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Rotationally Resolved Intramolecular Processes in Benzene

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Chemical Kinetics / Elementary Reactions / Gases / Multi-photon Processes / Spectroscopy, Ultraviolet

The influence of the molecular rotation on intramolecular processes is investigated for both a non-reactive and a reactive large polyatomic system. The non-reactive system chosen is the S_1 state of benzene, C_6H_6. Doppler-free spectra of the 14_0^1 band show isolated rotational perturbations due to a highly selective coupling of the "light" zero-order states to "dark" rovibrational states within the S_1 state. These perturbations are caused by J, K dependent Coriolis coupling, which will induce energy randomization in the excited molecule. The reactive process investigated is the unimolecular dissociation of rotationally selected excited benzene cations. It is found that energy is completely randomized and the benzene cations behave like a statistical system. Dissociation rates are found to decrease with rotational quantum number, J. It is concluded that rotational selection has to be included in precise experiments and theoretical models of intramolecular processes.

I. Introduction

The elucidation of the basic mechanism of intramolecular processes is only possible if the starting conditions for the intramolecular process under investigation are well defined. This condition can be fulfilled, if selected quantum states of the molecule are excited and the changes in the molecular system caused by the intramolecular process can be identified. In the past a great number of investigations has been performed in order to find out how intramolecular processes depend on vibrational quantum numbers and vibrational energy [1]. However, relatively little is still known about the influence of the molecular rotation, even though rotational states with high J quantum numbers are populated in samples of large molecules at room temperature.

In this work we report on the highly selective excitation of a large polyatomic system with a sufficient number of degrees of freedom to display a statistical behaviour. The selective excitation into specific rotational states allows us to investigate the influence of molecular rotation on different intramolecular processes.

In the first part of this work we would like to report on the intramolecular processes in a non-reactive system. Here the basic mechanisms are studied which can lead to an energy randomization within the excited molecule. In large systems with many degrees of freedom energy randomization is the primary process of a unimolecular reaction which can be described by statistical theories.

In the second part of this work the influence of rotation on unimolecular dissociation of a reactive system is investigated. Both investigations are performed for a single molecular species, benzene. Neutral benzene, when excited to the S_1 state at 40000 cm^{-1} does not dissociate and displays selective intramolecular couplings. On the other hand, the benzene cations, when excited to an only slightly higher energy dissociate on a μs time scale. Thus benzene is an ideal system for the investigation of different kinds of intramolecular processes in one large polyatomic system.

II. Intramolecular Couplings in S_1 Benzene

Intramolecular vibrational redistribution (IVR) in polyatomic molecules is caused by a coupling of the excited "light" zero order state to one, several or many "dark" background zero order states depending on the density of states. The density of states depends strongly on the vibrational excess energy. Particularly, in the low excess energy range it is very low and the intramolecular coupling is expected to be highly selective and may differ from state to state. For this reason the high resolution investigation of the low excess energy range can yield precise information on the nature and the strength of the coupling process if individual states are observed. For the observation of individual states Doppler-free techniques have to be used in the investigation of large molecules.

1. Experimental Techniques

The typical experimental set up for a Doppler-free two-photon experiment consists of a tunable laser light source with a frequency width narrower than the Doppler-width (typically a frequency sta-

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bilized single mode cw dye laser) and a gas cell that contains the low pressure molecular gas under investigation. Elimination of the Doppler-broadening is achieved by the absorption of two photons propagating in opposite directions [2]. Very high sensitivity can be accomplished by placing the gas cell within the standing light field of an external resonator. The scheme of a Doppler-free two-photon experiment with external cavity as used in our laboratory is shown in Fig. 1 [3]. Two-photon absorption is monitored by detection of UV-fluorescence from the excited level. At room temperature the

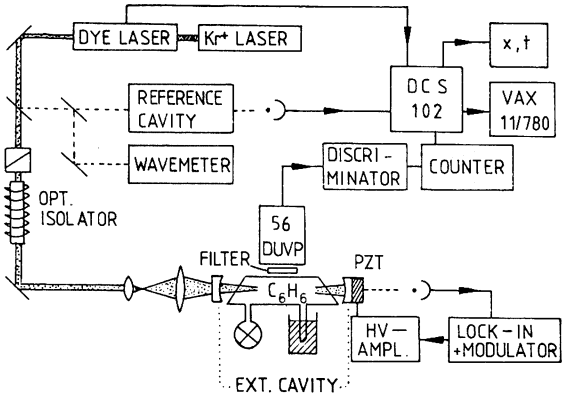

Fig. 1
Experimental set up used for the recording of Doppler-free two-photon spectra of benzene

Doppler-free spectrum of a polyatomic molecule consists of many thousands of rotational lines which arise from the large number of thermally populated ground state levels. The resulting tremendous number of data points is rapidly transfered to and stored in a lab computer with sufficient memory. A very precise and stable frequency calibration is provided by an evacuated and temperature-stabilized interferometer with a free spectral range of roughly 150 MHz which is known to 1 part in 10^5. With this experimental set up homogeneous lineshapes as narrow as 10 MHz can easily be measured [3].

