Rotational Dependence of the Unimolecular Decay Rate: Benzene Cation Dissociation

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We present the first example of unimolecular decay rates of a polyatomic system in which reactants are rotational state selected. Highly excited, but internal energy selected and J rotational quantum number selected benzene cations are produced in a two laser pump-pump experiment. Slow reactive decay of these ions is observed in a reflectron time-of-flight mass spectrometer and the total decay rate constant $k(E, J)$ is measured as a function of J. At constant internal energy E, $k(E, J)$ decreases with increasing J.

I. Introduction

The study of molecular ion dissociation is an important source of information for the elucidation of elementary chemical processes. Unimolecular fragmentation processes of molecular ions have been studied by electron impact [1], charge exchange [2], one photon absorption [3] and more recently multiphoton ionization [4–7]. One of the requirements for the precise elucidation of elementary kinetic processes is the selection of internal energy of molecular ions prior to dissociation [8]. The methods leading to the hitherto best energy selection in ions are the PIPECO technique [3, 9] and resonance-enhanced MPI [6, 10, 11] with an improved energy resolution.

Using the latter method, experiments were performed on the metastable dissociation of the benzene cation $C_6H_6^+$ [10, 11]; the total decay rate constants of this ion were determined as a function of well defined internal energy of the precursor ions. It has been shown that the benzene cation behaves with respect to dissociation like a large molecular system and that dissociation rates are well modelled by statistical theories [11, 12]. In these experiments the *vibrational* energy of the state selected benzene cations after two-photon ionization was sharply defined. However, the *rotational* energy distribution remained approximately thermal.

Detailed theoretical investigations have been performed on the influence of rotation on the decay rate according to the SAC model [13, 14] and a newly modified RRKM model [15], but no experimental information on the rotational dependence of unimolecular decay rates of large statistical systems has been available so far.

In this work we describe a two laser pump-pump experiment on the prototype molecule benzene, which leads to the production of internal energy selected and, for the first time, rotationally selected benzene cations. The unimolecular dissociation rate of these ions is measured in a reflectron time-of-flight mass spectrometer and the influence of the quantum number J of the total rotational angular momentum on the decay rate constant is investigated.

II. Experimental Set Up

The two laser pump-pump experiment for the measurement of unimolecular decay rate constants in a reflectron time-of-flight mass spectrometer (RETOF) was described in our previous work [10]. The corresponding excitation scheme is shown in Figure 1. The frequency-doubled output of laser 1 is focused onto the center of a molecular beam of benzene molecules. For selection of low J levels a cooled skimmed supersonic beam of benzene molecules seeded in He is used. For selection of high J levels the supersonic beam is replaced by an effusive thermal beam of pure benzene. The wavelength of the ionizing laser is tuned to the region of the 6_1^0 hot band transition ($\lambda_1 = 266.8$ nm) of C_6H_6 [16].

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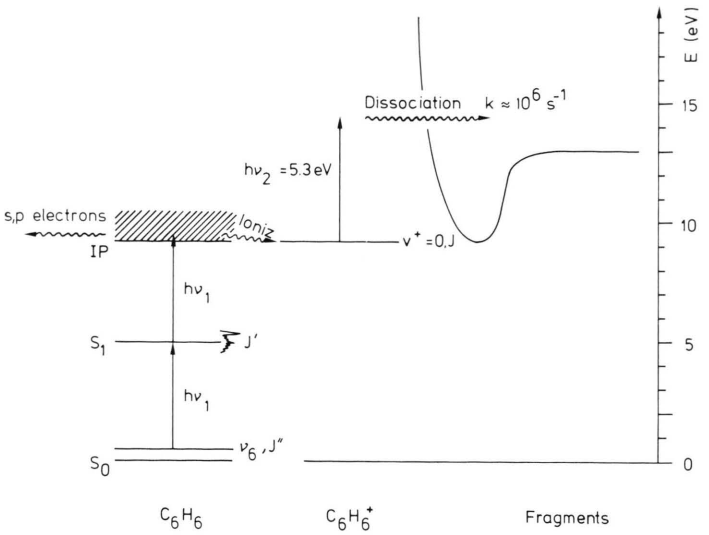

Fig. 1. Schematic energy diagram of the two laser pump-pump experiment for production of vibrational and rotational state selected benzene ions $C_6H_6^+$ in a resonance-enhanced two-photon ionization process via the 6_1^0 transition. J selection is achieved by tuning laser 1 to defined but varying positions in the rotational contour of the 6_1^0 band. 200 ns later a second laser with fixed energy $h\nu_2$ excites the so produced ions to an energy level above the dissociation threshold where metastable decay takes place.

Some 200 ns after the first laser pulse one-photon absorption from a second laser pulse excites the benzene cations from their vibrationless electronic ground state to an electronically excited state ($\tilde{C}(^2A_{2u})$, $\tilde{D}(^2E_{1u})$). In the present experiment laser 2 is kept at fixed wavelength $\lambda_2 = 233.92$ nm so that the energy gain of the ions is exactly 5.3 eV. This energy is then about 1 eV above the threshold of four low lying dissociation channels and leads to a metastable decay of the ions on a µs time scale [5, 17].

