

# Structural Isomers of the Benzene Dimer from Mass Selective Hole-Burning Spectroscopy

W. Scherzer, O. Krätzschmar, H. L. Selzle, and E. W. Schlag

Institut für Physikalische Chemie, Technische Universität München, Garching, Germany

Z. Naturforsch. **47a**, 1248–1252 (1992); received November 19, 1992

Mass selected hole-burning experiments in the gas phase are presented for the benzene dimer formed in a supersonic jet expansion. The observed spectra show three different ground state configurations for the dimer. From isotopically substituted dimers the structure of the most prominent conformer could be assigned to a very floppy T-shape like structure with two non-equivalent sites for the benzene molecules.

**Key words:** Benzene, Dimer, Cluster, Hole-burning spectroscopy, Mass spectroscopy.

## Introduction

The interaction between two benzene molecules to form the dimer cluster is of fundamental interest. Due to the lack of a rotationally resolved spectrum of the benzene dimer, its structure must be concluded from vibrational spectra and theoretical calculations. Several proposals can be found in the literature:

Janda et al. [1] showed that the dimer has a permanent dipole moment. From this a T-shaped structure was suggested, as it is found in solid benzene. Hopkins et al. [2] measured the UV R2MPI-spectra and Langridge-Smith et al. [3] the laser induced fluorescence spectrum. They also assumed a T-structure, but after the excitation to the  $S_1$ -state a rearrangement to a sandwich-structure in a low lying excimer state was postulated. However, as Shinohara and Nishi [4] pointed out, the behavior of the benzene dimer is not typical for an excimer. Therefore they postulated an excimer formation only for  $S_2$ -excitation.

Another structure, the “parallel displaced” dimer, was proposed by Bernstein et al. [5, 6] from both experimental and theoretical studies. In our laboratory the  $0_0^0$ -transition of the isotopically substituted benzene dimer was studied [7] and only a single peak was found for the heterodimer  $C_6H_6-C_6D_6$ , which shows that there is little interaction between the two halves and that the excitation is fully located in one benzene ring.

Reprint requests to Dr. H. L. Selzle, Institut für Physikalische Chemie, Technische Universität München, Lichtenbergstraße 4, W-8046 Garching, Germany.

Recently Henson et al. [8] reported the evidence for symmetrically non-equivalent benzene molecules in the electronic ground state of the dimer. From Raman vibronic double resonance spectroscopy of the benzene dimer [9] they concluded a T-shape equilibrium geometry for the benzene dimer with the benzene on top freely rotating.

In addition to these experimental investigations, several theoretical calculations were also performed. Forcefield calculation carried out by Williams [10] and Van de Waal [11] lead to a bent T-shape structure with an angle of only  $26^\circ$  between the two benzene molecules. In contrast to that, *ab initio* calculations of Pawliszyn et al. [12], Carsky et al. [13], and Hobza et al. [14] resulted in a floppy T-shape structure.

We recently introduced a mass selected hole-burning spectroscopy in the gas phase to the study of Van der Waals (VdW) complexes [15] and applied this here to study the benzene dimer. This method is superior to mass selected only spectroscopy, as VdW complexes can exist as several structural isomers at a given mass. This method was successfully applied to the benzene- $Ar_2$  complex [15] to identify the two conformers within the spectra which were proposed by Mons et al. from simulation of partially resolved rotational spectra [16] and ion threshold curves [17]. The important feature of hole-burning spectroscopy is that it offers the possibility of investigating different conformers of a cluster. The method is based on the fact that exciting a specific transition in the cluster with a first laser and ionizing from the resonant intermediate state will depopulate the ground state of the corresponding conformer without affecting the other possible conformers. A scan

0932-0784 / 92 / 1200-1248 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

with a second laser at a somewhat later time will find a reduced intensity for all transitions which have the depopulated ground state in common, and thus permits one to identify and separate the spectra of the different conformational isomers. With this method we now studied isotopically substituted benzene dimers, which now display two separate spectra due to different sites in the cluster and also demonstrates that there can be more than one ground state configuration formed in the jet expansion.

