Photoionization of benzene complexes

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Photoionization of Benzene Complexes

K. O. Börnsen, H. L. Selzle, and E. W. Schlag*

*Institute for Physical and Theoretical Chemistry, Technical University of Munich,
8046 Garching, West Germany (Received: February 24, 1988; In Final Form: April 26, 1988)*

The ionization potentials of isotopically mixed benzene dimers (d_0-d_0, d_0-d_6) and benzene–cyclohexane have been measured by using a two-color ionization technique in a molecular beam. The benzene dimer photoionization threshold spectra with mass selection cover a region of 800 cm^{-1}. The precision of the measurements here is ±30 cm^{-1} or 4 meV. It is shown that a linear extrapolation of the ion current gives different ionization potentials depending on the vibronic intermediate state. This clearly indicates that a linear technique gives the wrong ionization potential due to Franck–Condon shifts. A method for compensating for these shifts is applied to obtain the correct ionization potential.

Introduction

The intermolecular interactions of van der Waals clusters are of fundamental importance for a basic understanding of aggregated molecular systems. The benzene complexes are the simplest prototypes in which the energetic and structural interactions between aromatics and other molecules can be studied. van der Waals complexes of aromatic molecules have been the subject of a great number of studies.[1] Benzene complexes are formed at very low temperatures when they are expanded in a seeded supersonic beam. The exact composition of such complexes must be determined to disentangle the absorption spectra and to determine the effect of complexation onto the energy levels of the molecules.[2]

The weak van der Waals interactions in molecular clusters lead to a small shift of the resonant transitions. But in the ionization potentials of the complexes substantial changes appear. In the benzene dimer a red shift of about 3000 cm^{-1} is observed on ionization. Grover et al.[3] measured the ionization potential of the benzene dimer at 8.690 ± 0.023 eV with synchrotron radiation. They used an argon–benzene mixture in a supersonic jet experiment, which also makes it likely that clusters are formed together with the argon atoms. From other studies[4] of benzene clusters it is known that a large amount of higher clusters are formed in the jet as well. The ionization threshold for large clusters is strongly red-shifted at higher masses. Therefore, one cannot exclude photodissocation of these higher clusters, particularly since the excess energy rises with cluster size, which then will lead to the detection of smaller complexes. Thus even though the mass is correctly measured, the value of the ionization potential (IP) relates to a larger cluster. Using helium as the pressure gas reduces the amount of clusters with the noble-gas atoms. In this case one sees the higher benzene clusters, but no benzene–helium clusters. By cooling the benzene probe, one can avoid the higher clusters. The great advantage of these measurements is that we can prepare only the desired species via the resonant intermediate state. This state can be spectroscopically selected and allows for separation of the different clusters. In this way one can attain the correct ionization potential. Rühl et al.[3] have measured the ionization potentials of the benzene dimer also with synchrotron radiation (the wavelength resolution in this case was 3 Å or 150 cm^{-1}). The IP of the benzene dimer was found to be 8.84 eV. This very large change poses a question as to the reasons for such shifts.

Moreover, one observes in aromatic van der Waals complexes a very slow rise of the photoionization current in the spectra. For such a slow rise there exists a real problem as to what point on this curve represents the correct ionization potential. We show here that no point on these curves is correct. In contrast, the rise of the ionization current in the spectra of the benzene–argon clusters[5] is steep and exactly defined, providing field-delay excitation is employed.[6] In this report we measured for the first time the ionization potentials of different benzene clusters by a two-photon process using a pulsed field delay with a precision of ±30 cm^{-1}, but still corrections are demonstrated to be necessary.

Experimental Section

The supersonic jet used in this experiments has been described previously.[7] A skimmed arrangement was used. The benzene was cooled to −5 °C to reduce the seed ratio in the helium carrier gas at the 5 atm of pressure used. Thus only the monomer and dimer and a small amount of the trimer were present in the beam, higher complexes being avoided. The rotational temperature achieved is on the order of 3 K. Multiphoton ionization mass spectrometry (MUPI-MS) offers the possibility of studying the ionization potentials of each separate complex in the jet. In a two-photon experiment the first laser pulse excites a resonant S_1 state and the second color (laser) produces the ion. By scanning the second laser, one can measure the ionization potential of the complex. The two laser beams are collinearly aligned in opposite directions and perpendicular to the direction of the jet and flight path of the reflecting time-of-flight (RETOF) mass spectrometer. The first laser (unfocused) arrives 12 ns before the second ionization laser to avoid multiphoton processes. The ion optics of the mass spectrometer will be switched on 3 μs after the first laser pulse. Only under these field-free conditions can one observe steep and exactly defined rises of the IP.[6] Some contribution to the ion signal was produced from the multiphoton ionization from the first laser. This was checked periodically and subtracted from the two-color measurements. In this way we can be sure that the slow rise in the ionization spectra reflects the true potential. This method is desirable, since the efficiency of the dye used (rhodamine B) is not always constant in the long scanning range (700–900 cm^{-1}). The two-color ionization signal was normalized against the intensity of the two lasers. The present dye laser system has been described previously.[7] Two frequency-doubled pulsed dye lasers were used. The band width was 0.3 cm^{-1} in the UV. The ions were detected with a RETOF mass spectrometer of 75-cm length with a resolution of $M\Delta M$ of 2800. The ionization spectra are recorded with a dual-channel boxcar averager.

