The Interactions in the Benzene Dimer in a Supersonic Jet: Study of the S_1 level with isotopic labelling

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The S_1 energy levels of isotopically mixed benzene dimers are studied in a supersonic expansion. In the benzene dimer the O–O transition which is forbidden in the bare molecule is weakly allowed. The spectra show a small splitting for the homodimer and a single transition for the heterodimer, and an additional red shift of the homo dimer transition.

Introduction

Large molecules can be studied at very low temperatures when they are expanded in a seeded supersonic beam [1]. At higher pressure also weakly bound complexes with the carrier gas are formed [2] which are only stable at these low temperatures. At higher partial pressure of the molecules seeded into the beam one can also observe complexes of these molecules which each other [3]. The exact composition of such complexes must be determined in order to disentangle the absorption spectra and to determine the effect of complexation onto the energy levels of the molecules [4]. The separate determination of these complexes can be performed by soft ionisation with a two color experiment, where the first laser is tuned to the resonant transition which is studied and the second laser is used to ionize the complex. The wavelength of the second laser is chosen in a way that the energy of one photon just marginally exceeds the ionization threshold. The complexes then are only ionized and will not dissociate or fragment, which makes it possible to measure the bare complexes in a time of flight mass spectrometer. In this way one now can set the time window of detection on the appearance time at the desired mass and measure the excitation spectrum of a complex with a now known exact composition.

Of special current interest is the formation of dimers of large molecules like benzene, as there may be additional interactions besides the dispersive van der Waals interaction, namely due to an equal electronic structure and similar energy levels. To separate the different interactions it has been shown to be useful to use isotopically substituted molecules which then only differ in the vibrational frequencies but not in the electronic structure. Since the zero point energies differ, the energy levels are separated and resonance effects will be lowered.

The small interaction in the benzene dimer also makes the strictly forbidden O–O transition weakly allowed [5] and hence one can study the vibrationless ground state of the S_1 level. This now allows one to separate electronic effects from changes of vibrational frequences and vibrational coupling in the dimer which is seen in the degenerate ν_6-vibration, which is responsible for most of the observable one-photon transitions.

The benzene dimer is, of course, an interesting prototype interactive system, particularly in view of the large body of data available on the interaction of benzene in the crystal.

Experimental

The supersonic jet used in this experiment has been described previously [4]. The setup now is modified and a skimmed beam arrangement is used which gives a pressure of 2×10^{-6} Torr in the main chamber. Under these conditions isolated molecule conditions are maintained even with a backing pressure of 5 atm upstream the pulsed nozzle with an opening time of 400 μs. The rotational temperature achieved is in the order of 2 K. 99.69% perdeuterated benzene (Merck, Sharp & Dohme, Canada Ltd.) and perprotonated benzene was used in equal amounts for the isotope effect studies. The benzene was cooled to $-15\,°C$ to reduce the seed ratio to

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1.5×10^{-3} 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 18 cm downstream from the nozzle. The first laser (Coumarin 307) was used to scan the resonant state, and the wavelength of the second laser (Fluorescein) was set in a way that it would not ionize the bare benzene molecule but only the dimer which has a somewhat lower ionization potential [6]. The laser band width was 0.3 cm^{-1} in the UV and could be reduced to less than 0.1 cm^{-1} with an interactivity etalon. Absolute wavelength calibration was performed against the Ne line at 5203.895 Å.

The ions were detected with a TOF mass spectrometer of 75 cm length with a resolution $M/\Delta M$ of 150. Excitation spectra for selected different masses are recorded with a boxcar averager. In this way one can separate overlapping bands of the different isotopic species.

Results and Discussion

Figures 1a and 1b show the excitation spectra of benzene dimers in the region of the ν_6 excitation in the monomer with the excitation of the protonated half in the dimer ($d_0^* - d_0$ and $d_0^* - d_6$). The hetero dimer transition is shifted 41.3 cm^{-1} to the red relative to the monomer transition and a splitting of 3.8 cm^{-1} is observed. This splitting is the same for the homo dimer and the heterodimer. The homo dimer shows an additional red shift of 1.0 cm^{-1}.

The splitting of the degenerate vibration can arise from different sources like vibrational coupling, resonance splitting or splitting due to a nonsymmetrical dimer. To distinguish between these different possibilities we also measured the O–O transition. This transition, which is forbidden in the bare molecule is now weakly allowed in the dimer but the intensities are smaller by an order of magnitude.

