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Energy randomization in the benzene dimer ion

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An isolated benzene dimer is an ideal model system for the study of the interaction between two benzene moieties. It can be excited by choice locally in either of the benzene rings. By employing isotopically mixed benzene dimers, we study ionization of the dimer. Here we directly demonstrate that charge and energy are totally shared with the silent partner. Furthermore, fragmentation occurs at higher intensities – but this fragmentation happens without further communication among the two dimer halves.

1. Introduction

The interaction between two non-bonded aromatic molecules in absence of any interfering many-body effects is of fundamental interest. The benzene dimer is the simplest prototype system in which the interaction between two aromatic molecules can be studied. Benzene clusters become now widely studied in supersonic jets and fluorescence excitation spectra and mass-selected ionization spectra gave first information [1,2]. High-resolution spectra of isotopically substituted benzene dimers were presented by Fung et al. [3] and gave important information about the interactions between the two halves of benzene dimer and its structure. In the isotopic mixed benzene heterodimer the excitation was seen to be localized in either half of the dimer pumped, the other being essentially a silent partner. In the case of the homodimer there is a very weak electronic interaction which leads to a splitting of the transition [4].

Using this localized excitation in one of the benzene dimer halves we ionized the complex and followed the dissociation and fragmentation of the dimer ion. These intermolecular processes like energy randomization are of essential interest for the understanding of the dynamics of van der Waals complexes. The dissociation kinetics of the pure ionic benzene clusters have been measured by Kiermeier et al. [5]. In benzene–argon complexes the ioniza-

tion threshold is found to be lower by 171 cm^{-1} [6], which is due to an increase of bond energy caused by charge–dipole interaction. The stabilization energy D_0 for this cluster ion here was found to be 306 cm^{-1} [7], which is lower than the theoretical value obtained from calculations using model potential surfaces [8]. In this case the charge is still located in the benzene half of the complex. In the case of the benzene dimer, the ionization threshold is lowered by 4700 cm^{-1} [9], which can be understood from a model of a charge resonance interaction [10]. This strong interaction should give rise to a fast exchange of excitation in the ion. In the case of the isotopic substituted benzene dimer here the special case of ionization via an intermediate state with complete localization of excitation in one half is a very good test system for studying the multiphoton ionization-dissociation behavior of such a dimer cation. In contrast to experiments with identical dimer halves as in the case of the toluene dimer [11] where a non-statistical behavior is concluded [12], isotopic labelling is here used to follow the ion products and to identify the individual steps in these processes. In particular it is shown that, although excitation to the ion via an intermediate state is completely localized, excitation occurs on one half of the dimer, charge is completely randomized – both possible ions showing the same intensity.

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2. Experimental

The supersonic jet used in this experiment has been described previously [6]. A skimmed beam arrangement is used which gives a pressure of 2×10^{-6} Torr in the main chamber even with a backing pressure of 5 atm upstream the pulsed nozzle. The rotational temperature achieved is in the order of 4 K. The benzene was cooled to -9°C to reduce the seed ratio to $2.3 \times 10^{-3} \text{ mol}^{-1}$ in helium carrier gas at the highest pressure used. Thus only the monomer and dimers were present in the beam, higher complexes being avoided. Two frequency-doubled pulsed dye lasers were used which enter the jet chamber from opposite sides perpendicular to the jet and are combined in a common focus at 16 cm downstream from the nozzle. The first laser was used to scan the resonant state, and the wavelength of the second laser was set in a way that it would not ionize the bare benzene molecule but only the dimer which has a lower ionization potential [9]. The laser band width was 0.3 cm^{-1} in the UV and the intensity of the first laser was kept sufficiently low to avoid one color ion signal from this laser alone. The ions were detected with a time-of-flight mass spectrometer (TOF) of 75 cm length with a resolution of $M/\Delta M$ of 150 and the spectra were recorded with a dual channel boxcar integrator which allowed to observe two different mass selected spectra at the same time for comparing the relative product yields for the dissociation of the heterodimers. In our measurements of the excitation transfer for the benzene dimer a 1:1 mixture of benzene- h_6 (d_0) and benzene- d_6 (d_6) was used.

