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Infrared Spectroscopic and Ab-Initio Studies of the Benzene Dimer

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INTRODUCTION

Due to its high symmetry and small size, benzene serves as a model molecule for the symmetry properties of molecular vibrations in polyatomic molecules and research on its vibrational modes dates back 70 years. One would expect the fundamental frequencies of its 20 symmetry unique vibrational modes to be well known. However, for at least one mode, the B_{1u} C-H stretch mode, the until recently accepted value [1] was determined only indirectly. Performing experiments on the benzene dimer provides the first direct experimental determination of this mode [2]. Clusters of benzene have also attracted experimental and theoretical attention. Of special interest is the dimer, as it can serve as a prototype for $\pi - \pi$ interaction in aromatic systems and serves since long as a benchmark system to test our understanding of intermolecular interactions. There seems to be no clear consensus from theory if the dimer structure is a parallel or T-shaped structure, although recently, mostly (distorted) T-shaped structures are predicted as being the lowest energy structures. Raman experiments clearly indicate that for the observed species, the two moieties are symmetrically inequivalent [3] and microwave studies show the presence of a dipole moment [4]. Both these results thus support a T-shaped structure. However, it is not clear whether such a T-shaped structure is the exclusive structure or whether a parallel displaced and a T-shaped structure are is some equilibrium and only the T-shaped structure is visible to the experiment. Here, we present a mechanism in which higher energy gas-phase conformers can be converted into lower energy structures with rare gas atoms catalyzing the process [5].

CATALYTIC STRUCTURE CONVERSION

Benzene dimer complexes are generated in a supersonic expansion of benzene (0.03%) and helium or neon as a carrier gas at a stagnation pressure of two bars into vacuum. The molecular beam is skimmed and interrogated by two counterpropagating pulsed UV laser beams. In the IR experiments, the UV lasers are preceded in time by light from a tunable pulsed IR laser. The ions generated in a two-colour-REMPI process are detected perpendicular to the molecular beam axis in a time of flight (TOF) mass spectrometer. For electronic excitation in the REMPI process, the 0_0^0 transition to the first electronically excited state S_1 is used. The 0_0^0 transition is symmetry forbidden in benzene monomer, however, due to the broken symmetry weakly allowed in the benzene dimer. The experiments are performed using a 50:50 mixture of C_6H_6 and C_6D_6. Therefore, dimers of three different masses can be generated: the two homodimers $(C_6H_6)_2$ and $(C_6D_6)_2$ and the heterodimer $(C_6H_6)(C_6D_6)$.

In Figure 1 the UV spectra for the different benzene dimer species are shown in the region of the origin of the $S_1 \leftarrow S_0$ transition using either helium (left) or neon (right) as a carrier gas. When monitoring $(C_6H_6)_2$ with helium as a carrier gas, a peak around 38042 cm^{-1} with a partially resolved splitting of about 2 cm^{-1} is observed. For $(C_6D_6)_2$ a similar spectral feature is observed, shifted about 200 cm^{-1} to the blue. When performing the experiments using helium as a carrier gas and monitoring the mass of the isotopically mixed benzene dimer, two single peaks occur, slightly shifted to the blue compared to the corresponding homodimer transitions. A similar UV spectrum of the isotopically mixed

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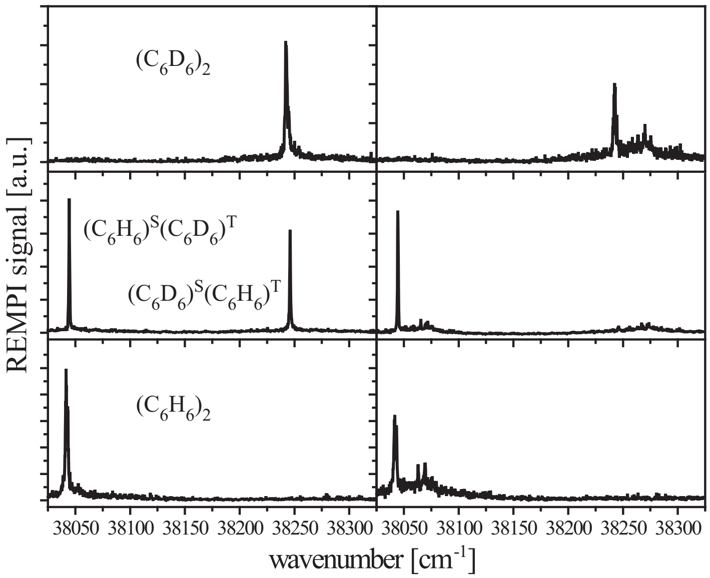

FIGURE 1. UV REMPI spectra of $(C_6H_6)_2$, $(C_6D_6)_2$ and $(C_6H_6)(C_6D_6)$ with helium and neon as expansion gases (left and right traces, respectively).

