An experimental value for the B_{1u} C–H stretch mode in benzene

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We here present experimental infrared spectra on two $(C_6H_6)(C_6D_6)$ benzene dimer isomers in the gas phase. The spectra show that the two benzene molecules in the dimer are symmetrically inequivalent and have distinct IR signatures. One of the two molecules is in a site of low symmetry, which leads to the IR activation of fundamental modes that are IR forbidden by symmetry in the monomer. In the spectra, all four fundamental C–H stretch modes of benzene are observed. Modes in the dimer are shifted up to 3 cm^{-1} to the red, compared to the modes that are known for the monomer. For the ν_{13} B_{1u} C–H stretch fundamental mode of benzene, a first experimental value of 3015^{+2}_{-5} cm^{-1} is determined, in excellent agreement with anharmonic frequency calculations presented here. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2198828]

Due to its high symmetry and small size, benzene serves as a model molecule to understand the symmetry properties of molecular vibrations in polyatomic molecules and research on its vibrational modes dates back 70 years.[1] Since then, the benzene molecule has been continuously in the focus of intense experimental and theoretical efforts. The fundamental frequencies of most of its 20 symmetry unique vibrational modes are well known.[2] However, for two of the modes, for which the frequency can only be determined indirectly, the currently accepted values are 50 years old.[3] One of them is the ν_3 (Wilson notation[1]) A_{2g} mode with a value near 1350 cm^{-1}. The other one is the ν_{13} B_{1u} C–H stretch mode. Both modes are neither Raman nor IR active. The ν_3 A_{2g} mode can be observed as a weak transition in liquid benzene as well as via combination bands.[3] For the fundamental frequency of the ν_{13} B_{1u} mode, a value of 3057 cm^{-1} is frequently cited as the experimental value. However, this value is deduced indirectly by applying product rules on modes of C_6H_6 and symmetrical $C_6H_3D_3$.[3] The application of such product rules is only valid for harmonic frequencies and will fail when modes are coupled via Fermi resonances. It is now known that such Fermi resonances play a role for the ν_{13} B_{1u} mode, as it strongly interacts with the $\nu_8 + \nu_{19}$ $(E_{2g} + E_{1u})$ combination band. One can thus put a question mark on the value of 3057 cm^{-1} for the ν_{13} B_{1u} mode.

Benzene also serves as a playground for theory and vibrational properties are investigated using empirical force-fields[1,4,5] as well as *ab initio* harmonic analysis at various levels.[6] Since recently, the role of anharmonicities is investigated. The resulting predictions of the value of the frequency of the ν_{13} B_{1u} fundamental mode range from 2988 cm^{-1} (Refs. 7 and 8) to 3083 cm^{-1} (Ref. 9). A value of 3028 cm^{-1} is predicted by *ab initio* theory as well as by recent empirical force fields[10,11] while another study predicts a value of 3045 cm^{-1}.[12]

Clusters of benzene have also attracted experimental[13–18] and theoretical[19] attention. Of special interest is the dimer, as it can serve as a prototype for π-π interaction in aromatic systems. There seems to be no clear consensus from theory if the dimer structure is a parallel or T-shaped structure. Raman experiments clearly indicate that the two moieties are symmetrically inequivalent[16] and microwave studies show the presence of a dipole moment.[18] Both these results thus support a T-shaped structure.

We here present experimental IR spectra on the benzene dimer as well as *ab initio* calculations that include anharmonic and Fermi corrections on the monomer. From this, we conclude that the benzene dimer has a structure with two inequivalent sites and that the fundamental frequency of the ν_{13} B_{1u} mode in the benzene monomer is at 3015^{+2}_{-5} cm^{-1}.

The IR spectra are obtained by performing ion dip spectroscopy on the benzene dimer complexes in a pulsed molecular beam in the region between 3000 and 3100 cm^{-1}. The complexes are generated by expanding a mixture of benzene (0.03%) in helium at a stagnation pressure of 2 bar into vacuum. The experiments are performed on a 50:50 mixture of C_6H_6 and C_6D_6. The molecular beam is skimmed and overlapped with the UV and IR lasers between the acceleration plates of a time of flight (TOF) mass spectrometer. Tunable UV light is obtained from two frequency doubled Nd:YAG pumped pulsed dye lasers. Tunable IR light is generated by difference frequency mixing of light from a dye laser near 800 nm with the 1064 nm of an injection seeded Nd:YAG laser that also served as the pump source for the dye laser. This IR laser setup is very similar to one described by Gerhards.[20] For electronic excitation, the 0^0_0 transition to the first electronically excited S_1 state is used. This excitation frequency is, depending on isotopic composition, between 38000 and 38300 cm^{-1}. The 0^0_0 transition is symmetry forbidden in the benzene monomer, however weakly allowed in the reduced symmetry of the dimer. For subsequent ionization, light from a second frequency doubled dye laser near 282 nm is used. Ions are then detected in the TOF mass spectrometer.