3. Results and discussion

In the benzene dimer the 0-0 transition which is strictly one- and two-photon forbidden in the benzene monomer is observed [1]. The 0-0 band of the non-deuterated homodimer d_0 - d_0 is shifted 45.4 cm^{-1} to the red relative to the forbidden monomer and shows a single peak under low resolution. At very low temperatures and high resolution the transition reveals itself as being two peaks [4]. The two peaks are separated by 1.7 cm^{-1} . In the case of the heterodimer d_0 - d_6 at the 0-0 transition of d_0 excitation only one single peak is observed, which is shifted 43.5

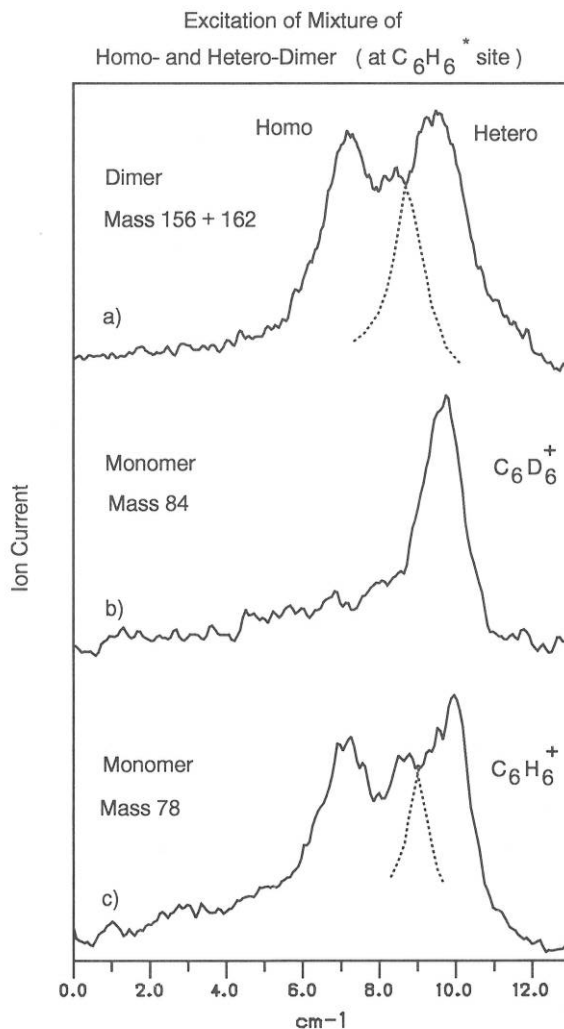


Fig. 1. Excitation spectra of benzene dimers with resonant excitation at the 0-0 S_1 transition of the d_0 benzene. A mixture of 50% perprotonated and 50% perdeuterated benzene was used. (a) Detection of dimer ions. The detection window was set to cover both the $d_0d_6^+$ ions. The spectrum shows both transition bands for the homo- and the hetero-dimer. (b) Detection of monomer d_6 ions. Signal is obtained only in the case of resonant heterodimer excitation. (c) Detection of monomer d_0 ions. Signal is obtained for both the homo- and hetero-dimer excitation. Equal intensity was found for d_0 and d_6 ions at the heterodimer absorption band.

cm^{-1} to the red of the forbidden 0-0 monomer transition. The energy of the vibrationless S_1 state of d_0 benzene lies 202 cm^{-1} below the vibrationless S_1 state of the d_0 benzene. Therefore no energy flow can oc-

cur after excitation of the d_0 half of the heterodimer, thus localizing the energy completely in this half. All processes which exchange energy and charge must thus be relegated to the ion after absorption of a photon from the same resonantly excited half. Thus energy flow in S_1 is precluded – the essentially complete flow observed thus can only occur in the ion. In the case of resonant excitation of the d_6 half of the heterodimer the vibrationless S_1 state lies 35 cm^{-1} below the lowest vibrational excited S_1 state of the d_0 half of the dimer. Thus energy transfer could only occur to the vibrationless S_1 state of the d_0 half which implies a simultaneous excitation of highly excited van der Waals modes, a rather improbable process. In this case the excitation will also stay localized. The resonant excited S_1 states in the clusters lie well above half of the ionization threshold. The second laser used for ionization, therefore, will not be absorbed by the ground state clusters and all ions observed are thus due to two color resonant intermediate state ionization, which in the case of the heterodimers is seen to occur in only one half of the dimer. For comparison with the dissociation and fragmentation spectra the detection mass window of the TOF was set to $M=156+162$ (d_0-d_0 and d_0-d_6 together). The observed spectrum is shown in fig. 1a. Under these conditions the splitting of the homodimer can also be seen but not as prominent as in a single dimer mass-resolved spectrum [4]. The peak for the heterodimer is 1.9 cm^{-1} red shifted relative to the main peak of the homodimer.