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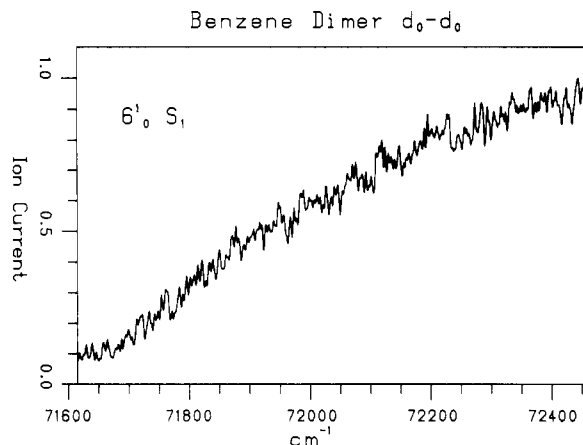
Figure 1. Two-photon ionization threshold of the benzene homodimer (d_0-d_0) by resonant excitation of the 6^1_0 transition.
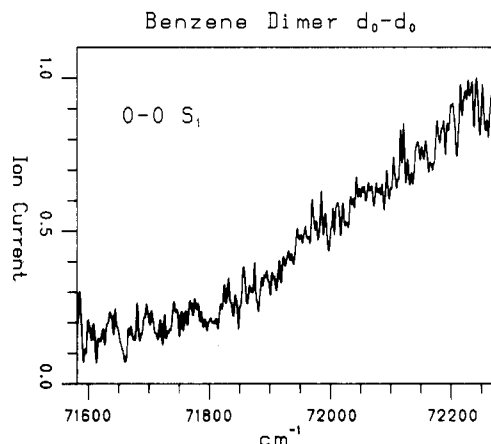

Figure 2. Two-photon ionization threshold of the benzene homodimer (d_0-d_0) by resonant excitation of the 0–0 transition.

Figure 3. Two-photon ionization threshold of the benzene heterodimer (d_0-d_6) by resonant excitation of the 0–0 transition in the benzene half of the complex.

Figure 4. Two-photon ionization threshold of the benzene–cyclohexane complex by resonant excitation of the 0–0 transition.

Results

Ionization Threshold for the Benzene Homodimer (d_0-d_0). The low-resolution spectra that were obtained by synchrotron radiation[3] encouraged us to do a two-photon experiment with field-free ionization to avoid any shifts of the IP and broadening of the onset due to electric fields. Figure 1 shows the photoionization spectra of the benzene dimer. The tail of the ionization threshold covers a long region of 800 cm^{-1}. In this measurement the 6^1_0 transition was excited and used as an intermediate state for the ionization. A linear extrapolation, the usual method of choice, would give an ionization potential of 71 650 cm^{-1}. This determination does not take into account the geometry change in the ion and is just an artificial threshold. If there are rather different Franck–Condon factors for the ionization via the 6^1_0 transition or the 0–0 transition, one can expect that the rise of the ionization signal changes under these conditions. The results of this measurement are shown in Figure 2. Here the range of the spectra is 700 cm^{-1}. One can clearly recognize again the slow rise. A linearly measured ionization threshold at 71 800 cm^{-1} is again an artifact, as mentioned above. This is most clearly seen if one compares the ionization potential in Figures 1 and 2 by doing the simple extrapolation; this produces two different ionization potentials for the same intramolecular vibrational ground state of the ion, which can hardly be. The differences in the observed threshold spectra can be explained only from the different intermediate states, as the final ion state is the same in both cases. This also means that one cannot obtain the IP from simple extrapolation of the onset of the ionization current. Hence we require a new method of analysis of the experimental data.