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
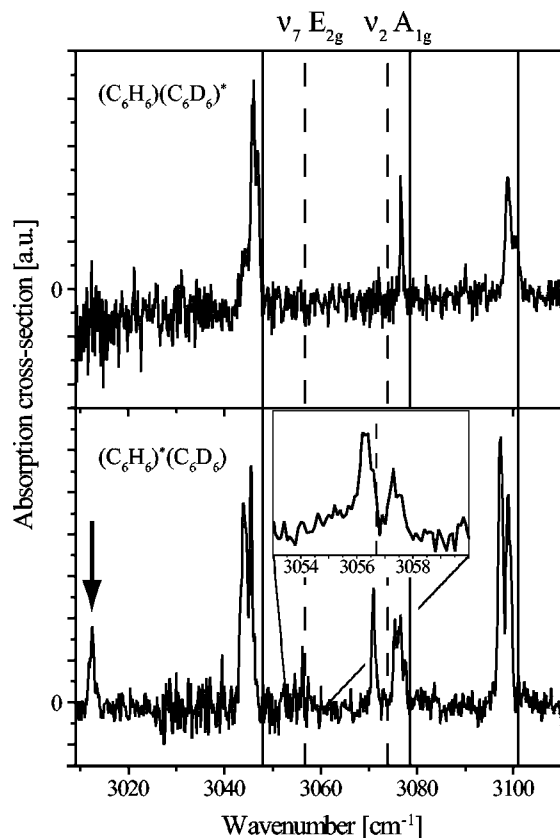
FIG. 1. IR spectra for $(C_6H_6)(C_6D_6)$ when detecting via UV excitation on the C_6H_6 (lower) and C_6D_6 (upper) moiety, indicated by " *". The frequency positions of the IR active modes for the benzene monomer are indicated as solid lines. The positions of two fundamental modes of the monomer that are not IR allowed in D_{6h} are shown as dashed lines. In the inset, the region between 3053 and 3060 cm^{-1} for $(C_6H_6)^*(C_6D_6)$ is shown, taken with a $10\times$ higher laser fluence. The peak indicated with an arrow in the spectrum of $(C_6H_6)^*(C_6D_6)$ is attributed to the ν_{13} B_{1u} mode of C_6H_6.

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.

The UV spectra of $(C_6H_6)_2$, $(C_6D_6)_2$, and $(C_6H_6)(C_6D_6)$ in the 0_0^0 transition range are known.[15] In the here studied UV range (38000 to 38300 cm^{-1}), two transitions at 38044.0 and 38246.4 cm^{-1} of about equal strength are observed for $(C_6H_6)(C_6D_6)$. The splitting results from the isotopic shift of benzene in the electronic transition upon deuteration.[15,16] It has been concluded that the UV spectrum

is in line with a T-shaped structure and that the UV excitation is always localized on the "stem" molecule.[16] Thus, when detecting $(C_6H_6)(C_6D_6)$ via excitation at 38044.0 cm^{-1} the T-shaped heterodimer with the C_6H_6 moiety in the "stem" is probed, while excitation at 38246.4 cm^{-1} probes the T-shaped heterodimer with the C_6H_6 moiety in the "top" position.