## Experimental

The supersonic jet was described previously [15]. A 50% mixture of benzene- $H_6$  and benzene- $D_6$  at  $-8^\circ C$  corresponding to 18 mbar seeded in He with 5.6 bar is expanded through a pulsed nozzle into the vacuum. A skimmer with a 1 mm opening placed 35 mm downstream the nozzle selects the center part of the molecular beam. The molecular beam enters the ionization region at a distance of 170 mm from the nozzle and is crossed by the hole-burning laser beam of a frequency doubled dye laser (Quanta Ray PDL-1) pumped by an Nd:YAG laser (Quanta Ray DCR1-A). With this, laser depletion of the ground state of a selected cluster is performed via REMPI by placing the frequency at the corresponding resonant  $6_0^1$  transition of benzene. Corresponding to the jet velocity, probing occurs 400 nsec later somewhat downstream from the position of the first laser beam. During the supersonic expansion different benzene clusters are generated simultaneously. To avoid contamination of the spectra from decomposition of simultaneously excited larger clusters, soft ionization has to be used for probing with a two color REMPI technique [7]. For this, the molecular beam is crossed by two frequency doubled dye laser beams (Quanta Ray PDL-1) which are simultaneously pumped by an Nd:YAG laser (Quanta Ray DCR1-A), where the first laser is scanned in the region of the  $S_1$   $6_0^1$  transition and the second laser is used at a fixed frequency slightly above the ionization threshold of the cluster. The ionizing laser is optically delayed by 20 nsec relative to the resonant scanning laser to separate one and two color contributions to the ion signal. The ions are extracted into a reflectron time-of-flight mass spectrometer (RETOF) with a resolution larger than  $2000 M/\Delta M$ . This allows in addition the separation of the ions produced by the different lasers and to obtain pure

two color spectra by detecting ions produced only by the second ionizing laser.

The hole-burning spectra are obtained in the way that the probing signal is recorded as the difference of the ion current signal with the hole-burning laser turned on and off for 40 laser shots. The scan of the probe laser thus directly gives the spectrum of a single conformer without contribution from the others.

## Results

### A) Heterodimer ( $C_6H_6$ ) ( $C_6D_6$ )

In benzene monomer the  $S_1$   $0_0^0$ -transition is forbidden, and in the dimer it is only weakly allowed and can be explained by the dipole moment of the dimer [1]. The dipole moment implies lack of a center of symmetry and therefore reduces the observability to only such structures. This is not true for allowed transitions, and therefore we chose the  $S_1 \leftarrow S_0$   $6_0^1$  transition. To distinguish between the two different benzene halves in the dimer the heterodimer ( $C_6H_6$ ) ( $C_6D_6$ ) is used which will form two different species in the case of non-equivalent sites in the cluster. In Fig. 1a the absorption band of the  $6_0^1$  transition is shown. The wavelength range covers the two bands separated by  $180\text{ cm}^{-1}$  which arise from exciting either  $C_6H_6$  (main peak at  $38563\text{ cm}^{-1}$ ) or  $C_6D_6$  (main peak at  $38743\text{ cm}^{-1}$ ) in the heterodimer. Every isotopic subband consists of a sharp double peak and a set of weaker peaks on both sides. To separate the spectra of the different possible conformers we applied the hole-burning laser first to the main peak A of the  $C_6H_6$   $6_0^1$  transition. This depletes the ground state of the corresponding conformer, and from scanning the probing laser and recording the difference spectrum with and without the hole-burning laser the entire contribution of this specific conformer to the  $6_0^1$  is obtained (Figure 1b). The spectrum of this conformer is now simpler and contains for the  $C_6H_6$  half excitation only one sharp double peak, whereas the excitation of the  $C_6D_6$  half gives rise to a sequence of smaller lines. The same behavior is found for the conformer where the hole-burning laser is set to the main absorption peak A' of the  $C_6D_6$  half (Figure 1c). This complementary behavior shows that there exists a structure for the benzene dimer with two-equivalent sites A and B. In the heterodimer the hole-burning of the species with  $C_6H_6$  in site A is thus reflected by the response of  $C_6D_6$  in site B and vice versa. The excita-