Figures 2a and 2b show the corresponding dimer transition in the O–O region of the benzene monomer.

The excitation here occurs in the perprotonated half of the dimer. Two important features of the dimer absorption can be seen: (i) the hetero dimer only shows a single peak but the homo dimer is split into a doublet with 1.3 cm^{-1} separation with an intensity ratio of about 10:8 comparing the lower to the higher energy level, (ii) the center of the homo transition doublet is red shifted relative to the hetero dimer by 1.9 cm^{-1} nearly double the value for the 6^1_0 excitation of the dimer. The transition of the hetero dimer is found 43.5 cm^{-1} to the red of the expected value of the O–O transition of the monomer, here the value of Callomon et al. [7] being given.

Figures 3a and 3b show the corresponding spectra for the excitation of the perdeuterated part of the dimer. The spectra are shifted to the blue due to the difference in the zero point energy of the d_0 and d_6 benzene of 203 cm^{-1}. In this case the homo dimer is also split but here the splitting is 2.5 cm^{-1} which is nearly twice that of the corresponding per-

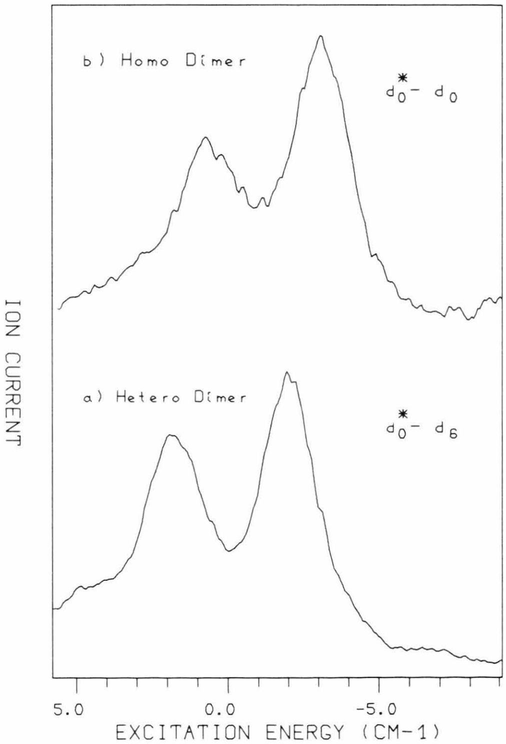

Fig. 1. Excitation Spectra of isotopic benzene dimer 6^1_0 transition. A mixture of 50% perprotonated and perdeuterated Benzene at −15 °C is seeded in He carrier gas at 5 atm. The center of the transition of the hetero dimer ν_0 is 38 567.2 cm^{-1}. a) Absorption of the hetero dimer ($d_0^* - d_6$). Excitation spectrum with detection of mass 162. b) Absorption of the homo dimer ($d_0^* - d_0$). Excitation spectrum with detection of mass 156.

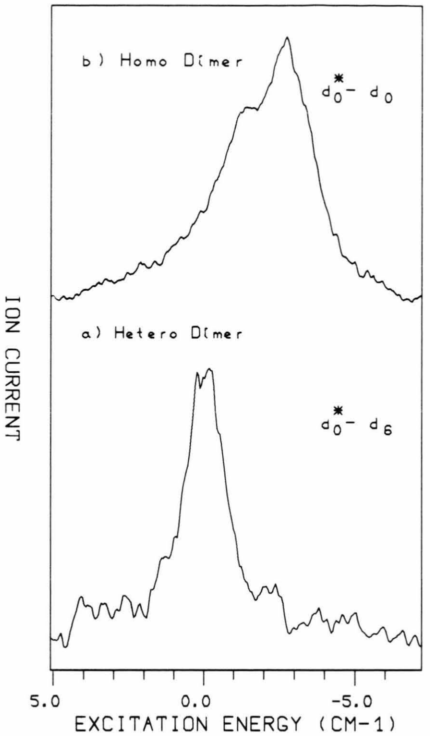

Fig. 2. Excitation spectra of isotopic benzene dimer O–O transition. A 50% isotopic mixture of benezne d_0 and benzene d_6 at −15 °C is seeded in He carrier gas at 5 atm. The center of the hetero dimer transition ν_0 is 38 042.6 cm^{-1}. a) Absorption of the hetero dimer ($d_0^* - d_6$) and detection of mass 162. Only a single transition is observed. b) Absorption of the homo dimer ($d_0^* - d_0$) and detection of mass 156. The transition is split by 1.3 cm^{-1}. Resolution is limited due to rotational temperature of 2 K.

