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Direct Infrared Absorption Spectroscopy of Benzene Dimer

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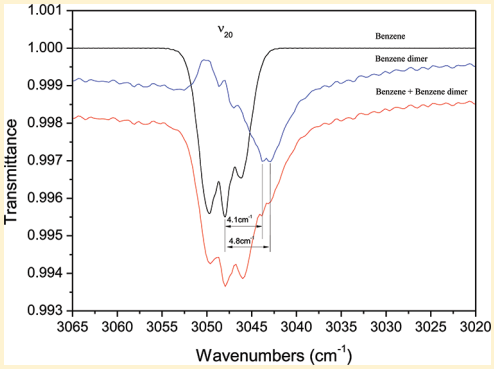
ABSTRACT: The *direct* infrared (IR) absorption spectrum of benzene dimer formed in a free-jet expansion was recorded in the 3.3 μm region for the first time. This has led to the observation of the C−H stretching fundamental mode ν_{13} (B_{1u}), which is both IR and Raman forbidden in the monomer. Moreover, the IR forbidden and Raman allowed ν_7 (E_{2g}) mode has been observed as well. These two modes were found to be red-shifted along with the IR allowed ν_{20} (E_{1u}) mode, as previously reported by Erlekam et al. [Erlekam; Frankowski; Meijer; Gert von Helden *J. Chem. Phys.* **2006**, *124*, 171101], using ion-dip spectroscopy, contrary to the blue-shift predicted earlier by theoretical studies. The observation of the ν_{13} band indicates that the symmetry is reduced in the dimer, confirming the T-shaped structure observed by Erlekam et al. Our experimental results have not provided any direct evidence for the presence of the parallel displaced geometry, the main objective of the present work, as predicted by theoretical calculations.



I. INTRODUCTION

The aromatic−aromatic interaction (the $\pi-\pi$ interaction) exists in various biological molecules such as DNA, proteins,[1] and in porphyrin aggregation and plays a major role in their structure and stability[2−6] and in molecular recognition.[7] Benzene is a prototype aromatic molecule and understanding its complexes in the gas phase can lead to a better understanding of the assembly phenomena between various aromatic groups, especially the dispersion forces that exist between the two aromatic molecules. Studying the benzene dimer in the gas phase could reveal the intrinsic properties of the $\pi-\pi$ interaction free from external environments.

The results from theoretical calculations vary and are highly dependent on the level of theory used.[8−14] However, almost all the theoretical calculations agree that two possible isomers for the benzene dimer could exist: a T-shaped (TS) and a parallel displaced (PD). Calculating the global minimum structure of the benzene dimer is more complicated as it is floppy in nature. The potential energy surface of the dimer is very flat and the interconversion barrier between the two isomers is predicted to be only about 0.1 kcal/mol.[8] The energy separation between the TS and PD isomers is calculated to be around 0.2 kcal/mol calculated at the CCSD(T) level of theory.[9] Recent calculations show that the TS structure should be the global minimum of the PES of the benzene dimer and that it is only slightly lower in energy than the PD one. Due to this particularly flat PES, the benzene dimer is used as a benchmark system for new theoretical approaches.[10] The importance of looking at the free energy change has been realized as well, and the recent on the fly ab initio molecular dynamics simulation predicts that both PD and TS structures should be present at 10 K.[14]