Similar spectra of the homo- and hetero-dimer of benzene are shown in fig. 2a for the 0–0 transition when the perdeuterated benzene dimer is excited. In this case the detection window of the TOF was set to $M=166+162$ (d_6-d_6 and d_6-d_0). In the homodimer d_6-d_6 a pure spectrum shows a splitting of 2.3 cm^{-1} and is shifted 44.8 cm^{-1} to the red relative to the forbidden 0–0 transition of the d_6 monomer. The heterodimer also shows only one single peak, 42.9 cm^{-1} shifted to the red of the forbidden 0–0 transition of the d_6 monomer. The large zero-point energy difference between the d_0 and the d_6 benzene now completely localizes the excitation in one half of the heterodimer upon $S_1 \leftarrow S_0$ excitation.

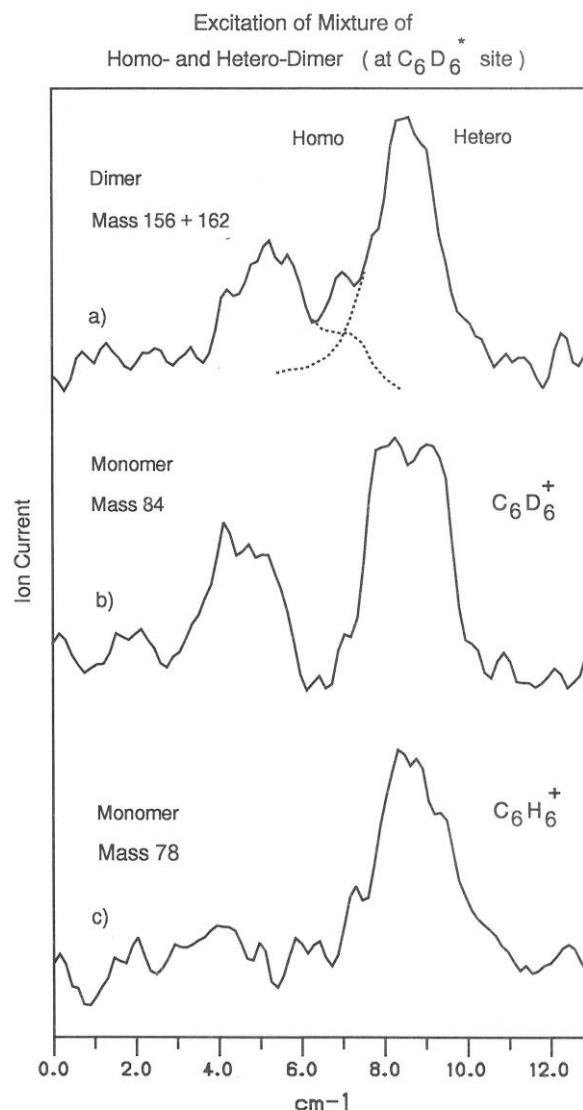


Fig. 2. Excitation spectra of benzene dimers with resonant excitation at the 0–0 S_1 transition of the d_6 benzene. A mixture of 50% perprotonated and 50% perdeuterated benzene was used. (a) Detection of dimer ions. The detection window was set to cover both the d_0d_0 and $d_0d_6^+$ ions. The spectrum shows both transition bands for the homo- and hetero-dimer. (b) Detection of monomer d_6^+ ions. Signal is obtained only for both the homo- and hetero-dimer excitation. (c) Detection of monomer d_0^+ ion. Signal is obtained only in the case of resonant heterodimer excitation. Equal intensity was found for d_0^+ and d_6^+ ions at the heterodimer absorption band.

