



The dissociation dynamics of state selected metastable aniline ions by single and multiphoton ionization

Tomas Baer and Thomas E. Carney

Citation: The Journal of Chemical Physics **76**, 1304 (1982); doi: 10.1063/1.443148 View online: http://dx.doi.org/10.1063/1.443148 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/76/3?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

State selective production of phosphorus ions via multiphoton ionization of atomic phosphorus J. Chem. Phys. **101**, 2659 (1994); 10.1063/1.467645

Multiphoton ionization photoelectron spectroscopy study of OCS: Rydberg vibronic structure and ion state selection J. Chem. Phys. **89**, 5527 (1988); 10.1063/1.455559

Dynamics of cluster dissociation following multiphoton ionization AIP Conf. Proc. **146**, 483 (1986); 10.1063/1.35919

Multiphoton metastable ion spectra and ion dissociation kinetics: Analysis of the decay channels of the aniline cation with a reflectron timeofflight instrument J. Chem. Phys. **82**, 5452 (1985); 10.1063/1.448579

Multiphoton ionization of ammonia clusters and the dissociation dynamics of protonated cluster ions J. Chem. Phys. **82**, 4076 (1985); 10.1063/1.448849



The dissociation dynamics of state selected metastable aniline ions by single and multiphoton ionization

Tomas Baer and Thomas E. Carney^{a)}

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514 (Received 1 October 1981; accepted 21 October 1981)

The lifetimes with respect to dissociation of state selected aniline ions have been investigated by photoion-photoelectron coincidence. Lifetimes between 0.3 and 100 μ s have been found when the aniline ion is prepared in energies ranging from 13.6 to 12.6 eV, respectively. These lifetimes are in good agreement with those of a recent study by Proch, Rider, and Zare, who observed metastable aniline ions in a UV multiphoton ionization (MPI) study in which three photons were required to reach the metastable ion energy range. By contrast, our visible MPI study of aniline shows no evidence for long-lived ions. This paradox is resolved by postulating that under the UV MPI conditions, a radiationless transition to the ground electronic state allows the 13 eV ions time to dissociate slowly, while under the much higher photon intensities needed in the visible MPI study, rapid up pumping of the excited ions prevents radiationless transitions. A lower limit for the radiationless transition rate of 2×10^8 s⁻¹ is derived.

I. INTRODUCTION

Long lived, or metastable, ions have been investigated by mass spectrometrists for many years. These polyatomic ions are ones which have lifetimes in the μ s time domain. They are long lived because of the time required for the vibrational energy to flow among the various normal modes before sufficient energy is deposited in one mode (the reaction coordinate) to dissociate the ion. The dynamics of this process, sometimes called vibrational predissociation, have been treated by the statistical unimolecular decay theories (RRKM^{1,2} and QET³) in terms of the phase space available to the molecular ion and the transition state. The microcanonical rate k(E) is expressed as

$$k(E) = \frac{\sigma \int_0^{E-E_0} \rho^*(E) dE}{h\rho(E)} , \qquad (1)$$

in which ρ and ρ^* are the densities of vibrational states of the molecular ion and transition state, respectively, E_0 is the activation energy, and σ is the number of equivalent dissociation paths. Conservation of angular momentum is neglected in Eq. (1). Often this neglect does not cause serious problems in unimolecular decay because the total angular momentum is small. However, in cases where the moments of inertia of the molecular ion and transition state are very different, the value of the effective E_0 will be significantly affected.

The decay rates as a function of ion internal energy of a number of ions such as $C_8H_{8,4}^{*4}$ $C_6H_{6,5}^{*5}$ $C_4H_{6,6}^{*6}$ $C_6H_5X^{*}$ (X = halogen), ⁷⁻⁹ $C_5H_5N^{*}$, ¹⁰ $C_4H_4X^{*}$, (X = O, S, NH)¹¹ have been measured by the technique of photoionphotoelectron coincidence (PIPECO) and the results interpreted in terms of the statistical theory. In this paper we present similar results on the dissociation of state selected aniline^{*} to form $C_5H_6^{*}$ + HCN.

