).

The spatial separation of ion *production* with laser 1 from the ion *excitation* with laser 2 exterior to the molecular beam assures that no additional parent ions are produced by the second laser. In this case the internal energy would no longer be defined.

Perturbing stable ions are suppressed by decreasing the reflecting voltage by some percent.[11] The metastable peak pattern as observed in the reflectron TOF instrument has been reported in our recent work.[12] All decay rate measurements reported in this work have been performed with partial correction for the kinetic energy shift of the daughter ions produced in a metastable decay. Under these conditions daughter ions produced by a metastable decay within the acceleration region (A) are distinguished from those produced in the drift region (B) and can be integrated separately with a transient digitizer (Tektronix R 7912) and a wave-form processing system (Tektronix WP 2221). The production rate k of the daughter ions is given by the measured ratio R of both integrated ion numbers and the parent ion residence time within the acceleration region (t_x) and the drift region before reflection (t_D), respectively, according to

$$R = (A + B)/A = (1 - \exp\{-k(t_x + t_D)\})/(1 - \exp\{-kt_x\}) \tag{1}$$

In our two-laser experiment the residence time t_x within the acceleration region has to be replaced by $t_x' = t_x - \Delta t$, where Δt is the time delay between ion production and ion excitation, the starting point for the metastable decay.

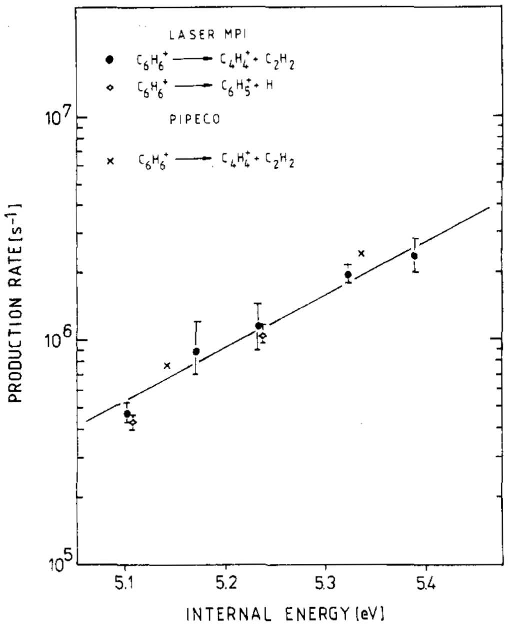

Figure 3. Measured production rate for $C_4H_4^+$ (●) and $C_6H_5^+$ (◇) as a function of the internal energy of $C_6H_6^+$ after two-laser excitation. For comparison, recent PIPECO results for the production rate of $C_4H_4^+$ (×)[16] are given.

Results and Discussion

The following metastable decay channels of the benzene cation can be observed in the range of 5.1–5.4-eV internal energy:

H loss:

$$C_6H_6^+ \rightarrow C_6H_5^+ + H \qquad \text{with } E_0 = 3.69 \text{ eV} \tag{2}$$

$$C_6H_6^+ \rightarrow C_6H_4^+ + H_2 \qquad \text{with } E_0 = 3.69 \text{ eV} \tag{3}$$

C loss:

$$C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2 \qquad \text{with } E_0 = 4.54 \text{ eV} \tag{4}$$

$$C_6H_6^+ \rightarrow C_3H_3^+ + C_3H_3 \qquad \text{with } E_0 = 4.60 \text{ eV} \tag{5}$$

Here E_0 is the thermodynamic threshold for the respective ion dissociation channel according to Rosenstock et al.[13] A fundamental question in the unimolecular decay behavior of the benzene cation is whether H-loss (eq 2 and 3) or C-loss (eq 4 and 5) channels originate from different electronic states and are thus noncompeting. Charge exchange measurements[14] revealed that the rates for $C_6H_5^+$ (eq 2) and $C_4H_4^+$ (eq 4) formation were very different, indicating that both dissociation channels are noncompeting. This result was corroborated by Rosenstock et al.[13] whereas from recent branching ratio measurements[15] of different C_6H_6 isomers it has been concluded that both channels are competing. Unfortunately, direct decay rate measurements for an H-loss channel have not been possible with the PIPECO method due to the small mass change, so that a direct test whether channels (2, 3) and channels (4, 5) are competing or noncompeting is still missing.

Due to the high resolution of the reflectron TOF mass spectrometer in this work, the production rate of a C-loss channel (eq 4) has been measured as well as that of an H-loss channel (eq 2). Our experimental points for the measured production rates are plotted in Figure 3 as a function of the internal energy which directly corresponds to the photon energy $h\nu_2$ of the delayed laser 2 since the ions are preferentially produced in their vibrationless ground state with laser 1. The experimental points have been

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(13) H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973).

(14) B. Andlauer and C. Ottinger, *Z. Naturforsch., A*, **27A**, 293 (1972).