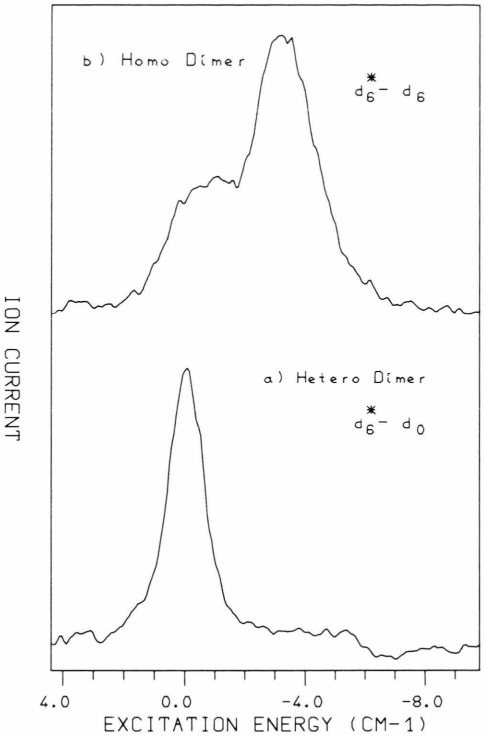

Fig. 3. Excitation spectra of isotopic benzene dimer O–O transition. A 50% isotopic mixture of benzene d_0 and benzene d_6 at −15 °C is seeded in He carrier gas at 5 atm. Center of the hetero dimer transition ν_0 is 38 246.1 cm^{-1}. a) Absorption of the hetero dimer ($d_6^* - d_0$) and detection of mass 162. Only a single transition is observed. b) Absorption of the homo dimer ($d_6^* - d_6$) and detection of mass 168. The transition is split by 2.5 cm^{-1}.

Table 1. Energy levels and splitting of the benzene dimer transition.

	Frequency [a] (cm^{-1})	Splitting (cm^{-1})
d_0^* (O–O)	38 086.1	
$d_0^* - d_6$	−43.5	0
$d_0^* - d_0$	−45.4	1.3
d_6^* (O–O)	38 289.0	
$d_6^* - d_0$	−42.9	0
$d_6^* - d_6$	−44.8	2.5
d_0^* (6^1_0)	38 608.5	
$d_0^* - d_6$	−41.3	3.8 [b]
$d_0^* - d_0$	−42.3	3.8 [b]

[a] The wavelength corresponds to the center of the observed band.

[b] K. Fung et al. [3].

protonated benzene, and a peak intensity ratio of 10:5 is found. The homo dimer is also red shifted by 1.9 cm^{-1} as in the case of d_0 benzene excitation in the dimer. The transition frequencies and shifts are given in Table 1.

The observed spectra now show clearly that the electronic interaction is very small and can only be observed in the O–O transition of the homo dimer. The hetero dimer shows only a single line which indicates that there is no observable site-splitting as in the solid phase [8], a fact which would argue against a T-shaped dimer. Hence the splitting of the ν_6 dimer transition is only a result of the vibronic interaction of the two dimer halves as the force field is changed and coupling via the van der Waals interaction occurs. There is no electronic interaction in the homo dimer of the ν_6 observable, as only a doublet and no quadruple peak is observed in this case. The results from studying isotopic mixed dimers has now revealed an electronic interaction of 1.3 cm^{-1} in the protonated and 2.3 cm^{-1} in the perdeuterated benzene dimer, which corresponds to the similar excitation splitting in the solid phase [9]. A possible vibronic exciton splitting and a site splitting could not be observed and must be less than 0.5 cm^{-1}, which is our detection limit. The additional red shift in the homo dimer transition compared to the heterodimer transition is not yet understood and an aim of further investigation.

In conclusion this work demonstrates that the use of isotopic labelling in multiphoton ionization mass detection enables one to sort the contributions in a mixed jet and provide new information on the elementary interaction between two benzene molecules in the gas phase.

Acknowledgement

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