3.1. Dissociation

Fig. 1c shows the dissociation spectra of the homo- and hetero-dimer ion at the 0-0 transition of the d_0 excitation with detection at mass 78 (d_0) with the first boxcar channel. For this measurement the intensity of the second laser was increased. The same two bands are found at the same position as in fig. 1a. By resonant excitation of the d_0 ring and further ionization of the complex with two photons of the second laser the dissociation of the complex ion can take place. Dissociation products are found detecting d_0^+ ions on both positions of the homo- and hetero-dimer. If one sets the second boxcar channel on the mass 84 (d_6) the spectrum in fig. 1b is observed. From the wavelength of this peak we can conclude that this d_6 ion originates from the excitation of the heterodimer d_0 - d_6 in which solely resonant excitation of the d_0 benzene ring in the dimer is available. The peak intensities of the d_0^+ and the d_6^+ ion signal originating from the heterodimer absorption are found to be nearly identical, which shows that the heterodimer ion dissociates with equal probability producing each different isotopic monomer ion.

The same results are found by resonant excitation of the d_6 half in the dimer as is shown in fig. 2. In this case the ion signal on the mass 84 (d_6) shows the excitation peak for the homo- and hetero-dimer at the 0-0 transition. The mass 78 (d_0) only shows the peak of the heterodimer (d_6 - d_0) although the excitation with the first ion took place only in the benzene- d_6 ring.

3.2. Fragmentation

In the same experiment we now have further increased the intensity of the second laser to induce the fragmentation of the dimer complex. The first photon excites one benzene ring in the dimer, the second red-shifted photon produces the ion of the complex by soft ionization and further absorption of more photons of this same color not only dissociates but also fragments the dimer. Fig. 3 shows the ion signal detected on the mass 56 (C_4D_4) at the 0-0 transition only in the case of resonant excitation of the benzene- d_0 ring in the heterodimer. The identification of mass 56 as C_4D_4 is unique as there is no fragment found with significant intensity for $n > 4$ for C_4H_n and C_4D_n fragments for the homodimers, thus

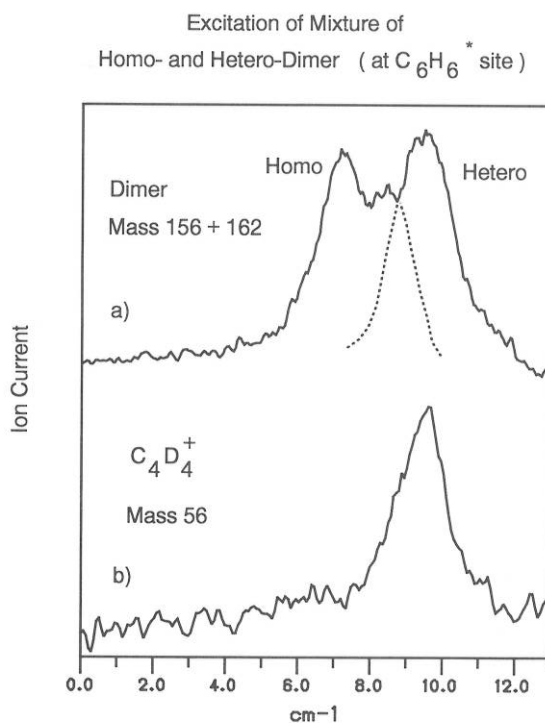


Fig. 3. Excitation-fragmentation spectra of benzene dimers via resonant excitation of the 0-0 S_1 transition of the d_0 benzene. (a) Detection at the dimer mass of d_0d_0 and d_0d_6 simultaneously shows the position of the homo- and hetero-dimer absorption band. (b) Detection at the mass of C_4D_4 . Signal is obtained only at the heterodimer absorption band.

excluding C_4H_8 , C_4H_6D , $C_4H_4D_2$ and $C_4H_2D_3$ and thus being uniquely attributable to the fragmentation of the d_6 half of the dimer. This measurement is of particular interest in that it shows that even if local resonant excitation is in the d_0 half of the heterodimer, fragments of the d_6 half are observed.

The converse result is obtained from resonant excitation of the d_6 half in the heterodimer which is shown in fig. 4. In this case the detection was set on mass 51 which is identified as $C_4H_3^+$, a result that shows also fragmentation of the nonexcited half of the heterodimer. In this experiment a mixed fragment C_4HD_2 could not be precluded as yet.