To study the time decay behaviour of individual states, pulsed excitation with high spectral resolution and defined coherence width is necessary. Light with these properties is produced in our laboratory by pulsed amplification of the cw laser rather than by a pulsed oscillator with several frequency selecting elements. Typically, the amplifier system contains three stages pumped by an excimer laser [4]. The light pulses resulting from the amplification process possess Fourier transform-limited bandwidth and therefore their coherence width is equal to the width of the frequency distribution and inversely proportional to the pulse length. Typically, pulses with a peak power of 300 KW and a frequency width of 80 MHz are obtained with our set up [4].

2. Spectroscopic Results

Part of the 14_0^1 band of C_6H_6 is shown in Fig. 2 at a resolution of 10 MHz [5]. The upper state of this electronic transition it at 1570 cm^{-1} vibrational excess energy. More than 600 rotational lines of the Q-branch are observed in the 8 cm^{-1} wide spectral range. Every line represents a transition to a single, defined rotational

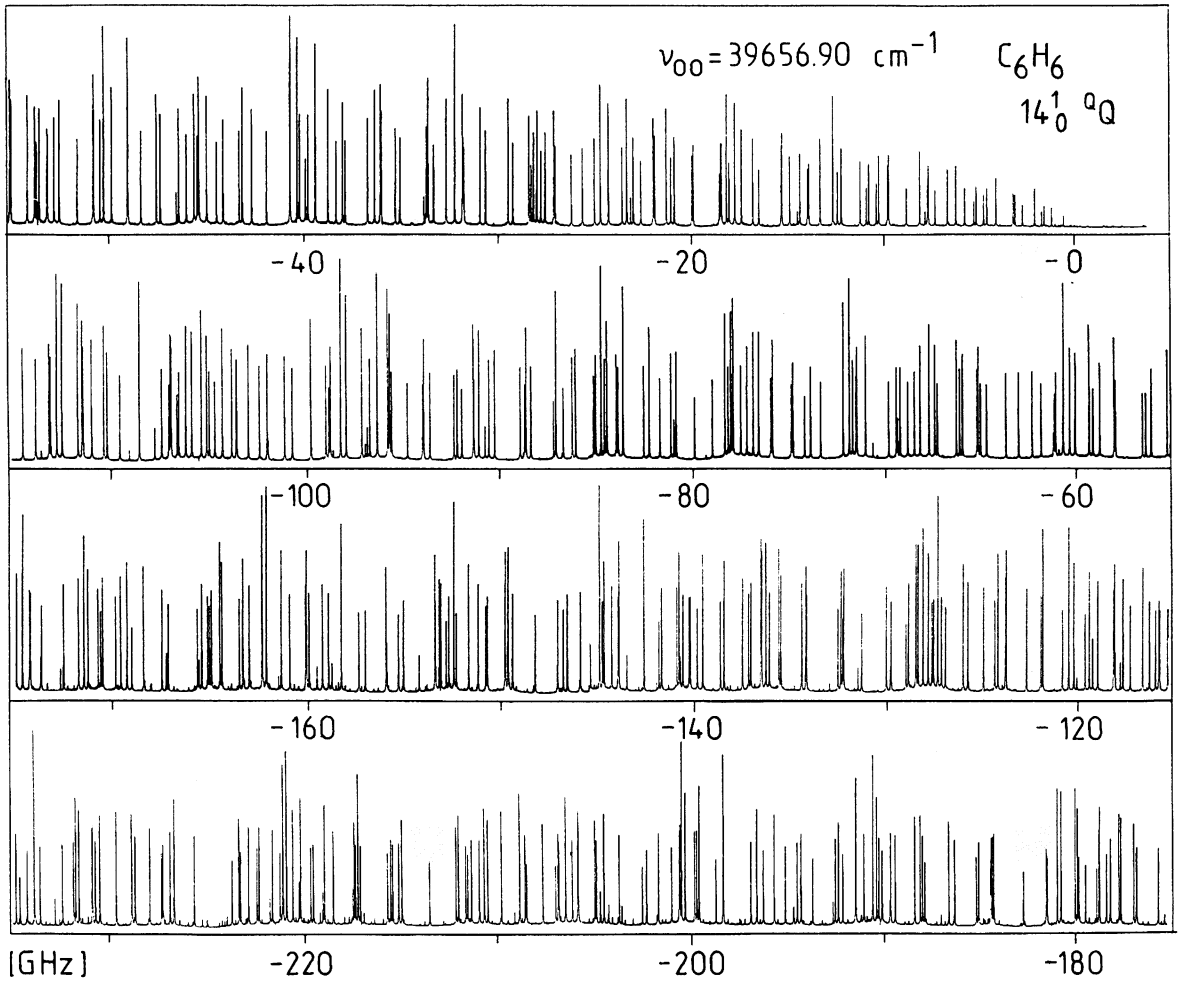

Fig. 2
Part of the Doppler-free room temperature spectrum of the Q-branch of the 14_0^1 band of C_6H_6. Every line corresponds to an individual rovibronic transition. All of these lines have been assigned