During the past two years, numerous molecules have been investigated by resonantly enhanced multiphoton ionization (REMPI). Among them are C_6H_6 , ¹²⁻¹⁴

 C_6H_5X , ¹⁵ C_4H_4S , ¹⁶ and $C_6H_5NH_2$, ^{17–21} Although parent ions of these molecules at appropriate internal energy ranges have been shown to decay via long lived, metastable, precursor ions when ionized by a single vacuum UV photon^{5,7,11} or by electron impact, no metastable ions have been observed when the ions are formed by REMPI.

Recently, Proch, Rider, and Zare²² have reported the first observation of a metastable ion in REMPI. The unfocused (266-300 nm) output of a tunable frequency doubled dye laser, pumped by a Nd: YAG laser, was used to ionize aniline. Numerous fragment ions were observed in the time-of-flight (TOF) mass spectrum. All had narrow and symmetric shapes except for m/e 66, which was asymmetrically broadened toward the long TOF, a peak distortion characteristic of fragment ions originating from long lived parent ions in the acceleration region of the TOF spectrometer. The m/e 66 peak was identified as $C_5H_6^*$ by comparison with deuterium labeled spectra. The lifetimes ($\approx 1 \ \mu s$) were shown to vary with laser wavelength. However, the internal energy of the aniline ion was not known precisely because in the ionization step at the two-photon level, the electron carries off an unknown amount of kinetic energy. Nevertheless, the observation of such metastables is of great importance for our understanding of the fragmentation mechanism in REMPI. It is clear evidence that the aniline ion is produced at a certain energy and that it remains in that energy state during the 5 ns long intense laser pulse without further photon absorption.

In this paper, we present REMPI data on aniline using visible light from a dye laser pumped by a pulsed N_2 laser. We will compare the production of metastable aniline ions of the same total energy but prepared by one, three, and five photons with approximate wave-lengths of 92, 275, and 460 nm, respectively. Although the spectroscopic aspects of aniline REMPI have been reported^{17,18} and the REMPI mass spectra have been in-vestigated, ¹⁹⁻²² none of the investigators searched for a metastable ion using visible laser wavelengths.

0021-9606/82/031304-05\$02.10

^{a)}Present address: E. I. duPont de Nemours & Co., Inc. Experimental Station, Wilmington, Delaware 19898.

II. EXPERIMENTAL

A. Photoion-photoelectron coincidence (PIPECO)

The PIPECO technique has been discussed previously¹¹ in detail and will be only reviewed here. Ions are formed by vacuum UV radiation produced by a H_2 low pressure discharge, and dispersed by a 1 m normal incidence monochrometer. In the electric field of about 12 V/cm, electrons and ions are accelerated in opposite directions. The time difference between the electron and ion signals is converted to a voltage pulse by a time to pulse height converter. These pulses are collected in a multichannel pulse height analyzer.

Initially, zero energy electrons are detected by passing the electrons through a stainless steel collimated hole structure. Energetic electrons, which in general have velocity components perpendicular to the hole axes, do not pass through the hole structure. State selection of the ions is achieved by detecting only those ions which are in coincidence with the zero energy electrons.

All the dynamical information is contained in the ion TOF distribution. In particular, the TOF distributions of product ions, originating from metastable parent ions, are asymmetrically broadened as a result of dissociation events which occur while the parent ions are accelerating.

B. Multiphoton ionization

A description of the experimental setup has been previously published.²³ Briefly, light from a pulsed nitro-



FIG. 1. Coincidence time of flight (TOF) distributions of $C_5H_6^*$ ions produced from parent ions with the indicated energies in eV. The solid lines are calculated TOF distributions in which the indicated decay rates are assumed.



FIG. 2. The dissociation rate as a function of the $C_6H_5NH_2^*$ internal energy. The solid lines are RRKM/QET statistical theory calculations assuming tight and loose transition states.

gen laser pumped dye laser is focused to a small area on the order of 10^{-5} cm². The ionization takes place in an electric field of 100 V/cm. The ion TOF spectrum is obtained by using the laser pulse as a start input and the ion signal as a stop input to a time to pulse height converter. The data are then collected in a multichannel pulse height analyzer.