In Fig. 1, the IR spectra of $(C_6H_6)(C_6D_6)$, when excited at 38044.0 cm^{-1} $[(C_6H_6)^*(C_6D_6)]$ and at 38246.4 cm^{-1} $[(C_6H_6)(C_6D_6)^*]$, are shown. Indicated with solid lines are the three well known IR transitions of the benzene monomer that occur in this range.[17,21,22] 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}.[23]

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 wave numbers to the red, compared to the benzene monomer (see also Table I). The exact positions and detailed structures of the peaks that are common in the spectra differ from each other, this point will however be discussed elsewhere.[24] More importantly, one can see that in the $(C_6H_6)^*(C_6D_6)$ 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 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 time scale between IR excitation and UV excitation/ionization, which is, in the present experiment, about 30–70 ns. If the two rings were equivalent and/or able to interchange on a 70 ns time scale, identical IR spectra for $(C_6H_6)^*(C_6D_6)$ and $(C_6H_6)(C_6D_6)^*$ would result. Similar conclusions were also obtained from Raman experiments.[16]

The IR spectra shown in Fig. 1 thus represent the C–H stretch IR spectra of the two nonequivalent sites in the benzene dimer. One of the two spectra resembles that of the benzene monomer,[17,21,22] while the other spectrum shows the presence of additional transitions (see Table I). What is the nature of those transitions? The present experiment produces

TABLE I. Experimental and calculated vibrational frequencies (cm^{-1}) for the benzene monomer and dimer.

	Experiment			Theory	
	$(C_6H_6)^*(C_6D_6)$	$(C_6H_6)(C_6D_6)^*$	C_6H_6	C_6H_6 harmonic	C_6H_6 anharmonic
ν_{13} (B_{1u})	3012.4	—	3015[a,b]	3159.2	2993.2[c]
ν_{20} (E_{1u})	3044.0/3045.6	3043.6/3046.0	3047.9[d]	3184.4	3030.1[c]
ν_7 (E_{2g})	3056.2/3057.3	—	3056.7[b,e]	3169.3	3034.8
ν_2 (A_{1g})	3070.9	—	3073.9[b,e]	3194.9	3053.2[f]

[a]This study.
[b]Not IR active.
[c]In Fermi resonance with the $\nu_8 + \nu_{19}$ mode.
[d]Reference 21.
[e]Reference 23.
[f]In Fermi resonance with the $\nu_8 + \nu_8$ mode.

spectra for $(C_6H_6)_2$ (not shown) that are nearly identical to spectra observed previously.[17,25] There, in one experiment two[17] and in the other experiment all three[25] transitions were observed as well. As tentative assignment for the two stronger transitions visible in Fig. 1, combinations with intermolecular vibrations were suggested.[17] We propose here a different assignment.

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 Fig. 1 result from those modes that become IR allowed upon symmetry reduction; the spectrum shown in the top of the figure is attributed to the higher symmetry "top" molecule while the one below is attributed to the lower symmetry "stem" molecule, consistent with the interpretation that UV excitation always occurs on the "stem" molecule.[16]

Based purely on symmetry considerations, it is not possible to say whether those newly allowed IR transitions would be strong enough to be observable and, if they are observable, whether they are significantly shifted from the positions of their unperturbed counterparts. Qualitatively, the strength of the symmetry reducing perturbation (the intermolecular interaction) will affect both, the strength and the shift of the newly allowed transitions. For the benzene dimer, this intermolecular interaction is very weak, compared to the intramolecular interactions. This is expected from theory[19] and can also be seen from the shifts and/or splittings of the bands in Fig. 1. For the modes in the dimer which correspond to IR active modes in the benzene monomer, the observed splittings have a maximum of 2.5 cm^{-1} and the shifts compared to the monomer are not larger than 4 cm^{-1}. For the modes that correspond to IR dark modes in the monomer, the mode at 3070.9 cm^{-1} in $(C_6H_6)^*(C_6D_6)$ 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 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.

To further test this assignment, we have performed calculations of the vibrational modes of benzene that include the effects of anharmonicities. The calculations are performed with GAUSSIAN03 using the B3LYP DFT functional and the cc-pVTZ basis set. The resulting frequencies for the C–H stretch modes are shown in Table I. Relevant for the direct comparison to the experiment are anharmonic modes, which also include the effect of Fermi interactions. Comparing those with the known bands of benzene shows that the calculated modes are between 0.6% and 0.7% too low in frequency. Correcting the calculated value for the B_{1u} mode at 2993.2 cm^{-1} for this, results in a predicted value of 3013.0 cm^{-1} for the B_{1u} mode. This is in excellent agreement with the transition in the dimer observed at 3012.4 cm^{-1}. Comparing the positions of the transitions observed in the dimer to those in the monomer shows that in the dimer, transitions are up to 3 cm^{-1} shifted to the red. This shift is of course not known for the B_{1u} mode, it would, however, be surprising if this shift would be vastly different for this mode. We thus include an estimated empirical shift of 2–3 cm^{-1} for this band and conclude that the fundamental frequency of the ν_{13} B_{1u} mode in the benzene monomer is at 3015^{+2}_{-5} cm^{-1}.