Hence to obtain more information for the correct assignment of the fragment mass spectra these were recorded for both cases either ionizing the homodimer d_0d_0 or the heterodimer d_0d_6 . This could always be achieved by setting the first resonant laser to the corresponding absorption band. The mass

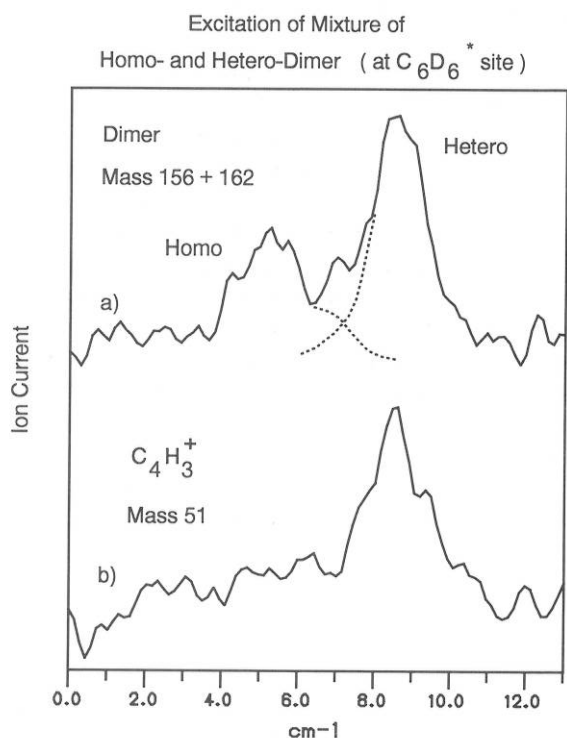


Fig. 4. Excitation-fragmentation spectra of benzene dimers via resonant excitation of the 0-0 S_1 transition of the d_6 benzene. (a) Detection at the dimer mass of d_0d_0 and d_0d_6 simultaneously shows the position of the homo- and hetero-dimer absorption band. (b) Detection at the mass of C_4H_3 . Signal is obtained only at the heterodimer absorption band.

spectra for the homodimer are shown in fig. 5a and for the heterodimer in fig. 5b. In the case of the homodimer the fragmentation pattern for the C_4 fragments only shows C_4H_n fragments with $n \leq 4$. The small feature at mass 53 is due to the natural abundance of ^{13}C . A more complex spectrum is obtained when one sets the first laser on the heterodimer resonant intermediate state. When one analyzes this pattern one can see that this spectrum is the superposition of a fragment spectrum of the protonated benzene containing only $C_4H_n^+$ ions and an identical spectrum with double spacing between the peaks and thus consisting of $C_4D_n^+$ ion peaks. The peaks at mass 49 and 51 are from fragmentation of d_0^+ and the peaks at mass 54 and 56 are due to fragments of d_6^+ . The peaks at mass 48, 50 and 52 are the superposition of fragmentation of either d_0^+ or d_6^+ ions. From fig. 5a it is seen that the peaks for