III. RESULTS

The $C_5H_6^*$ TOF distributions at various vacuum UV photon energies are shown in Fig. 1. The points are the experimental data, while the solid lines are the calculated ion TOF distribution in which the one adjustable parameter is the mean parent ion lifetime. It was varied until the fits shown in Fig. 1 were obtained. The resulting k(E) values as a function of the energy are shown in Fig. 2.

The ion TOF distribution of the fragment ion from aniline obtained in REMPI at 462 nm is shown in Fig. 3. This spectrum is typical of all the ones obtained at a number of laser wavelengths from 587 to 364 nm. Of particular significance is the shape of the m/e 66 peak which is symmetric, indicating that it is produced from a short lived parent ion. We estimate a parent ion lifetime of less than 0.1 μ s, since this is the TOF of the parent ion in the acceleration region of the mass spectrometer.

IV. DISCUSSION

A. RRKM/QET calculations

In order to learn more about the dissociation mechanism of aniline ions with energies between 12.5 and 14



FIG. 3. The REMPI mass spectrum at a photon wavelength of 460 nm at a laser energy fluence of greater than 1000 MW/cm^2 .

eV, we calculated the parent ion lifetimes with the statistical theory. In order to calculate this rate, we must evaluate the density of vibrational states in Eq. (1). This is done by specifying the vibrational frequencies of the molecular ion and the transition state. The Hase-Bunker program²⁴ was used to evaluate the state densities and the resulting decay rates.

Because the statistical theory is based only on vibrational predissociation, it is also necessary to specify the electronic state of the aniline ion from which dissociation occurs. The dissociation reactions of all carefully studied metastable ions⁴⁻¹¹ have been shown to proceed from the ground electronic state. This means that radiationless transitions from the electronically excited

state to the ground electronic state and the associated conversion of electronic into vibrational energy are faster than direct dissociation from the excited state. The photoelectron spectrum (PES) of aniline (Fig. 4), which is sketched from the PES of Debies and Rabalais.²⁵ indicates that the initially excited states of aniline* in the metastable energy range are those with vertical ionization energies at 12.5 and 14 eV. We assume that these states are strongly coupled to the ground electronic states and that dissociation proceeds from the latter. In the case of the aniline dissociation, the activation energy, E_0 is an unknown parameter because the dissociation rate at the dissociation limit is so slow as to be unmeasurable except perhaps by the ion trapping technique. We therefore treated E_0 as an adjustable parameter. We assumed that the molecular ion maintains its aniline structure and used the aniline vibrational frequencies.²⁶ For one of the transition states, we used the aniline molecule vibrational frequencies. This corresponds to a moderately tight transition state. A set of frequencies characteristic of a linear structure with a number of low lying vibrational modes was used as a loose transition state.

The fits of the rates derived with the tight and loose transition states to the experimental points are shown in Fig. 2. The assumed E_0 's are 2.9 and 3.5 eV, respectively. The fit to the data is better for the loose transition state so that the 3.5 eV value would appear to be more realistic. However, there are other considerations.

The dissociation limits to various $C_5H_6^*$ product²⁷ ions are shown in Fig. 4. If we consider only the five isomers in the figure, it is clear that the $C_5H_6^*$ product ion cannot be any of the open chain isomers because the calculated activation energy is too low. This is contrary



FIG. 4. The potential energy curve for the dissociation of aniline. The photoelectron spectrum (PES) is taken from Ref. 25. The transition state energy range (hashed region) was determined from the RRKM/QET calculation fit to the measured decay rates. Multiphoton energy levels are for 275 and 460 nm.

J. Chem. Phys., Vol. 76, No. 3, 1 February 1982

to what had been assumed in previous electron impact and MPI studies.^{22, 28} The reason for the discrepancy is very simple. In any electron impact or PI scan of $C_5H_6^*$ from aniline, an onset at around 12.5 eV will be obtained. The onset is at 12.5 eV not because the dissociation limit is at that energy, but because the rate of dissociation reaches a sufficiently high value so that the aniline ions will fragment before they are detected. As we see here, this shift of the observed onset from the dissociation limit, commonly called the kinetic shift, is about 1.5 eV.