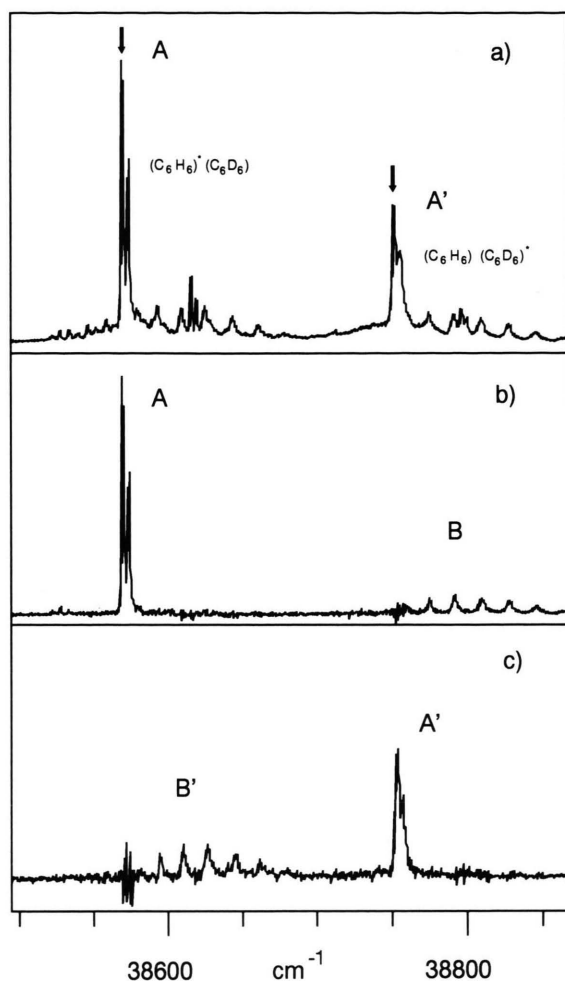


Fig. 1. Hole-burning spectra of the  $(\text{C}_6\text{H}_6)(\text{C}_6\text{D}_6)$  heterodimer. Benzene- $\text{H}_6$  and benzene- $\text{D}_6$  at  $-8^\circ\text{C}$  are seeded in He at 5.6 bar. a) Excitation spectrum of the heterodimer at the  $6_0^1$ -transition with soft ionization detection and mass selection of the heterodimer. b) Difference spectrum with the hole-burning laser set to peak A.  $\text{C}_6\text{H}_6$  at position A corresponds to  $\text{C}_6\text{D}_6$  at position B. c) Difference spectrum with the hole-burning laser set to peak A'.  $\text{C}_6\text{D}_6$  at position A' corresponds to  $\text{C}_6\text{H}_6$  at position B'.

tion of the two different sites gives rise to a double peak from lifting the degeneracy of the  $\nu_6$  vibration in site A and to a VdW progression for the other site B. This finding is consistent with the dipole moment for the dimer [1] and supports a T-shape like structure.

#### B) Homodimer $(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_6)$

The excitation spectrum of the benzene dimer can now be seen as the superposition of the spectra of