Ionization Threshold for the Heterodimer (d_0-d_6). To be able to exclude the exciton interaction,[7] as found in the homodimer (d_0-d_0), as a possible reason for the slow rise of the ionization potentials, we measured the IP of the heterodimer (d_0-d_6). Figure
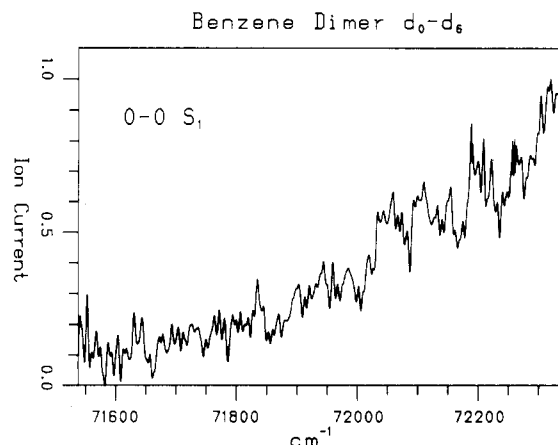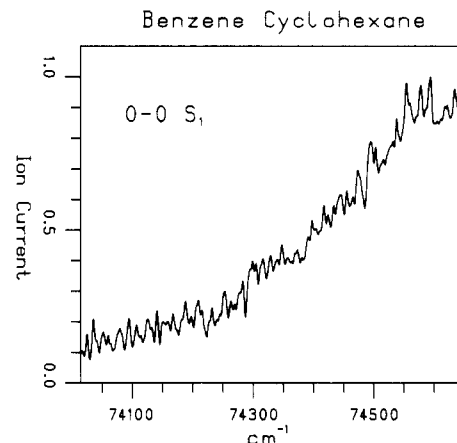
3 shows the ionization threshold for the heterodimer (d_0-d_6). One can see only small changes in the behavior compared to the case of the threshold of the homodimer. Also the ionization potential at 71 820 cm^{-1} obtained by simple extrapolation is barely moved compared to the homodimer. In this spectrum the 0–0 transition is used as an intermediate state (S_1) to produce the ion. The S_1 state of the heterodimer is shifted -43 cm^{-1} to the red relative to the benzene monomer.[7] The similarity of the data indicates that no complications arise from the exciton splitting.

Ionization Threshold for the Benzene–Cyclohexane Complex. The complex benzene–cyclohexane is a further cluster system that might shed some light on the slow rise and the red-shift of the ionization threshold. This complex stands with its qualities between a benzene–argon complex and the benzene dimer. The benzene–cyclohexane complex represents a molecular cluster, but the electronic states of cyclohexane lie some 20 000 cm^{-1} above those of the benzene molecules,[8] which means that there is no exciton interaction in the excited resonant intermediate state in the complex. The cyclohexane ring acts, seen in a spectroscopic way, as a bystander to the benzene molecule. The spectrum for the measurement of the ionization potential is shown Figure 4. Here the first laser excites the 6^1_0 transition. In this case the ionization potential determined from a linear extrapolation is found at 74 200 cm^{-1} and is lowered by 270 cm^{-1} compared to the benzene monomer. The rise of the signal again is slow and develops in a region of 355 cm^{-1}.

In Table I all ionization potentials are listed together with the intermediate states for the ionization. The ionization potentials are given from the analysis of the threshold spectra when one takes

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TABLE I: Ionization Potentials[a]

		S_1, cm⁻¹	IP, cm⁻¹	shift, cm⁻¹	range, cm⁻¹
d_0	6^1_0	38 608.5	74 555[b]	4	4[b]
d_0-d_0	6^1_0	38 565.7	71 504 ± 30[c]	−3051	700
d_0-d_0	0–0	38 044.8	71 550 ± 50[c]		700
d_0-d_6	0–0	38 046.2	71 550 ± 50[c]		700
d_0-Cy[d]	0–0	38 562.8	74 150 ± 20[c]	−405	350

[a] In all cases the ionization occured via the S_1 intermediate state of the C_6H_6 molecule in the complex with vibrational excitation as indicated. IP is the ionization potential of the vibrational ground state of the complex ion. The shift of the ionization potential is given relative to the bare benzene molecule, and the range gives the length of the slope of the observed onset. [b] Direct measurement by Müller-Detlefs et al.[6] [c] Value obtained from the fit with our model. [d] Cy = cyclohexane.

into account the geometry change in the ion.