Even though benzene is a nonpolar molecule, the benzene dimer was found to be polar using a molecular beam deflection study, indicating the TS structure.[15] Law et al. had measured the optical absorption spectra of the first excited singlet state of the benzene dimer and reported that the dimer structure could be PD.[16] Bornsen et al.[17] studied the isotopically mixed dimers in the S_1 electronic state and suggested that the dimer displays a V-shaped structure. However, almost all the experimental results after these have supported only the TS structure of the benzene dimer. Hanson et al.[18] performed Raman-vibronic double resonance technique and reported that the benzene dimer consists of two unequivalent sites, indicating a T-shaped structure. Their results also suggest that the benzene moiety in the top is free to rotate around its C_6 axis. The same group had recorded the intermolecular stretches of the dimer and other bands were assigned to some of the intermolecular motions.[19] In the same year, Arunan and Gutowsky[20] reported the microwave spectra of the benzene dimer and provided unambiguous evidence for the T-shaped structure. The observed spectrum could be fit as a symmetric top confirming the prediction by Hanson et al. of nearly free rotation of benzene in the dimer. Microwave spectrometers are sensitive only to polar molecules and so the presence or absence of other nonpolar isomers like PD cannot be confirmed. Recently, Erlekam et al.[21] measured the IR spectra of the benzene

Special Issue: Pavel Hobza Festschrift

Received: May 18, 2011
Revised: August 8, 2011
Published: September 20, 2011

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Table 1. Experimental Conditions Used for the Investigation of the Benzene Dimer[a]

expt conditions	P_0 hPa	P_b hPa	Q(He) slm	Q(C_6H_6) slm	T_{rot} (K)	number of scans (LR)	number of scans (HR)
b	860	0.145	50	0.5 (0.99%)	~21	250	
c	1430	0.350	140	0.5 (0.35%)	~10	1100	800
d	1450	0.361	140	0.89 (0.6%)		750	

[a] P_0: reservoir pressure. P_b: background pressure. Q(He): flow rate of helium (carrier gas). Q(C_6H_6): flow rate of benzene. T_{rot}: rotational temperature of benzene in the expansion. LR and HR represent low and high resolutions, respectively. Expt conditions *b* are found to prevent clustering while expt conditions *c* limit the clustering to dimer.

dimer using ion dip spectroscopic technique and their interpretation of the observed spectrum indicated that the dimer is T-shaped. Clearly, most of the existing experimental data positively identify the presence of the TS structure. However, none of them could rule out the presence of PD structure.

Bare benzene has four C−H stretches ν_{13}, ν_{20}, ν_7, and ν_2. In that only ν_{20} is IR allowed, ν_7 and ν_2 are Raman active, and ν_{13} is neither IR nor Raman active. When symmetry is lowered on dimerization, all four bands are IR allowed. The signatures of these bands should be different for the PD or TS structure. Moreover, if rotationally resolved IR absorption spectrum can be recorded, the PD and TS structure could be positively identified. Thus, a careful analysis of the low and high resolution IR spectrum of the dimer in the C−H stretch regions would give valuable information about its structure. The direct infrared spectrum would be a suitable technique to study the presence of various isomers of the dimer formed by adiabatic cooling. However, as the shifts in band positions are expected to be small, recording the absorption spectrum of the dimer has been a big challenge. In this work, the benzene dimer was formed in a planar free jet expansion and its IR spectrum was recorded in the CH spectral range by carefully choosing the jet conditions. Some of the bands that are forbidden in the monomer could be observed in our experimental spectrum of the dimer. The observation of these bands indicates a reduction of symmetry, pointing out again to the T-shaped structure.

II. EXPERIMENTAL SECTION

The experimental setup is fully described elsewhere.[22] Benzene complexes are formed in a planar free jet expansion using a slit nozzle[22] supplied with helium. Benzene (99.99%) was obtained from Aldrich and used without any further treatment. In the slit-jet experiment, a controlled amount of benzene is evaporated and mixed with the carrier gas using a Bronkhorst Controlled Evaporating and Mixing (CEM) system prior to being injected in the slit nozzle reservoir. The cluster size is monitored by varying both the pressure and the benzene/carrier gas concentration in the stagnation reservoir, that is, by monitoring the mass flow rate of carrier gas and benzene vapor injected into the slit. The 24 cm long slit nozzle is adjusted to its smallest width, around 15 μm, in order to achieve stagnation pressure up to 1400 hPa for a maximum continuous flow rate of 140 slm (slm = standard liter per minute, i.e., at 0 °C and 1 atm) permitted by the set of Roots blowers available in Rennes. The temperature of the slit reservoir and the gas inlet tubing is regulated to some 20 °C higher than the one corresponding to the vapor pressure of benzene to prevent its condensation. The planar expansion is probed by a single pass infrared beam produced by a tungsten lamp a few millimeters downstream the nozzle exit. The diameter of the IR beam remains smaller than 1 cm along the absorption path length. The infrared absorption takes place before the injection of the infrared beam into the spectrometer Bruker IFS120HR. The spectra are recorded using a CaF_2 beam splitter and an InSb detector, cooled at liquid nitrogen temperature. This latter combination leads to the best signal-to-noise ratio in the CH stretching region located around 3 μm.