Born-Oppenheimer state possessing its own individual dynamic behaviour. Even though the spectrum looks very complex it can be analyzed on the basis of a simple symmetric rotor approximation. After a computer-aided assignment of the lines, a fit to thousands of line positions yields values for the rotational and centrifugal constants with a precision two orders of magnitude greater than that obtainable from conventional Doppler-limited UV spectroscopy [6]. The accuracy of these constants even exceeds those of the ground electronic state determined from high resolution infrared measurements.

More than 90% of all rotational lines of the 14_0^1 band can be explained using the simple symmetric rotor Hamiltonian including centrifugal distortion. The remaining lines deviate from their expected positions. Obviously they are perturbed. This is illustrated in Fig. 3 where parts of the experimental spectrum (upper trace) are compared with the calculated one (lower trace) [7]. Instead of the predicted peaks $J'_{K'} = 21_{17}$ and $J'_{K'} = 22_{17}$ two peaks appear in each case, shifted by about 0.5 GHz from the calculated position. The two peaks are due to the coupling between pairs of zero order states. One member of each pair is the optically accessible light state. The other is a dark rovibronic state within the same electronic potential (S_1), which is in accidential resonance with the light zero order state [7]. The identity of the "dark" background state will be subject of further investigations described below. The observation that infrequent coupling occurs only between pairs of levels is reasonable in view of the low density of S_1 vibrational states (1.2 states/cm^{-1}) at the relatively low excess energy (1570 cm^{-1}) of the 14^1 state.

Perturbations like those shown in Fig. 3 are observed in several parts of the band. The analysis of the residuals of the perturbed lines yields the avoided crossing curves shown in Fig. 4 [5]. The ultra high resolution of Doppler-free two-photon excitation and the good signal to noise ratio achieved with the external cavity makes possible the identification of very low intensity perturbed lines. As a result the observation of both eigenstates resulting from the mixing of the zero order states is possible near the crossing point (Fig. 3) [6, 7]. From the exact position of the eigenstates the coupling matrix element of each pair can be determined. The dependence on the J, K quantum numbers tells us about the nature of the coupling process. It is found that perpendicular Coriolis coupling is responsible for the perturbations analyzed in the 14_0^1 band. The according coupling matrix element

$$V = V_0\sqrt{(J+K)(J-K+1)} \tag{1}$$

depends strongly on the rotational quantum numbers J, K and it is seen that the rotation strongly enhances the intramolecular coupling. The J and K independent coupling matrix element V_0 was found to be in the order of 30 MHz which is typical for a higher order coupling process. Already at this early stage of the investigations it is noticed that rotations seem to induce the intramolecular coupling and hence play a by no means secondary role in energy redistribution processes.

After having analyzed the nature of the coupling process, the symmetry selection rules and the symmetry of coupled background states can be evaluated. For perpendicular Coriolis coupling it holds

$$\Gamma_{\nu_{14}} \otimes \Gamma_{\nu_x} \otimes \Gamma_{R_{x,y}} = a_{1g}. \tag{2}$$

Here $\Gamma_{\nu_{14}}$ (b_{2u}) is the symmetry of the light 14^1 state, $\Gamma_{R_{x,y}}$ is the symmetry of a rotation perpendicular to the figure (z) axis of benzene, and Γ_{ν_x} is the symmetry of the coupled background state. Evaluation of relation (2) yields $\Gamma_{\nu_x} = e_{2u}$.

In Tab. 1 all combination states with a component of e_{2u} symmetry and vibrational energy near the light 14^1 state are listed. Their position was calculated in the harmonic approximation. Even within the limited accuracy of this calculation we can be sure that there are only two states close enough to the 14^1 state to be coupled by matrix elements in the order of 1 GHz. These are the $6^2 11^1$ and the $5^1 10^1 16^1$ states with a calculated energy mismatch of -7 cm^{-1} and -11 cm^{-1}. Due to the $\Delta K = \pm 1$ selection rule of perpendicular Coriolis coupling and slightly different rotational constants