Discussion

The ionization potential of a molecule decreases when it goes from the gas phase to the condensed phase, and the shift depends on the size of the system. Parallel to this, one often observed a long tail in the onset of the ionization signal. In earlier experiments the reason for this shift and the lack of a step function in the ionization process was partly explained as being due to the effect of the electric field on the ionization threshold.[9] This lowering due to an electric field can be quite large and is now avoided by a field-free ionization technique.[6]

For clusters between aromatic molecules and a noble-gas atom, one also finds a lowering on the order of 100 wavenumbers, which can be explained by a model that contains pairwise atom–atom interactions between atoms in the molecule and the noble-gas atoms, including charge-induced dipole interaction.[10] This model is adequate for complexes with noble-gas atoms but not for the interaction of aromatic molecules with each other. Theoretical studies have shown that in the case of identical molecules in the dimer there can be a resonance charge-transfer interaction that will lead to a lowering of the energy levels. In the case of the benzene dimer a charge resonance energy contribution of 2630 cm⁻¹ was calculated.[11] This value is in good agreement with the experimental results and explains the mechanism in the benzene homodimer.

It is now interesting that the spectrum of the heterodimer threshold is nearly at the same wavelength as that of the homodimer. In the neutral monomer molecules one has a change in the zero-point energy difference of 179 cm⁻¹ for the S_0 and the S_1 states when one goes from benzene-d_0 to benzene-d_6. The excitation to the resonant intermediate state is predominately localized in the excited d_0 half of the dimer, due to the very small exciton interaction in the benzene dimer compared to the energy difference for the $S_1 \leftarrow S_0$ transition in and benzene-d_0 and -d_6, and further absorption to the ionization occurs thus from the d_0 half of the complex. In benzene-d_0 and -d_6, monomer ions the difference in the 0–0 transition is only 20 cm⁻¹.[12] In this case the resonance charge-transfer interaction of 2630 cm⁻¹ is much larger than the energy difference between the two benzene ions whether isotopically different or not. Hence the charge is completely delocalized for either dimer, which leads to a nearly identical ionization spectrum for both cases.

In the case of the benzene–cyclohexane complex the excitation of the intermediate S_1 state is also seen to be completely localized in the benzene half.[7] The ionization potential of cyclohexane is 5200 cm⁻¹ higher than the ionization potential of the bare benzene molecule. The ionization potential in the benzene–cyclohexane complex lies only 270 cm⁻¹ below that of the pure benzene mo-

nomer. This has an explanation similar to the case of complexes with noble-gas atoms. In this case a possible resonance charge-transfer interaction gives only a small contribution to the observed shift, and the ion charge is localized in the benzene half of the complex ion. This then explains the comparative steepness of the ionization yield curve.

The long tail in the onset of the ionization current that is observed for the benzene dimer and in a smaller amount for the complex with cyclohexane also gives interesting new information about the complex. The measurements here are performed in a supersonic jet at very low temperatures in the isolated gas phase. Therefore, effects from thermal population of higher vibrational states cannot explain the long tails. There are no further collisions of the complexes in the jet, which negates any collision-induced ionization of Rydberg states. These long tails then must be attributed to the special features of the weakly bound van der Waals complexes. In a previous paper[13] a theoretical model for the photoionization of weakly bound complexes was established. In this model the photoionization threshold spectra can be explained from the geometry change in the complex on ionization and from the low-frequency van der Waals modes in the complex. This model is based on the assumption that the ionization cross section is mainly governed by Franck–Condon factors. For a large intermolecular geometry change in the complex between the neutral and the ion, a perpendicular transition to the ground state of the intermolecular potential of the complex is expected to have a nearly vanishing Franck–Condon factor, and one will mainly observe a transition to excited van der Waals modes of the complex. These Franck–Condon factors will strongly depend on the intermolecular geometry. When one now excites an intramolecular vibration in the intermediate resonant state, a small geometry change in the neutral complex will occur, which will then lead to a different onset of the ionization current. A relaxation in the intermediate resonant state is ruled out, as the spectra stayed the same when one delayed the second ionizing laser. We now have analyzed the spectra with the assumption that only one van der Waals mode will have oscillator strength. In this case a staircaselike ionization should be observed that will be smeared out by the other thermally populated very low frequency van der Waals modes.[13] The analysis is performed by fitting the observed spectra with the model by varying the frequency of the optically active van der Waals mode and also the displacement of the potential for this normal coordinate. The best fit was obtained with a frequency of 80 cm⁻¹ for the van der Waals mode and for a displacement of −0.36 Å. This model then also predicts the position of the ionization threshold, which is considerably further to the red than the value that one would obtain from a linear extrapolation of the slope of the ion current spectrum. For the benzene dimer we now find a value of 71 504 ± 30 cm⁻¹ for the ionization potential from the fit of the spectrum with the 6^1_0 intermediate state. The assumption of only one mode that is responsible for the long tail is reasonable, as only the van der Waals mode with the direction of the bond between the two molecules will show a large enough displacement due to the geometry change in the ion from the resonance charge-transfer interaction. The spectrum of the ion current onset for the ionization via the 0–0 intermediate state shows a somewhat different shape in the rise, which is probably due to different Franck–Condon factors if no intramolecular vibration is involved. A fit for these spectra gives a value of 71 550 ± 50 cm⁻¹ for the ionization potential. The accuracy is less because of the short spectral range that could be used for the fit. The interesting observation is that these two values agree, as they must, whereas the observed ionization onsets differ.