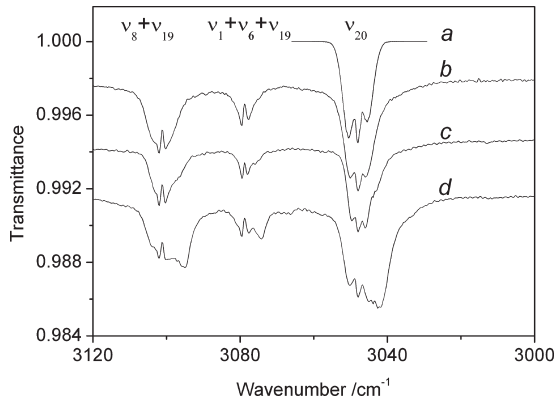

Figure 1. Jet-cooled spectra of benzene. The top trace is a simulation of the ν_{20} band of the monomer at 21 K. Spectrum *b* corresponds to the pure monomer. The red-shifted shoulders observable on each absorption bands of spectrum *c* are assigned to the dimer. Spectrum *d* corresponds to larger clusters.

III. RESULTS AND DISCUSSION

We measured the 3.3 μm infrared direct absorption spectrum corresponding to the C−H fundamental stretch region of jet-cooled benzene using the experimental conditions given in Table 1 and the corresponding low resolution spectra (0.5 cm^{-1}) are shown in Figure 1. Spectrum *b* corresponds to the benzene monomer. It was obtained by expanding the benzene vapor, with a reservoir pressure low enough (860 hPa) to prevent its condensation in the expansion. The band at 3047.9 cm^{-1} corresponds to the $\nu_{20}(E_{1u})$ mode of the C−H fundamental stretch. The ν_{20} state is in anharmonic resonance with the $\nu_1 + \nu_6 + \nu_{19}$ and $\nu_8 + \nu_{19}$ states located, respectively, at 3080 and 3101 cm^{-1}. The reservoir pressure was then increased up to the growth of new absorptions bands. These absorptions, attributed to benzene clustering, are red-shifted compared to the above-mentioned monomer bands. Spectrum *c* was recorded for a reservoir pressure of 1430 hPa corresponding to the minimum observed red-shift. A higher resolution spectrum (0.015 cm^{-1}) was also recorded under the same reservoir pressure conditions (see Figure 4). The ν_{20} band of the benzene monomer was simulated to extract the rotational temperature of the observed spectra *b* and *c*. For that purpose, the spectroscopic constants of ν_{20} were taken from the work of Domenech et al.,[23] and the simulation was performed using the software Pgopher.[24] The absorption lines were