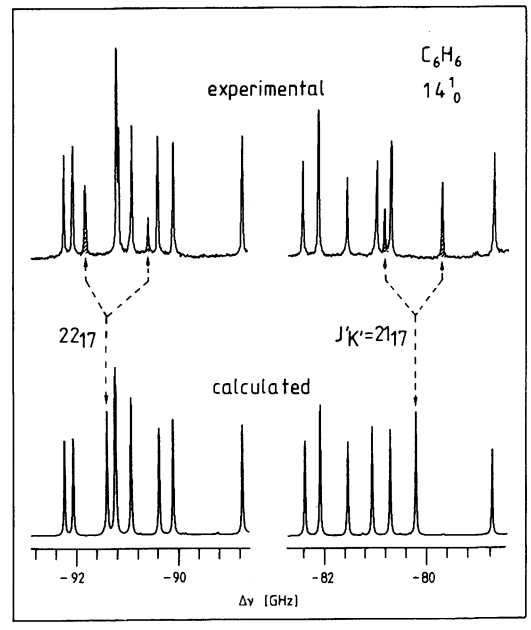

Fig. 3
Two small parts of the Q-branch of the 14_0^1 band of C_6H_6 under Doppler-free resolution. Upper traces: measured spectra; lower traces: calculated spectra. Instead of the predicted peaks $J'_{K'} = 21_{17}$ and $J'_{K'} = 22_{17}$ two peaks appear shifted from the calculated position in each case. (Taken from Ref. [7])

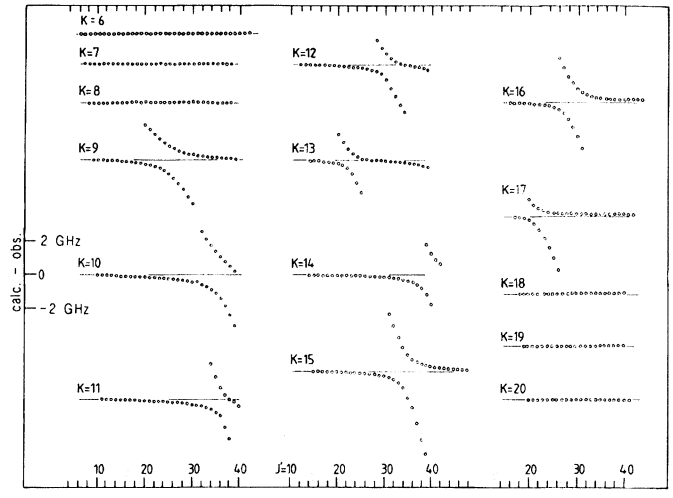

Fig. 4
Avoided crossings found from the analysis of the highly resolved 14_0^1 band of C_6H_6 shown in Fig. 2. The avoided crossings are caused by the Coriolis interaction of the (light) rotational states (labeled by the quantum numbers J and K) in the 14^1 vibronic state with dark background states in the S_1 potential energy surface

of the two vibrational states only a small number of rotational states will be in close energy match and thus give rise to the isolated perturbations observed. It is interesting to note that both vibrational states contain out-of-plane modes (ν_{11} and ν_{16}). Out-of-plane modes are known to be good accepting modes for the electronic nonradiative relaxation processes Internal Conversion (IC) and Intersystems Crossing (ISC) [8]. This point will turn out to become important when the dynamic behaviour of the perturbed states is studied.

A direct test of the identity of the background states which are responsible for the coupling process would be to study the dispersed emission from the mixed states [9]. The admixture of the dark states should produce additional bands in the emission spectrum which

Table 1
e_{2u} vibrational states of S_1 C_6H_6 near the 14^1 state. The energies of the states were calculated in harmonic approximation

energy [cm^{-1}]	deviation from 14^1 ($1570\ cm^{-1}$)	state
1500	−70	$10^1 18^1$
1512	−58	$6^1 11^1 16^2$
1517	−53	$10^1 12^1$
1559	−11	$6^2 11^1$
1563	−7	$5^1 10^1 16^1$
1636	66	$1^1 16^3$
1641	71	$1^1 17^1$

are fingerprints of the coupled state. The high resolution spectroscopy of this work has shown that the intramolecular coupling depends strongly on the rotational state. Therefore dispersed emission from *single rotational* states has to be observed. This requires, that the dye laser frequency remains in resonance with the molecular transition frequency for about 1 h, typically to a precision of 1 MHz/h. These problems have recently been solved in our laboratory. First emission spectra of single rovibronic states are presented in a separate publication [10]. They show that both the $6^2 11^1$ and the $5^1 10^1 6^1$ state are mixed into the 14^1 state at different positions of the 14^1_0 band.