To summarize, it is clearly observed that the two benzene moieties in the benzene dimer are symmetrically inequivalent and have distinct IR signatures. One of the two molecules is in a site of low symmetry, which leads to the IR activation of fundamental modes that are IR forbidden by symmetry in the monomer and all four fundamental C–H stretch modes of benzene are observed. When comparing to the modes that are known for the monomer, modes in the dimer are shifted up to 3 cm^{-1} to the red. "Blue-shifting hydrogen bonds" are predicted by theory for the benzene dimer[26] and can be experimentally found in other gas-phase clusters.[27] In agreement with previous studies,[25] they are not observed here. For the ν_{13} B_{1u} C–H stretch fundamental mode, a first experimental value of 3015^{+2}_{-5} cm^{-1} is determined.

[1] E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

[2] For a review see: L. Goodman, A. G. Ozkabak, and S. N. Thakur, J. Phys. Chem. **95**, 9044 (1991).

[3] S. Brodersen and A. Langseth, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, 1 (1956).

[4] See, for example: E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (Dover, New York, 1955).

[5] S. Rashev, Int. J. Quantum Chem. **99**, 894 (2004).

[6] J. M. L. Martin, P. R. Taylor, and T. J. Lee, Chem. Phys. Lett. **275**, 414 (1997) and references therein.

[7] A. Miani, E. Cané, P. Palmieri, A. Trombetti, and N. C. Handy, J. Chem. Phys. **112**, 248 (2000).

[8] A. D. Boese and J. M. L. Martin, J. Phys. Chem. A **108**, 3085 (2004).

[9] K. Yagi, K. Hirao, T. Taketsugu, M. W. Schmidt, and M. S. Gordon, J. Chem. Phys. **121**, 1383 (2004).

[10] E. Cané, A. Miani, and A. Trombetti, Chem. Phys. Lett. **340**, 356 (2001).

[11] S. Rashev, J. Phys. Chem. A **107**, 2160 (2003).

[12] M.-L. Senent, P. Palmieri, S. Carter, and N. C. Handy, Chem. Phys. Lett. **354**, 1 (2002).

[13] J. B. Hopkins, D. E. Powers, and R. E. Smalley, J. Phys. Chem. **85**, 3739 (1981).

[14] P. R. R. Langridge-Smith, D. V. Brumbaugh, C. A. Haynam, and D. H. Levy, J. Phys. Chem. **85**, 3742 (1981).

[15] K. O. Börnsen, H. L. Selzle, and E. W. Schlag, J. Chem. Phys. **85**, 1726 (1986).

[16] B. F. Henson, G. V. Hartland, V. A. Venturo, and P. M. Felker, J. Chem. Phys. **97**, 2189 (1992).

[17] R. H. Page, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **88**, 4621 (1988).

[18] E. Arunan and H. S. Gutowsky, J. Chem. Phys. **98**, 4294 (1993).

[19] See, for example: M. O. Sinnokrot and C. D. Sherrill, J. Phys. Chem. A **108**, 10200 (2004) and references therein.

[20] M. Gerhards, Opt. Commun. **241**, 493 (2004).

[21] J. Plíva and A. S. Pine, J. Mol. Spectrosc. **126**, 82 (1987).

[22] R. H. Page, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **88**, 5362 (1988).

[23] A. B. Hollinger and H. L. Welsh, Can. J. Phys. **107**, 974 (1978); **107**, 1513 (1978).

[24] U. Erlekam, M. Frankowski, G. Meijer, and G. von Helden (unpublished).

[25] B. Reimann, Ph.D. thesis, Frankfurt/M, Germany 2002.

[26] P. Hobza, V. Špirko, H. L. Selzle, and E. W. Schlag, J. Phys. Chem. A **102**, 2501 (1998); P. Hobza and Z. Havlas, Chem. Rev. **100**, 4253 (2000).

[27] P. Hobza, V. Špirko, Z. Havlas, K. Buchhold, B. Reimann, H.-D. Barth, and B. Brutschy, Chem. Phys. Lett. **299**, 180 (1999).