There is a slight inconsistency in the results of Figs. 2 and 3. This is that a loose transition state is usually associated with a reaction having no reverse activation energy. Yet the loose transition state, which gives an excellent fit to the data of Fig. 2, implies a transition state energy of 11.2 eV, considerably above the dissociation limit to the cyclopentadienyl ion (10.43 eV). These results therefore suggest the existence of yet another $C_5H_6^*$ ion, with a $\Delta H_f^0 = 1010$ kJ/mol. We carried out a number of *ab initio* calculations using the Gaussian 76 program at the STO-3G level to minimize the energy of various $C_5H_6^+$ structures. However, the three and four membered ring structures were found to be about 2 eV less stable (4-31G basis set) than the five membered ring structure. We conclude that there are probably no other $C_5H_6^*$ structures in between the cyclopentadienyl ion and the open chain structures of Fig. 4, and that the ion formed in the aniline dissociation has the cyclopentadienyl structure.

B. Multiphoton ionization/dissociation

1. UV MPI

The REMPI mass spectrum of Proch et al.²² at 266 nm shows that a metastable aniline ion with a lifetime of about $0.5 \ \mu s$ is formed. Figure 4 indicates that two photons are necessary to form the ion. An additional photon absorbed by the ion would reach the metastable states and result in the slow dissociation of $C_{g}H_{5}NH_{2}^{+}$. However, the observation of numerous other higher energy fragments shows that some of the aniline ions absorb more photons to reach higher energy states, which produce fragments such as $C_2H_3^+$, $C_2H_4^+$, $C_3H_2^+$, and $C_3H_3^+$. These ions are produced by fast dissociation steps. Because the laser pulse is only 5 ns long, it is clear that two kinds of excited aniline ions are formed between 13 and 14 eV. One class of ions remains at that energy to dissociate sometime after the laser pulse is over, while the other class of ions absorbs more photons to dissociate to higher energy fragments. Furthermore, there is competition between these two classes of ions. That is, the higher the laser flux, the greater is the yield of high energy fragments relative to the $C_5H_6^+$ ions formed via the metastable parent ions.

Using the rate constant of $2 \ \mu \mbox{s}^{-1}$ at 266 nm calculated by Proch *et al.*, we see by comparison with our PIPECO data that the third 266 nm photon must prepare parent ions at 13.6 eV total energy. Subtracting the energy of one photon then shows that the parent ions are initially formed at 8.9 eV (1.2 eV above the I. P.) after ionization by the second photon. Although there is probably a distribution of ionic states formed, this calculation shows that the parent ions are produced with considerably vibrational energy in the ionization step.

These results can be interpreted best by a mechanism [Eqs. (2)-(6)]:

$$C_6H_5NH_2 + 2h\nu - C_6H_5NH_2^+ + e^-$$
, (2)

$$C_6H_5NH_2^+ + h\nu - C_6H_5NH_2^{+*}(\tilde{E})$$
, (3)

$$(-C_6H_5NH_2^{++}(X)),$$
 (5)

$$C_6H_5NH_2^{**}(\tilde{X}) \xrightarrow{slow} C_5H_6^{+} + HCN , \qquad (6)$$

in which the excited state, termed \tilde{E} here, is depleted competitively by either further absorption of photons or a radiationless transition to the ground state (\tilde{X}) . Once in the ground state with over 5 eV of vibrational energy, we assume that photon absorption is improbable because of small Franck-Condon factors.