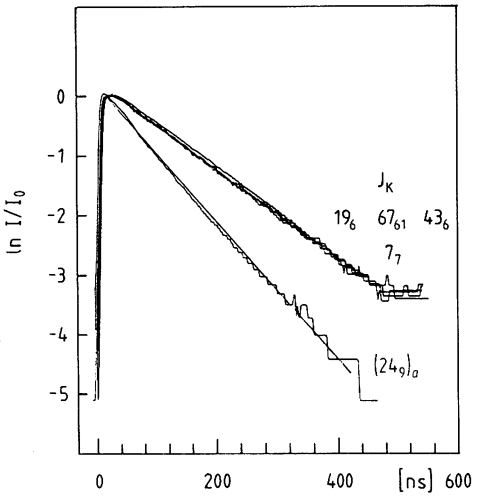

Fig. 5
Decay behaviour of different individual rotational states in the 14^1 vibronic state of C_6H_6 measured by fluorescence detection. All unperturbed states display an exponential decay with the same decay time. Perturbed states such as $J_K = (24_9)_a$ show a considerably faster decay due to the shorter decay time of the coupled, dark zero-order state

3. Dynamic Behaviour of Individual Quantum States

So far we have discussed the coupling to other rovibrational levels within the same electronic potential (intrastate coupling). This is highly selective, but it does not lead to any irreversible dynamic IVR process in the low excess energy region discussed. The coherent excitation of both quasi-eigenstates resulting from the coupling process (see Fig. 3) would lead to an oscillatory behaviour of the zero order state population and quantum beats would be observed. However, the information obtainable from such a time-resolved measurement with large coherence width has already been obtained from the spectroscopic analysis of the line splitting and no additional information is expected from this coherent excitation. Instead we are interested in the decay of the individual quasi-eigenstates resulting from the coupling to the dark background state. If a dark state and a light state are mixed the decay behaviour of the resulting quasi-eigenstates should differ from that of the light state, because the dynamic behaviour of the background state is expected to be different from that of the light state. This is due to the different vibrational nature of the dark and the light states. With the pulsed set up individual rotational levels in the 14^1 vibronic state can be populated and their decay behaviour observed under collisionless conditions [4, 11]. This is demonstrated in Fig. 5, where the decay behaviour of several individual rotational states ($J_K = 19_6$, 67_{61}, 43_6, 7_7) within the 14^1 state is shown [5]. For all states that were found unperturbed in the spectroscopic analysis a single exponential decay is found and the decay time of $\tau = 135$ ns is independent of the rotational quantum numbers J and K. This is in good agreement with the assumption that the decay of the levels is determined by the radiative decay and more strongly by the coupling to the T_1 triplet state in the statistical limit [4].

On the contrary, for states found to be perturbed a significantly shorter decay time is found [4]. For example, the $J_K = (24_9)_a$ state resulting from the coupling of the $J_K = 24_9$ rotational state of the 14^1 vibronic state to the dark rovibronic state has a decay time of only 87 ns. The decay is again single exponential. It can be concluded that the dark zero order state decays much faster and due to the mixed vibronic nature of the observed quasi-eigenstate its shorter decay time results. The corresponding coupling scheme is shown in Fig. 6 [4]. A light zero order state with narrow bandwidth is coupled to a broader dark state. The linewidth of the zero order states is due to an electronic nonradiative process (ISC, IC) in the statistical limit. At the crossing point of the term curves the resulting linewidth of the quasi-eigenstates is just the average of the zero order state linewidths. It is seen that there exist vibrational states in S_1 at the vibrational excess energy of the light state that possess much faster decay rates. These states can not be directly

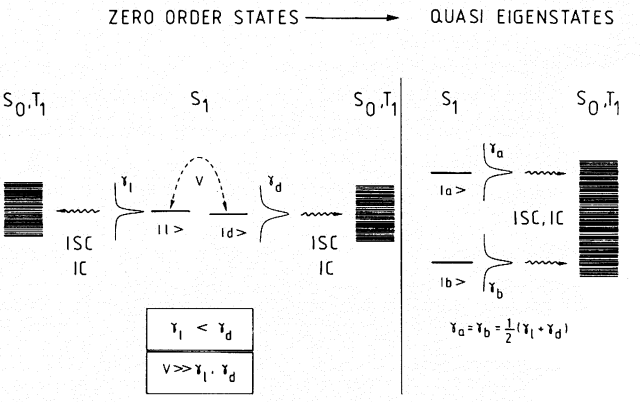

Fig. 6
Coupling scheme of the light zero-order state $|l\rangle$ with the dark zero-order state $|d\rangle$. Both zero-order states have different linewidths due to a faster electronic nonradiative relaxation process of the dark zero-order state ($\gamma_d > \gamma_l$). The linewidths γ_a and γ_b of the resulting quasi-eigenstates are shown on the right side for degenerate zero-order states, i.e. at the crossing point. (Taken from Ref. [4])

excited and their observation is only possible through the analysis of perturbations. A reasonable explanation for the broader linewidth (or shorter decay time) of the dark background state is given by the vibrational character of these states. The spectroscopic analysis described above has shown that the coupled dark states contain quanta of out-of-plane modes. These are known to strongly enhance the electronic nonradiative relaxation process and decrease the decay time [8].