The resulting metastable peak shape, as observed in the RETOF, was reported in previous work [17]. The reflecting field acts as an energy analyzer, hence daughter ions produced by metastable decay in the acceleration region and daughter ions produced in the field-free drift region can be distinguished. The total decay rate constant of the benzene cations was measured by an analysis of kinetic energy as described in our previous work [11].

III. Experimental Results and Discussion

In previous work it has been shown by a photoelectron energy analysis [18, 19], that state selection in benzene cations is achieved if resonant two-photon ionization is performed via the 6_1^0 "hot band" transition of benzene. More than 90% of all ions are produced in the vibrationless electronic ground state ($v^+ = 0$, $\tilde{X}(^2E_{1g})$). In previous experiments [10–12] the ionizing laser frequency was tuned to the maximum of the 6_1^0 hot band transition. The J distribution in the benzene cation resembled the distribution at room temperature. In the present work, laser 1 is operated with an intracavity etalon. This results in a laser frequency width of 0.04 cm^{-1}. J selection is achieved by tuning the laser frequency to defined positions in the rotational contour of the 6_1^0 intermediate state spectrum of neutral benzene [20]. In the supersonic beam experiment low J levels ($2 \leqq J \leqq 20$) and in the effusive beam experiment bunches of high J-levels ($20 \leqq J \leqq 58$) are selected in the $S_1(J') \leftarrow S_0(\nu_6, J'')$ transition. In addition to the narrow J distribution there is superimposed a distribution of K quantum numbers (i.e. the projection of the total rotational angular momentum onto the figure axis). Hönl-London factors are largest for K approaching J so that the strongest contributions to the selected transitions originate from $|K| \lessapprox J$ levels. As shown in [20] a certain J value once chosen in the $S_1 \leftarrow S_0$ 6_1^0 transition is almost preserved up to the highly excited ionic state.

Decay rate constants have been measured for various selected J levels. This leads to different rotational energies E_{rot} of the ion, depending on the J value excited. Therefore also the total energy ($E = 5.3\ \mathrm{eV} + E_{\mathrm{rot}}$) in the ion is slightly changing with J. For an oblate symmetric top the rotational energy E_{rot} is given by [16]

$$E_{\mathrm{rot}} = B\,J(J+1) + (C-B)\,K^2\,. \tag{1}$$

We estimate the rotational energy of the ion for $K = J$ using the rotational constants of the S_1 state [16].

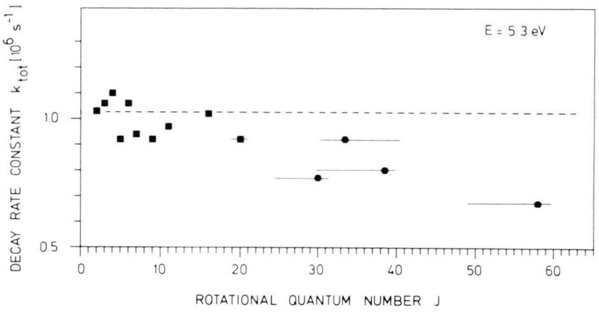

Fig. 2. Measured rotational dependence of the total dissociation rate constant of $C_6H_6^+$. Experimental results are normalized to a constant total energy $E = 5.3$ eV. J selection is achieved by resonance-enhanced two-photon ionization in a cooled supersonic jet (■) and in a room temperature effusive molecular beam (●). For explanation of the horizontal error bars see text. The dashed horizontal line indicates a J independent decay rate constant.

In order to compare the experimental results with theory, the measured decay rate constants have to be normalized to constant total energy E. This is done using the energy dependence of the total decay rate constant of our previous work [11]. The normalized values for k_{tot} are shown in Figure 2. They represent the measured J dependence of the decay rate constant for constant total energy ($E = 5.3$ eV) which will be directly compared with theoretical results according to a modified RRKM model [15] in our forthcoming work [20]. We observe a decrease in the decay rate constant of more than 30% when J is increased from 2 to 58. The horizontal bars in Fig. 2 represent the width of the J distribution achieved for high J levels [20].

IV. Summary and Conclusion

In this work we present the first J selected measurements of the unimolecular decay rate of a large statistical system. In these experiments not only the internal energy of the reactant but also its total rotational angular momentum (J quantum number) is defined. Vibrational state selection in the benzene cations was achieved by two-photon ionization via the 6^0_1 hot band transition. Rotational ($2 \leq J \leq 58$) J selection was performed by tuning the laser to different positions in the rotational contour of this vibronic band under the different rotational temperature conditions of an effusive and a supersonic beam. Further excitation of vibrational state- and J selected benzene cations drives them beyond the threshold for dissociation and leads to their slow decay which is detected by analysis of their kinetic energy in a reflectron mass spectrometer.

We found that there is a measurable rotational effect in the total decay rate even though the experiments have been performed for a relatively large internal energy of 5.3 eV. For an energy of more than 1 eV above threshold the total decay rate decreases by about 30% as J is increased from 0 to 50. A strongly increasing rotational dependence of the decay rate is expected when approaching the dissociation threshold.

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