This mechanism raises the possibility of determining the rates of radiationless transitions or the cross section of further photon absorption if either one of these rates is known. However, even in the absence of additional data we can calculate an approximate lower bound of the radiationless transition rate. The stated power of 20 MW/cm^2 at 266 nm corresponds to a photon flux of 2.66×10²⁵ photons/s cm². From the REMPI mass spectrum of Proch et al., 22 we estimate that 50% of the product ions absorb photons beyond the three-photon level at 13.5 eV during the 5 ns long laser pulse. From the relation N/No = exp[$-\sigma It$], where σ , I, and t represent the absorption cross section, the laser flux, and the laser pulse width, we calculate a $\sigma = 5 \times 10^{-18} \text{ cm}^2$. This is a lower limit because if we take into account the competition from radiationless transitions to the \tilde{X} state the calculated σ will increase. The minimum rate of the radiationless transition is 2×10^8 s⁻¹. Both of these rates are reasonable insofar as these are known. A radiationless transition rate has been measured for the case of the $\tilde{A}^2 E$ state of 2, 4-hexadiyne⁺ from the branching ratio between fluorescence and dissociation, and found to be 4×10^7 s⁻¹.²⁹ Because of the more closely spaced energy levels of aniline and its less rigid structure, we would expect radiationless transition rates to be higher in aniline than in 2, 4-hexadiyne, as is indeed confirmed by this approximate calculation.

2. Visible REMPI

The visible laser REMPI mass spectrum (Fig. 3) shows a fragmentation pattern similar to the UV REMPI mass spectrum, except that there is no evidence for a metastable $C_6H_5NH_2^+$ ion. An analysis of the competition between further photon absorption and radiationless transition by the parent ion shows immediately why no metastable ions are expected under these conditions. Because a two-photon transition is required to excite the aniline molecule to the resonant state, rather than a one-photon transition for the case of UV REMPI, a considerably higher photon flux is needed in order to ionize aniline. In fact, the laser was tightly focused to

about a 100 μ m spot which gives a power in excess of 1000 MW/cm². This means that the photon density is greater than 3×10^{27} photons/s cm², or over 100 times greater than under the UV REMPI conditions. As a result, the photon absorption rate far exceeds the radiationless transition rate. Hence, no metastable ions are produced. From this analysis, we conclude that the chance of observing a metastable ion in two- or three-photon resonant MPI spectra is extremely small.

There is one aspect to the REMPI mass spectrum of Fig. 3 which is extremely intriguing. It is that the largest peak in the spectrum is that of the parent ion. Now, if the laser intensity is so great as to create very high energy ions such as C⁺, how is it possible for some parent ions to absorb no photons? It is particularly puzzling in that the REMPI mass spectra of benzene at similar wavelengths and laser intensities have no parent ions. Aniline and benzene are very similar in that both require two photons above the ionization limit in order to fragment. One explanation is that not all aniline molecules ionize after the absorption of three photons, but that an additional photon is absorbed to some autoionizing state. The aniline ion resulting from the autoionization may be highly vibrationally excited (2-3 eV)and have small Franck-Condon factors for further photon absorption. Photoelectron spectra may shed some light on this problem.

V. CONCLUSION

Aniline ions with selected internal energies between 12.5 and 14 eV have been prepared by photoion-photoelectron coincidence. The lifetimes with respect to the dissociation to $C_5H_6^*$ + HCN have been measured by analyzing the asymmetric flight time distribution. The measured lifetimes (0.2 to 100 μ s) are in good qualitative agreement with those determined by Proch, Rider, and Zare who prepared the ions by multiphoton ionization using a UV pulsed laser (≈ 266 nm). Our own MPI study using a much more intense visible pulsed laser source (≈ 460 nm) shows that no long lived (metastable) ions are produced. These findings are interpreted with a model in which electronically excited ions at $\approx 13.5 \text{ eV}$ can undergo either a radiationless transition to the ground electronic state or absorb more photons during the 5 ns laser pulse. According to this model, once the ions are in the ground electronic state with over 5 eV of vibrational energy they absorb no further photons because of poor Franck-Condon factors, but instead dissociate with a slow rate to $C_5H_6^+$ and HCN. We estimate from this model that the lower limit of the radiationless transition rate is 2×10^8 s⁻¹, and the lower limit of the cross section for further photon absorption from the excited electronic state is 5×10^{-18} cm². In the higher power visible REMPI study, the larger laser flux favors photon absorption over the radiationless transition so that no long lived aniline ions of 13.5 eV are formed. It is, however, intriguing that the major peak in the visible MPI peak is the parent ion. Why it is not photodissociated in the intense laser field is not clear.