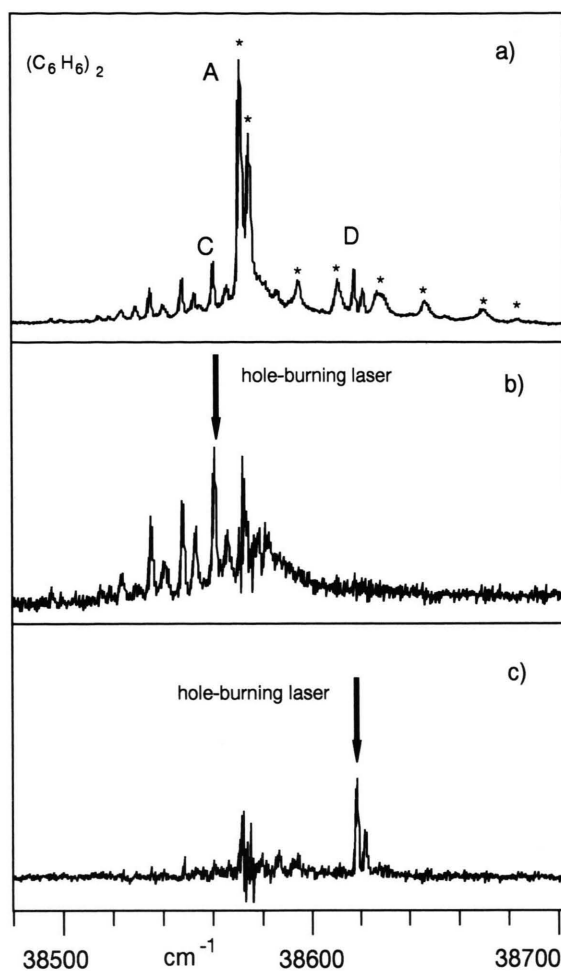


Fig. 2. Hole-burning spectra of the  $(\text{C}_6\text{H}_6)_2$  homodimer. Experimental condition are as for Figure 1. a) Excitation spectrum of the homodimer at the  $6_0^1$ -transition with soft ionization detection and mass selection of the homodimer. The lines arising from the T-shape like structure are indicated with \*. b) Difference spectrum with the hole-burning laser set to peak C. A group of five doublets can be identified to represent the spectrum of conformer C. c) Difference spectrum with the hole-burning laser set to peak D. The spectrum of this conformer consists of a sharp double peak and a set of three weaker peaks at about  $-30\text{ cm}^{-1}$  to the red. The signal at about  $38575\text{ cm}^{-1}$  is residual noise from the difference between hole-burning laser on and off.

different conformers. The hole-burning in the case of the heterodimer permits one to identify the conformers due to two non-equivalent sites. However, there remain lines in the spectrum which do not belong to this conformer and hence must be considered separately. In Fig. 2a the excitation spectrum of the  $(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_6)$  is shown and the transitions of the T-shape structure

are indicated. To identify further conformers, hole-burning was performed using the first strongest transition C to the red side of the main peak A. The resulting difference spectrum, which contains a sequence of double peaks, is shown in Figure 2b. This spectrum clearly shows a contribution from a new ground state configuration and has to be assigned to a further conformer. The remaining two sharp peaks D on the blue side have none of the other ground states in common and were also used for a hole-burning experiment. The resulting difference spectrum is shown in Figure 2c. From this it is found that the two peaks belong to the same conformer, together with some weak peaks on the low energy side of this double peak. It is interesting to note that these peaks are only visible at jet conditions at a high driving pressure and a low seed ratio which leads to a stronger cooling in the jet.

## Discussion

These new results obtained for the benzene dimer  $6_0^1$ -transition now lead to a new discussion and interpretation of the structure of the benzene dimer. The experiments using the heterodimer show that the most probable structure found in the jet is a conformation where the two benzene molecules are arranged in two non-equivalent sites. This is consistent with the known dipole moment of the dimer and the high level *ab initio* calculation. The structure therefore will be best described as T-shaped or near T-shaped. The two different sites give rise to a sharp double peak for site A and a VdW progression for site B. The appearance of a double peak shows that the degeneracy of the  $\nu_6$  vibration is lifted in the excited state. This implies that for this site the symmetry is lowered and therefore this band A can be tentatively assigned to the stem of the T-shape structure. The other site B, which manifests itself in a VdW progression, is the top of the T. Exciting the benzene to the  $S_1$  state increases the size of the ring, and in this case the benzene molecule of the stem can approach somewhat, which is enhanced by the higher polarizability in the excited state. This change in the geometry gives rise to a displacement in the VdW coordinate between the ground and the excited state and explains the observed strong VdW progression with a frequency of about  $17\text{ cm}^{-1}$  for this vibra-

tion. A force field calculation using the potential and parameters from Williams [10] shows only two bending vibrations in this frequency range and explains the mode as a bending of the T-shape. This bending vibration influences the in-plane  $\nu_6$  vibration only weakly, and therefore no splitting but only a broadening of the lines is observed.