4. Summary

In this section we have shown that intramolecular coupling in a large polyatomic molecule can be highly selective if the excess energy is not too high. Using Doppler-free high resolution techniques we were able to investigate not only the coupling process but also the dynamic behaviour of selected states. In this way the nature of the coupling and the size of the coupling matrix elements were found. It was shown that the intrastate coupling depends strongly on the rotation of the molecule. Two effects were found to be responsible for the rotational selectivity:

i) Accidental resonance of the excited light state with dark background states are only present for some of the rotational states and missing for others. This produces a strong variation of the coupling from one rotational level to the other which cannot be described in a simple way.
ii) It has been found for benzene that all perturbations observed in the rotational structure of the bands at low excess energy are due to Coriolis forces. These are strongly dependent on the rotation and therefore the coupling matrix element itself depends strongly on the rotational quantum number.

The first effect is a general property of every molecule as long as the intramolecular process under consideration is not in the statistical limit, i.e. the density of background states is not too high. This situation is always given for small molecules but we have shown that it is also present in large molecules if the excess energy in the electronic state under consideration is sufficiently low.

The second effect is typical for a Coriolis coupling process and would not be expected e.g. for anharmonic coupling. Even though only a couple of bands have been analyzed in detail, Doppler-free spectra have shown that most of the couplings involving matrix elements below 1 GHz are due to Coriolis interaction rather than to anharmonicity. Additional information from low resolution techniques has also suggested Coriolis coupling in many other molecules [12]. Coriolis coupling is of particular importance in energy randomization as it can lead not only to a change of vibrational quantum numbers but also of K rotational quantum numbers. Randomization of K quantum numbers (K-mixing) is often assumed in unimolecular reaction according to a statistical model [13].

III. Rotationally Resolved Unimolecular Decay Rates

1. Statistical Decay of $C_6H_6^+$

In the preceding section rotational effects were studied for intramolecular couplings in a non-reactive system. Now we would like to investigate whether rotation also has an influence on the unimolecular dissociation rate of a large statistical system. For a statistical system energy randomization over all vibrational degrees of freedom prior to dissociation is generally assumed. This randomization is believed to be caused by a large number of intramolecular couplings, probably in the statistical limit, which lead to a complete mixing of all vibrational levels for each J quantum number. It is the purpose of this section to clarify whether there is still a rotational dependence of the reactive decay rate under these conditions.

The molecular system chosen for this investigation is the benzene cation. Charged molecules like the benzene cation are very suitable for the study of unimolecular reactions due to a number of experimental advantages. Ionized systems can be detected with high sensitivity in a mass spectrometer. Also charged products of a dissociation reaction are nearly automatically monitored in the mass spectrum. The only major difficulty in this type of experiment is to produce molecular ions with a defined internal energy and in a selected rotational state, the prerequisite for a precise investigation of an intramolecular process, i.e. the dissociation of $C_6H_6^+$. Conventional ion sources do not easily allow this selection.

Recently, however, we were able to show that vibrational state selected benzene cations can be produced by resonance-enhanced two-photon ionization via selected intermediate states [14–16]. The state selection was proved by energy analysis of the photoelectrons [17, 18]. These state-selected ions are further excited with a second laser of variable photon energy (5.0–5.5 eV) to a defined internal energy slightly above the threshold of the four dissociation channels of lowest energy [19]:

$$C_6H_6^+ \rightarrow C_6H_5^+ + H \quad (3)$$

$$C_6H_6^+ \rightarrow C_6H_4^+ + H_2 \quad (4)$$

$$C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2 \quad (5)$$

$$C_6H_6^+ \rightarrow C_3H_3^+ + C_3H_3 \quad (6)$$

The decay rate constant of the excited ions was measured with a special technique based on a kinetic energy analysis in the reflecting field of a reflectron time-of-flight mass spectrometer [15, 20]. A slow metastable decay of the ions on a μs time scale was observed. It was found that H-loss channels (Eqs. (3), (4)) as well as C-loss channels (Eqs. (5), (6)) show the same dissocation rate constant and thus are competing and originate from the vibrationally highly excited electronic ground state of the cation.

The total decay rate constant was measured as a function of variable but sharply defined energy. As all four channels are competing the total decay rate is given by the sum of the individual decay rates of all channels. The individual decay rate constants were derived from the total decay rate constant and the individual branching ratios. The results are shown in Fig. 7. A smooth increase of the decay rate constants as a function of internal energy is seen. This is typical for a statistical decay. The solid lines in Fig. 7 represent the results of RRKM fits to the experimental data.

The frequencies and threshold energies have been chosen so that they are in line with isotopic results [21]. For this reason we believe to have established a reliable set of parameters. In particular, it turned out that all vibrations have to be taken into account and thus participate in the energy redistribution process. In addition to the vibrational energy selection discussed so far, also experiments with rotational selection were performed at 5.3 eV internal energy (dashed line in Fig. 7). This is explained in the following section.