benzene dimer has been measured several years ago by Bernstein and coworkers [6]. In the T-shaped complex, the chromophore in the "top" is considerably more perturbed relative to the free benzene chromophore than the one in the "stem". In REMPI experiments, therefore, a narrow spectral feature is only observed when the excitation occurs on the "stem" molecule [3]. Since the isotopic composition of the "stem" is different for the two isomers of the mixed benzene dimer, they can be selectively excited by choosing the appropriate UV frequency and thus detected separately. Ions generated using 38042 cm^{-1} light thus originate from dimers with a perprotonated "stem", indicated from now on as $(C_6H_6)^S(C_6D_6)^T$, whereas ions generated using light at 38246 cm^{-1} correspond to the isomer in which the "stem" is perdeuterated, $(C_6D_6)^S(C_6H_6)^T$. In helium, both isomers occur with similar intensities in the spectrum. Using neon as an expansion gas, and monitoring $(C_6D_6)_2$ or $(C_6H_6)_2$, again two slightly split peaks (Fig. 1 right half) at the same spectral positions as in the case of helium are observed. However, in contrast to the measurements in helium, for $(C_6H_6)(C_6D_6)$, only one peak is observed. This peak corresponds to the $(C_6H_6)^S(C_6D_6)^T$ isomer and it appears that the other isomer with the "stem" deuterated and the "top" hydrogenated is completely absent.

When the benzene molecules expand into vacuum, the adiabatic expansion causes a rapid cooling. Dimerization occurs, however, the incipient benzene dimer molecule is initially warm and cools via collisions with the buffer gas. As long as the internal energy of the dimer is above the isomerization barrier, the two subunits rapidly interchange. Once the energy drops to below this barrier, isomerization stops and the conformational distribution is frozen in. At the height of the barrier, the small difference in zero-point energy of about 2 cm^{-1} between the two heterodimer isomers should have a negligible effect on the relative populations and one would expect a near equal abundance of the two conformations. This is indeed observed when helium is used as an expansion gas. Why is now the conformer distribution completely different when neon is used as an expansion gas? When the benzene dimer molecules expand into vacuum, the collision rate drops very fast. A few nozzle diameters downstream, this rate gets so low that three-body collisions and clustering become unimportant. However, two-body collisions between the dimers and carrier gas atoms still occur frequently. As the translational temperature is then already low, those collisions occur with low energy. In such a cold collision between a benzene dimer molecule and a rare gas atom, a short lived complex is formed. The internal energy of this complex is the sum of the collision energy, the internal energy of the colliding partners before the collision and the binding energy of the complex. Late in the expansion or in the cold environment of the molecular beam, the last contribution is dominating by far. In the absence of a third collision partner, this complex will dissociate back to the reactants very fast (within a few pico- to nanoseconds, depending on the system) after the formation of the complex. Usually, such collisions and the formation of transient collision complexes are thus of little consequence. However, when the internal energy of the transient complex is higher than the barriers separating the conformers, isomerisation can occur. This is exactly what can happen when a benzene dimer collides with a neon atom. As an estimate for the internal energy of the benzene dimer-rare gas complex, the binding energy D_0 of a rare gas atom to the benzene monomer molecule can be taken, which is about 48 cm^{-1} [7] and 120 cm^{-1} [8] for helium and neon, respectively. A transient complex of the benzene dimer with neon thus has enough energy for the exchange of the monomer units while a complex with helium has not. If the complex is initially formed in the "high energy" conformer $(C_6D_6)^S(C_6H_6)^T$, complexation with neon can induce isomerization to the "low energy" conformer $(C_6H_6)^S(C_6D_6)^T$. The difference in zero-point energy of about 2 cm^{-1} is then available as kinetic energy for dissociating the complex, strongly enhancing the dissociation rate in that channel. Under the cold conditions of the molecular beam, the initial collision energy between the dimer and the rare gas atom is on the order of 1-3 cm^{-1} so that the reverse "low to high energy" isomerization is strongly disfavoured. The neon atoms thus effectively acts as a catalyst for the isomerization in the benzene dimer, forming selectively the low energy isomer $(C_6H_6)^S(C_6D_6)^T$. This mechanism, in combination with calculated energies [7, 9], also predicts that the parallel displaced sandwich isomer should not survive in the molecular beam, as already helium would catalyse its destruction.

C-H STRETCH VIBRATIONS OF THE BENZENE MOLECULE

IR spectra are obtained by irradiating the molecular beam with the IR laser about 60 ns prior to UV radiation. When the IR laser is resonant with a vibrational transition in the complex, ground state complexes are depleted and a dip in the ion signal is observed. Monitoring the ion yield at a fixed UV wavelength as a function of the IR frequency gives thus the IR spectrum of the complex.

In Figure 2, the IR spectra of $(C_6H_6)(C_6D_6)$, when excited at 38044.0 cm^{-1} $(C_6H_6)^S(C_6D_6)^T$ and at 38246.4 cm^{-1} $(C_6H_6)^T(C_6D_6)^S$, are shown. Indicated with solid lines are the three well-known IR transitions of the benzene monomer that occur in this range [10, 11, 12]. These are the ν_{20} E_{1u} fundamental mode at 3047.9 cm^{-1}, the $\nu_1\nu_6\nu_{19}$ combination band at 3078.6 cm^{-1} and the $\nu_8\nu_{19}$ combination band around 3101 cm^{-1}. Shown as dashed lines are the positions of two other, not IR active fundamental C-H stretch modes of the benzene monomer: the ν_7 E_{2G} mode at 3056.7 cm^{-1} and the ν_2 A_{1g} mode at 3073.9 cm^{-1} [13].