In the case of the benzene–cyclohexane complex the onset of the ion current at the threshold is steeper than for the benzene dimer. The fit with our model gives a value of 60 cm⁻¹ for the optically active van der Waals mode and a displacement of −0.30 Å. The ionization potential could also be determined by this method and is found to be 74 150 cm⁻¹, whereas a linear ex-

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trapolation would have given an ionization potential of 74 200 cm⁻¹. The lower frequency and the smaller displacement can be explained from the much weaker interaction between the molecules in the ion as here no resonance charge-transfer interaction is active.

Conclusion

In this paper we have shown that the determination of the adiabatic ionization threshold for complexes of organic molecules will lead to wrong results when one uses just a linear extrapolation of the onset of the ionization current. The long tail in the rise of the ion signal must be analyzed in a more sophisticated manner and gives new information on the structure and bonding of the complex ion. From a simple model with one optically active van der Waals mode, a self-consistent value for the ionization potential can be obtained. In addition the geometry change in the ion and the frequency of the van der Waals mode can be predicted.

Registry No. Benzene, 71-43-2; cyclohexane, 110-82-7.

Photodissociation Dynamics of *tert*-Butyl Nitrite (S₂) and *tert*-Butyl Hydroperoxide at 248–250 nm

J. August, M. Brouard, M. P. Docker, C. J. Milne, J. P. Simons,*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

R. Lavi, S. Rosenwaks, and D. Schwartz-Lavi

Department of Physics, Ben-Gurion University, 84105 Beer Sheva, Israel (Received: December 28, 1987; In Final Form: February 25, 1988)

The technique of Doppler-resolved laser-induced fluorescence spectroscopy has been employed to study the scalar and vector properties of fragments generated via photodissociation of two large polyatomic molecules, *tert*-butyl nitrite excited into its S₂ state at 250 nm and *tert*-butyl hydroperoxide photolyzed at 248 nm into its first absorption continuum. Experiments on the former system confirm the planar nature of the dissociation, which generates NO fragments with $v_{NO} \perp J_{NO}$, and the A′ symmetry of the parent molecular S₂ state. For *tert*-butyl hydroperoxide, the energy disposal in the OH fragments is similar to that found for H₂O₂ photolyzed at 248 nm, but both β, the OH fragment translational anisotropy, and $\beta_0^0(22)$, the (v_{OH}, J_{OH}) correlation, are significantly smaller than for H₂O₂. These differences (and others) in the photofragment vector properties are discussed in terms of changes in the kinematics and the potential energy surfaces for the two systems. In particular the low translational anisotropy found in *tert*-butyl hydroperoxide can be explained in terms of angle bending, leading to "slingshot" photodissociation dynamics.

1. Introduction

High-resolution molecular spectroscopy is concerned principally with structure, while molecular reaction dynamics is concerned principally with its loss or transformation. The loss of resolved structure in the electronic absorption spectrum associated with excitation into a dissociative continuum is a reflection of that transformation. From a dynamical viewpoint the critical question is the manner of its transformation: necessarily, high-resolution spectral analysis of a molecular absorption continuum is neither helpful, nor sensible! Translational[1] or optical[2] spectroscopy of its separated fragments or spectral analysis of the weak, redistributed radiation emitted by the parent molecule during the course of fragmentation[3] is much more helpful. The combination of translational and optical spectroscopy using Doppler-resolved, laser-induced fluorescence[4] (LIF) or ionization[5] techniques to probe the recoiling fragments is better still. These techniques attain their fullest expression when the polarization properties of the pump and probe lasers are exploited to reveal both the scalar distributions (energy disposals) *and* the vector correlations (linear and angular momentum directions) among the recoiling fragments.[6-8] The scalar and vector patterns provide three-dimensional reflections of the structural changes that occur during dissociation, and their study is an important branch of the newly emerging field of dynamical stereochemistry.[9]

One of the first systems to which the new techniques were applied has been (and continues to be) H₂O₂,[10-13] where the Doppler analysis is greatly facilitated by the very narrow spread of recoil velocities among the separating OH fragments. The sensitivity of the Doppler-resolved profiles of P, Q, or R rotational features in the OH(A←X) LIF excitation spectrum to changes

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