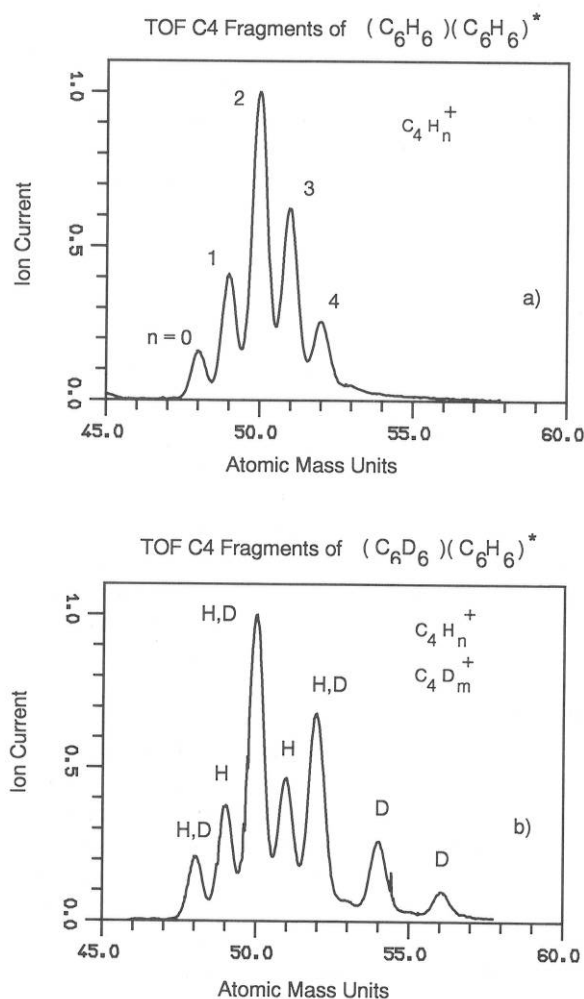


Fig. 5. Multiphoton mass spectrum of C_4 fragments of benzene dimer with excitation at the 0-0 transition. (a) Spectrum obtained when resonantly exciting only the benzene homodimer showing $C_4H_n^+$ ions with $n=0,1,2,3,4$. (b) Spectrum obtained when resonantly exciting the heterodimer only. H denotes peaks related to $C_4H_n^+$ ions, D denotes peaks related to $C_4D_m^+$ ions.

C_4H_n for $n \leq 4$ are very prominent and therefore we focused our interest on mass 53 in the heterodimer case which could possibly be constructed from $C_4H_nD_m^+$ ions for sets of $\{n, m\} = \{1, 2\}$ and $\{3, 1\}$ with the condition $n+m \leq 4$. There one should find a peak with a reasonable intensity if the fragmentation starts from a highly excited dimer ion entity. This peak at mass 53 is missing as well as the peak at mass 55, both of which are only possible for isotopic mixed fragments. The small features observed

at these masses are due to the natural abundance of ^{13}C in the benzene dimer. This analysis demonstrates that no isotopically mixed fragments are formed in this process and hence that the isotopic integrity of each benzene half is preserved in the dissociation of the dimer ions even though the energy is shared.

4. Conclusion

The measurements for the ionization, dissociation and fragmentation of the benzene dimer ion as a prototype of an aromatic dimeric system gives a clear example of the primary photochemical processes which occur after absorption of photons here. The special technique of using isotopic substituted molecules allows, in the case of the heterodimer d_0d_6 , to locally excite one half into a resonant intermediate state from which further absorption takes place. The absorption of the next photon therefore occurs in the same half of the dimer. If one chooses the energy of this second photon to be less than the dissociation limit of the dimer, soft ionization with stable dimer ions is performed. When one now increases the intensity of the ionizing laser multiphoton, absorption takes place where the excess energy readily dissociates the complex. Here we found the important result that when probing the heterodimer d_0^+ and d_6^+ , ions are produced with the same probability in the spite of the prior localized excitation process. This shows that the charge exchange process in the dimer ion is faster than the dissociation process and can be understood from a large resonant charge transfer interaction associated with the lowering of the ionization threshold in the dimer by 4700 cm^{-1} .

When the intensity of the second laser is still increased further, more photons can be absorbed in the ion and fragmentation is observed. The important feature here is the fact that fragments of either half of the dimer are observed with equal probability in spite of the local excitation and also demonstrates the fast charge and energy delocalization in the dimer ion after ionization. If further photons are absorbed, only fragments of either the protonated or perdeuterated ring are found, the integrity of each ring is preserved. This leads one to conclude that the dissociation of the dimer ion occurs faster than fur-

ther absorption, thus preserving the integrity of each ring. The fragmentation now starts from an already separated monomer which has absorbed further photons. This very fast dissociation is consistent with the fact that no mixed fragments of the type $\text{C}_4\text{H}_n\text{D}_m^+$ are observed even at higher intensities of the ionizing laser. This would therefore negate a model involving a superexcited dimer cluster ion. The primary process in the dimer ion therefore is a fast resonant charge exchange, which is followed by a rapid dissociation after absorption of a further photon which prevents the formation of a longer-lived superexcited ion state. The further absorption therefore leads to a photochemical decomposition of already separated monomer ions. Within this picture a statistical behavior is maintained and a non-statistical behavior due to a superexcited cluster could be excluded.

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