In both benzene dimer spectra, the three resonances that are IR active in the bare benzene are observed. In all cases, they are observed a few wavenumbers to the red, compared to the benzene monomer. In the $(C_6H_6)^S(C_6D_6)^T$ spectrum additional resonances are observed, one at 3012.4 cm^{-1}, one at 3070.9 cm^{-1} and a weak split peak (shown enlarged in the inset) at 3056.2 cm^{-1} and 3057.3 cm^{-1}. Two important consequences arise from the observed difference between the two spectra: 1) the two benzene rings must be symmetrically inequivalent and 2) the two rings do not interchange on the timescale between IR excitation and UV excitation/ionization, which is, in the present experiment, about 30-70 ns.

Our observations of two different dimer IR spectra are in agreement with a T-shaped complex. In such a structure, two sites are present of which one, the stem, has C_{2v} (or lower) symmetry. The other site, the top molecule, has formally C_s symmetry. However, the barrier for rotation of this molecule around its C_6 axis (or, equivalent, rotation of the stem around its C_2 axis) is expected to be very low, so that it can be viewed as a free rotor. In that case, the symmetry of the top molecule is C_{6v} and that of the stem remains unchanged C_{2v}. Benzene in D_{6h} symmetry has four C-H stretch vibrations with symmetries B_{1u}, E_{1u}, E_{2g} and A_{1g}. In D_{6h}, only the E_{1u} mode is IR allowed. Upon reduction of the symmetry, more modes can become active. It can be shown that upon reduction to C_{6v}, the A_{1g} mode becomes an A_1 mode, which is IR-allowed as well. When the symmetry is reduced to C_{2v}, all four modes become IR-allowed and the degeneracy in the E_{1u} as well as in the E_{2g} mode is lifted. We propose that the additional lines observed in the lower spectrum of Figure 2 result from those modes that become IR allowed upon symmetry reduction.

For the modes that correspond to IR dark modes in the monomer, the mode at 3070.9 cm^{-1} in $(C_6H_6)^S(C_6D_6)^T$ is only 3 cm^{-1} shifted to the red from the position of the A_{1g} mode in C_6H_6. The modes at 3056.2 cm^{-1} and 3057.3 cm^{-1} can be compared to the E_{2g} mode in C_6H_6 at 3056.7 cm^{-1}. In the dimer, the degeneracy is lifted and therefore, a splitting is observed. Consistent with the (negligible) shift and splitting, the band is observed to be very weak in the dimer. The third "dimer" transition observed at 3012.4 cm^{-1} we here assign to correspond to the only other fundamental C-H stretch mode in benzene that is left in this range, the B_{1u} mode. This new assignment is also agreement with *ab-initio* calculations which will be presented. It should be noted that this new value is significantly shifted from the previously accepted value of 3057 cm^{-1} [1] which, however, has been determined only indirectly and was most likely less correct.

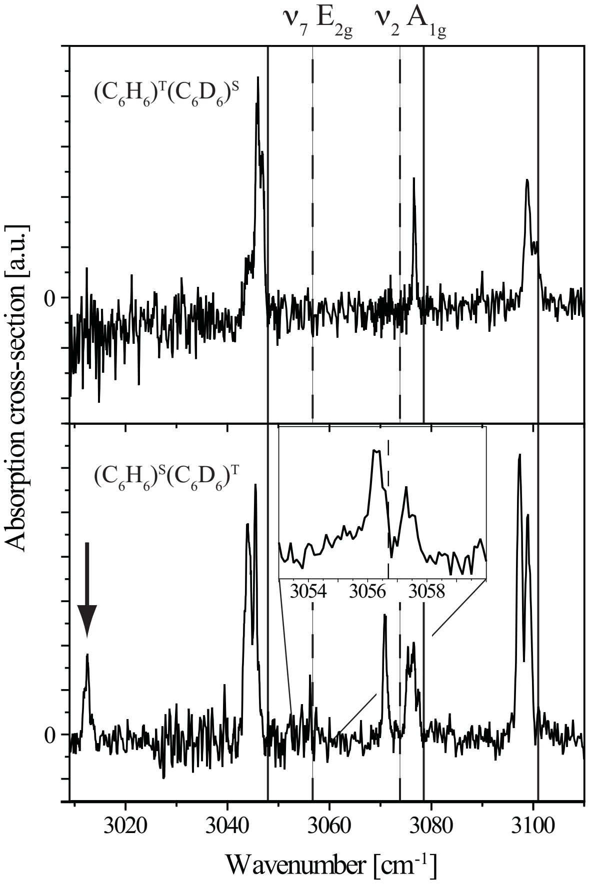

FIGURE 2. IR spectra of $(C_6H_6)(C_6D_6)$ with C_6H_6 being in the "Top" position (upper trace) and in the "Stem" position (lower trace).

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