ACKNOWLEDGMENTS

We are grateful to Professor John Holmes for providing us with the heats of formation of the linear $C_5H_6^+$ isomers. This work was supported by grant CHE77-28321 from the National Science Foundation and by the facilities of the University of North Carolina Laser Laboratory supported by the National Science Foundation Instrumentation grant CHE77-14547.

- ¹(a) O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927); (b) L. S. Kassel, J. Phys. Chem. **32**, 225 (1928).
- ²R. A. Marcus and O. K. Rice, J. Phys. Colloid Chem. 55, 894 (1951).
- ³H. M. Rosenstock, M. B. Wallenstein, A. L. Warhaftig, and H. Eyring, Proc. Natl. Acad. Sci. U.S.A. **38**, 667 (1952).
- ⁴D. Smith, T. Baer, G. D. Willett, and R. C. Ormerod, Int. J. Mass Spectrom. Ion Phys. **30**, 155 (1979).
- ⁵T. Baer, G. D. Willett, D. Smith, and J. S. Phillips, J. Chem. Phys. **70**, 4076 (1979).
- ⁶A. S. Werner and T. Baer, J. Chem. Phys. **62**, 2900 (1975).
- ⁷T. Baer, B. P. Tsai, D. Smith, and P. T. Murray, J. Chem. Phys. **64**, 2460 (1976).
- ⁸H. M. Rosenstock, R. Stockbauer, and A. C. Parr, J. Chem. Phys. **71**, 3708 (1979).
- ⁹S. A. Pratt and W. A. Chupka, Chem. Phys. (in press).
- ¹⁰J. H. D. Eland, J. Berkowitz, H. Schulte, and R. Frey, Int. J. Mass Spectrom. Ion Phys. 28, 297 (1978).
- ¹¹(a) J. J. Butler and T. Baer, J. Am. Chem. Soc. 102, 6764 (1980); (b) G. D. Willett and T. Baer, *ibid.* 102, 6769, 6774 (1980).
- ¹²U. Boesl, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. **72**, 4327 (1980).
- ¹³L. Zandee and R. B. Bernstein, J. Chem. Phys. 71, 1359 (1979).
- ¹⁴T. Carney and T. Baer, J. Chem. Phys. **75**, 477 (1981).
- ¹⁵T. G. Dietz, M. A. Duncan, M. G. Liverman, and R. E. Smalley, J. Chem. Phys. **73**, 4816 (1980).
- ¹⁶T. Carney and T. Baer (unpublished data).
- ¹⁷L. Goodman and R. P. Rava, J. Chem. Phys. **74**, 4826 (1981).
- ¹⁸T. G. Dietz, M. A. Duncan, M. G. Liverman, and R. E. Smalley, Chem. Phys. Lett. **70**, 246 (1980).
- ¹⁹J. H. Brophy and C. T. Rettner, Chem. Phys. Lett. 67, 351 (1979).
- ²⁰C. T. Rettner and J. H. Brophy, Chem. Phys. 56, 53 (1981).
 ²¹U. Boesl, H. J. Neusser, and E. W. Schlag, Chem. Phys.
- 55, 193 (1981). ²²R. Proch, D. M. Rider, and R. N. Zare, Chem. Phys. Lett. 81, 430 (1981).
- ²³T. E. Carney and T. Baer, J. Chem. Phys. 75, 4422 (1981).
- ²⁴Available as program 234 through the Quantum Chemistry Exchange, Indiana University.
- ²⁵T. P. Debies and J. W. Rabalais, J. Electron Spectrosc. 1, 355 (1972).
- ²⁶These frequencies were constructed by combining those from benzene and methylamine taken from T. Shimanouchi, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. **39** (1972).
- ${}^{27}\Delta H_f^0$ (cyclopentadiene⁺) = 960 kJ/mol [H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data **6**, 1 (1977)]. The heats of formation of the open chain C₅H₆⁺ ions were obtained from Professor J. Holmes, University of Ottawa.
- ²⁸J. L. Occolowitz and G. L. White, Aust. J. Chem. **21**, 997 (1968).
- ²⁹M. Allan, J. P. Maier, O. Marthaler, and E. Kloster-Jensen, Chem. Phys. **29**, 331 (1978).