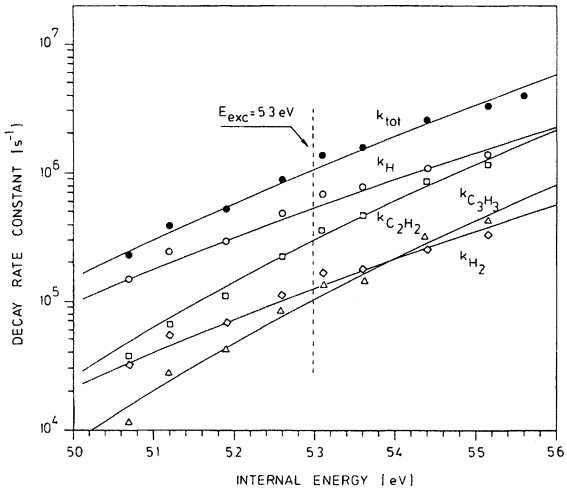

Fig. 7
Decay rate as a function of the internal energy. Details see text

2. Rotational Selection

For two-photon ionization via the 6_1^0 hot band photoelectron energy analysis has shown, that the benzene cations are produced almost exclusively in their vibrational ground state [17,18]. Additional rotational selection is achieved by tuning the first laser to different parts in the rotational contour of the band [22]. For selection of low J levels up to $J = 20$ a cooled supersonic beam is used. Higher J levels are excited in an effusive molecular beam.

In Fig. 8 a Fortrat analysis (top) of the R-branch of the 6_1^0 hot band transition is shown for a rotational temperature of 25 K. The middle trace represents the corresponding calculated spectrum, whereas at the bottom the experimental spectrum is shown. It is clearly seen that in the R-branch various transitions with constant J'' and different K'' are superimposed at certain transition frequencies and give rise to the series of peaks in the spectrum. These peaks represent transitions with constant J''. When the laser frequency is tuned to one of the peaks, J levels are selectively excited in the S_1 intermediate state of neutral benzene. This J selection is largely conserved in the following two absorption steps. In the photoionization there is a low probability for electron waves with large angular momentum (p,d-waves) and associated large change of J. The one-photon excitation of the ions changes their J quantum number by at most ± 1. As a result slowly dissociating benzene cations are produced in a small range of J levels. The variation of their dissociation rate as a function of J can be observed by variation of the frequency of the first laser. The steps of excitation discussed above are summarized in Fig. 9.

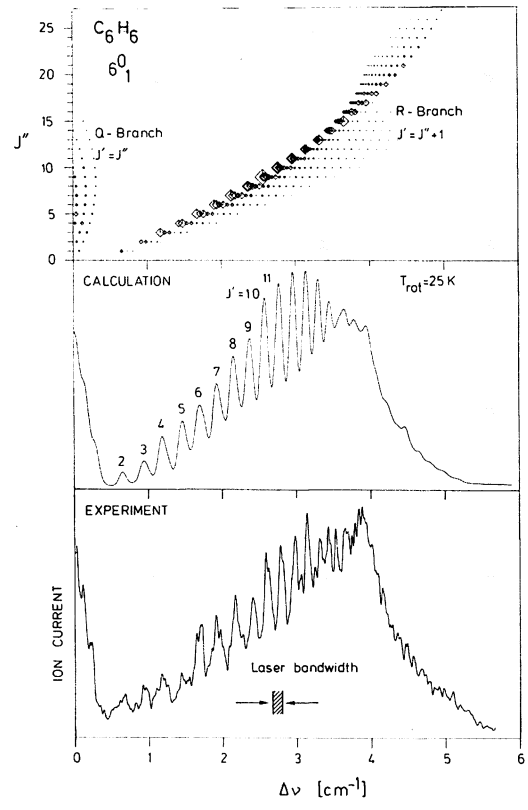

Fig. 8
Fortrat analysis (top), calculated spectrum (middle) and measured spectrum (bottom) of the R-branch of the 6_1^0-hot band transition in benzene, C_6H_6. The size of the squares in the Fortrat analysis reflects the intensity of an individual rovibronic transition. The superposition of rotational transitions with common J forms a peak in the spectrum. The rotational temperature is 25 K. (Taken from Ref. [22])