The hole-burning spectroscopy now shows that there are two more ground states available in the jet for the benzene dimer. One possible explanation could be that these are no new configurations but simple dimers which are vibrationally excited in the electronic ground state. Such clusters would also give rise to hole-burning spectra with the populated vibronic level in common. This can be safely excluded, as these additional hole-burning spectra become more prominent the stronger the cooling and thus are not related to hot band transitions. This is supported from the fact that there is no benzene vibration with the proper frequency change from ground to excited state to give the observed spectral positions. The spectra therefore represent two further conformers of the benzene dimer. It is interesting to note that these spectra cannot be obtained for the  $0_0^0$ -transition, which indicates that they are symmetry forbidden in this case. The bands C and D show a splitting of the peaks which is comparable to the splitting when the benzene in the stem position of the T-shape structure is excited. For this configuration the degeneracy of the  $\nu_6$  vibration is also lifted and implies a lower symmetry environment in the cluster.

The hole-burning experiment in the case of the benzene dimer clearly identifies several different and separate conformers of a single size cluster. Simple mass resolved spectroscopy fails here. From the isotopic substitution one conformer can be assigned as a floppy T-shape structure with two non-equivalent sites. In addition to this, two further structures can be identified in the jet with smaller concentration and are observed only under extreme cooling conditions.

## Acknowledgement

This work was supported by the Binational German-Israeli James-Franck program for laser-matter interaction.

- [1] K. C. Janda, J. C. Hemminger, J. S. Winn, S. E. Novick, S. J. Harris, and W. Klemperer, *J. Chem. Phys.* **63**, 1419 (1975).
- [2] J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Phys. Chem.* **85**, 3739 (1981).
- [3] P. R. R. Langridge-Smith, D. V. Brumbaugh, C. A. Haynam, and D. H. Levy, *J. Phys. Chem.* **85**, 3742 (1981).
- [4] H. Shinohara and N. Nishi, *J. Chem. Phys.* **91**, 6743 (1989).
- [5] K. S. Law, M. Schauer, and E. R. Bernstein, *J. Chem. Phys.* **81**, 4871 (1984).
- [6] M. Schauer and E. R. Bernstein, *J. Chem. Phys.* **82**, 3722 (1985).
- [7] E. W. Schlag and H. L. Selzle, *J. Chem. Soc. Faraday Trans.* **86**, 1 (1990).
- [8] B. F. Henson, G. V. Hartland, V. A. Ventura, R. A. Hertz, and P. M. Felker, *Chem. Phys. Lett.* **176**, 91 (1991).
- [9] B. F. Henson, G. V. Hartland, V. A. Ventura, and P. M. Felker, *J. Chem. Phys.* **97**, 2189 (1992).
- [10] D. E. Williams, *Acta Cryst. A* **36**, 715 (1980).
- [11] B. W. van der Waals, *Chem. Phys. Lett.* **123**, 69 (1986).
- [12] J. Pawliszyn, M. M. Szczésniak, and S. Scheiner, *J. Phys. Chem.* **88**, 1726 (1984).
- [13] P. Carsky, H. L. Selzle, and E. W. Schlag, *Chem. Phys.* **125**, 165 (1988).
- [14] P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Chem. Phys.* **98**, 5893 (1990).
- [15] W. Scherzer, H. L. Selzle, and E. W. Schlag, *Chem. Phys. Lett.* **195**, 11 (1992).
- [16] M. Schmidt, M. Mons, J. Le Calvé, and P. Millié, *Chem. Phys. Lett.* **183**, 69 (1991).
- [17] J. Le Calvé, M. Schmidt, and M. Mons, *J. Phys. Chem.* **96**, 4131 (1992).