(15) T. Baer, G. D. Willett, D. Smith, and J. S. Phillips, *J. Chem. Phys.*, **70**, 4076 (1979).

obtained after averaging over several independent measurements. The error bars indicate the largest deviation of an individual result from the average value. The solid line represents a straight line found from a least-squares fit procedure for the experimental points (●) of the C-loss channel (eq 4). For comparison the result for the decay rate of the same channel (eq 4) as obtained from recent PIPECO measurements by Eland and Schulte[16] are given in Figure 3 (×). From the good agreement of both results it is clear that the time scale of our reflectron TOF mass spectrometer is well calibrated. In addition, the decay rate of one H-loss channel (eq 2) has been measured with our reflectron TOF mass spectrometer for two internal energies. The experimental points (◇) are found to be in good agreement with the measured rates of the C-loss channel (eq 4). From this result it is clear that both C-loss and H-loss decay channels are competing and originate from the same electronic state. Most likely this is the ground electronic state ($^2E_{1g}$) of the ion, and indeed our recent branching ratio measurements of the four decay channels discussed above[17] and the branching ratios of Baer et al.[15] strongly support this model. Thus, it is concluded that after the absorption of one photon with energy $h\nu_2$ $C_6H_6^+$ is excited to the $^2A_{2u}$ or $^2E_{1u}$[18] electronic state, and then a fast electronic relaxation process (IC) takes place. The metastable decomposition into the four competing decay channels then occurs from the highly vibrationally excited electronic ground state.

In conclusion, in this work we have demonstrated that multiphoton ionization in a two-laser pump–pump experiment represents a new method for the preparation of internal energy selected polyatomic molecular ions. The unimolecular decay constant of the monoenergetic metastable parent ions can then be measured as a function of this well-defined internal energy in a reflectron time-of-flight mass spectrometer. In this way valuable information about unimolecular ion kinetics can be obtained. A further prospect of this method is that due to the resonance-type two-photon excitation process within the neutral molecules, not only the internal energy selection is feasible but also a rotationally selective excitation should be possible. In this way ions in defined rotationally selected states could be prepared in the near future.

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(16) J. H. D. Eland and H. Schulte, *J. Chem. Phys.*, **62**, 3835 (1975).

(17) H. J. Neusser, H. Kühlewind, U. Boesl, and E. W. Schlag, *Ber. Bunsenges. Phys. Chem.*, in press.

(18) J. H. D. Eland, "Photoelectron Spectroscopy", Butterworths, London, 1984, p 116.

Mode-Specific Intramolecular Vibrational Energy Redistribution: Direct Picosecond Measurements

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In this Letter, we report on the direct picosecond measurement of mode-dependent, dissipative IVR rates in jet-cooled *trans*-stilbene. It is found that excitation of different bands in the $S_1 + 1250\text{-cm}^{-1}$ energy region of the molecule gives rise to different IVR rates, as determined by the temporal evolution of vibrationally unrelaxed fluorescence. The results are discussed in terms of the spectroscopic assignments for the excitation bands.

The characterization of intramolecular vibrational energy redistribution (IVR) in the high-energy regime is presently one of the most challenging problems in intramolecular dynamics.[1] An issue of particular importance concerns the dependence of IVR dynamics on the *character* of the initially excited vibrational motion. One would like to know whether certain types of levels couple more efficiently than other types to the intramolecular bath of vibrational states. Such dependences, if they were to exist in the high-energy regime, would show that dissipative IVR need not be solely governed by excess vibrational energy and would help to pinpoint the molecular parameters influencing the IVR process.

Recently, (time-integrated) dispersed fluorescence measurements have indicated the presence of spectroscopic features that are consistent with mode-dependent vibrational coupling in *p*-difluorobenzene.[2] However, the time scales for the selective IVR of different modes have not been reported yet, since this requires direct picosecond temporal resolution of the IVR.

In this Letter, we report on the direct measurement of mode-dependent, dissipative IVR rates in jet-cooled *trans*-stilbene. It is found that excitation of different bands in the $S_1 + 1250\text{-cm}^{-1}$ energy region of the molecule gives rise to different IVR rates, as determined by the temporal evolution of vibrationally unrelaxed fluorescence. The results are discussed in terms of the spectroscopic assignments for the excitation bands.

The experimental system has been described in detail elsewhere.[3] *trans*-Stilbene (Eastman scintillation grade, or Aldrich > 96%) at 125 °C was expanded with 30 to 40 psig of He through a 100-μm pinhole into an evacuated chamber. The frequency-doubled output ($\Delta\tilde{\nu} \simeq 2\ \text{cm}^{-1}$) of a synchronously pumped, cavity dumped dye laser (Rhodamine 6G as dye) excited the jet at x = 3 to 8 mm from the pinhole. Fluorescence was detected at right

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[‡] Contribution No. 7113.

(1) For a review see: C. S. Parmenter, *Faraday Discuss., Chem. Soc.*, **75**, 7 (1983).

(2) M. Fujii, T. Ebata, N. Mikami, M. Ito, S. H. Kable, W. D. Lawrance, T. B. Parsons, and A. E. W. Knight, *J. Phys. Chem.*, **88**, 2937 (1984).

(3) W. R. Lambert, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.*, **81**, 2217 (1984).

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