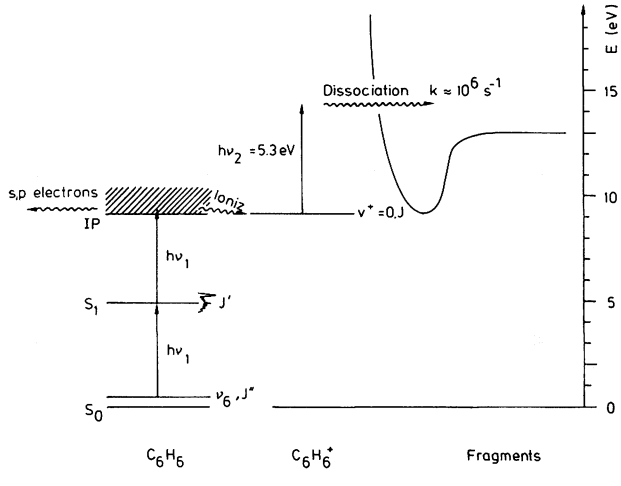

Fig. 9
Schematic energy diagram of the two-laser pump-pump experiment for production of vibrational and rotational state selected benzene ions $C_6H_6^+$ in a resonance enhanced two-photon ionization process via the 6_1^0-transition. J selection is achieved by tuning laser 1 to defined but varying positions 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 dissociation threshold, where metastable decay takes place

3. Decay Rates

Total decay rates have been measured for various selected J levels and a constant photon energy (5.3 eV) of the second laser. For increasing J quantum numbers (and rotational energy) of the benzene cation the total energy increases since the frequency of the second laser is kept constant. To compensate for this effect the measured decay rate constants were normalized to a constant total energy. This can be readily performed using the energy-dependence of the total decay rate shown in Fig. 7. In Fig. 10 the normalized decay rate constants are plotted as a function of J. We observe a decrease of the decay rate constant by more than 30% when J is increased from 2 to 58. The horizontal lines in Fig. 10 represent the width of the J distribution. For $J > 20$ (effusive beam) a complete J selection is no longer possible and bunches of J are excited.

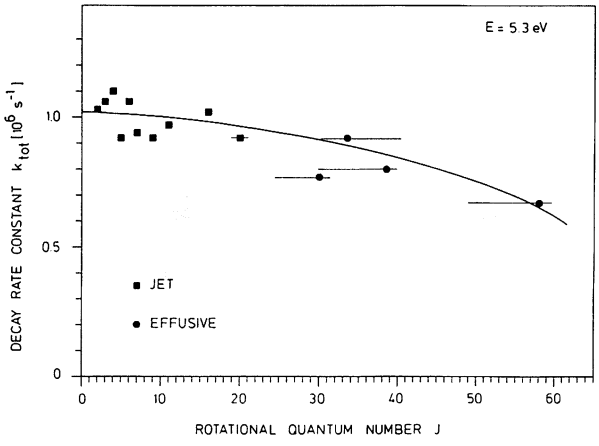

Fig. 10
Measured rotational dependence of the total decay rate constant. Experimental results are normalized to a constant total energy $E = 5.3$ eV. J selection is achieved by resonance enhanced two-photon ionization in a cooled supersonic jet (■) and in a room temperature effusive molecular beam (●). The solid line is a numerical result from a modified RRKM model

The solid line in Fig. 10 represents the theoretical J dependence of the total decay rate obtained from a RRKM model modified to include the J dependence of the decay rate [22]. In these calculations tight activated complexes and a complete randomization of K quantum numbers have been assumed. Theory shows that the main contributions to the rotational effect in the total decay rate originate from the H-loss (Eq. (3)) and the C_2H_2 loss (Eq. (5)) channels. This is due to a moderate rotational effect but a large branching ratio of the H-loss channel and to a strong rotational effect in the C_2H_2 dissociation with a relatively small branching ratio [15, 22]. In view of the assumptions made in the model calculations surprisingly good agreement of the theoretical and experimental results is found.

4. Summary

The technique of resonance-enhanced two-photon ionization enabled us to produce J selected benzene cations with an energy content of 5.3 eV. This internal energy is 1.1 to 1.6 eV above the thresholds of four dissociation channels and sufficient to induce a slow reactive decay of the ions. Measurement of the J dependence of the decay rate allowed us for the first time to investigate the influence of the molecular rotation on the unimolecular dissociation of a large statistical system. It was found that there exists a measurable rotational effect in the total decay rate even for the relatively high internal energies of our experiment. The decay rate is found to decrease by about 30% when J is increased from 2 to 58. This rotational effect can be described by a modified RRKM model assuming tight activated complexes and K-mixing. Theory predicts an even stronger rotational dependence closer to the dissociation threshold [22, 23].

IV. Concluding Remarks

The investigation of rotationally resolved intramolecular processes in neutral benzene and benzene ions yields basic information on the underlying general mechanisms. Rotation was found to induce the energy randomization by J, K dependent Coriolis coupling. Moreover, even, if energy is completely randomized in a statistical system independent of the rotational quantum numbers excited, rotations are by no means negligible in the unimolecular dissociation kinetics. Dissociation rates are found to decrease with rotational quantum number J even for moderate excess energy above threshold. Hence it is evident that rotational selection has to be included in forthcoming experiments and theoretical models.

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