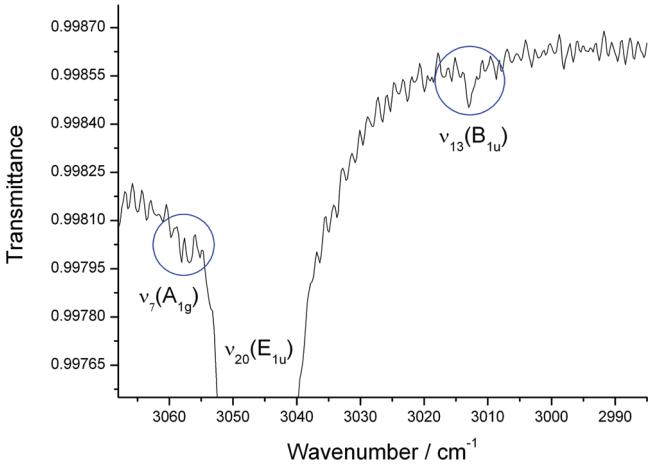

Figure 2. Encircled portions of the spectrum, recorded using experimental conditions *c* in Table 1, highlight the very weak ν_{13} and ν_7 bands of benzene dimer observed at 3012.9 cm^{-1} and around 3056 cm^{-1}, respectively. The observed spectrum corresponds to the minimum redshift observed for the ν_{20} band, obtained by tuning the jet conditions very carefully.

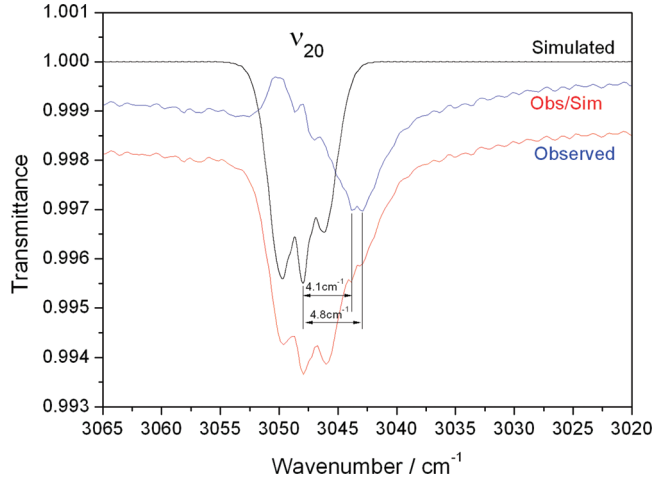

Figure 3. Enlarged view of the ν_{20} band region recorded using experimental conditions *c* in Table 1, favorable to the dimer formation (red curve). The black curve is a simulation of the monomer band at 10 K. The blue curve is the ratio of the observed to the simulated spectra. It is assumed to correspond to the ν_{20} band of the dimer and shows two distinct peaks red-shifted from the monomer by 4.1 and 4.8 cm^{-1}. The observed spectrum corresponds to the minimum redshift observed for the ν_{20} band, obtained by tuning the jet conditions very carefully.

convoluted by a line profile, taking into account both Doppler broadening and instrumental apparatus function (NBW apodization). As a result, a rotational temperature of about 21 K is associated with spectrum b, while spectrum c is a little bit colder, with a temperature of about 10 K.

As shown in Figure 1, spectrum *b* is correctly reproduced by the simulated spectrum at 21 K, thus, indicating the absence of significant clustering in the expansion that is explained by the low reservoir pressure (860 hPa) used in this case. On the other hand, a small red-shifted shoulder is observed in the ν_{20} band and in the two combination bands $\nu_8 + \nu_{19}$ and $\nu_1 + \nu_6 + \nu_{19}$ of the observed spectrum *c*, recorded using a higher reservoir pressure (1430 hPa) and the same injected flow of benzene. As the red-shift depends on the cluster size, the minimum red-shift is likely to be the signature of the dimer. Actually, spectrum *b* corresponds to the smallest shift ever obtained by tuning the reservoir pressure in our experiment. At a lower pressure, the red-shifted shoulders vanish, and at a higher pressure and higher benzene concentration, the red-shift increases (increase of the size distribution) together with the intensity of the shoulder (increase of the fraction of aggregated molecules), as it can be seen in spectrum *d*. Therefore, it is reasonable to assume that the extra absorptions visible in spectrum *b* correspond to the infrared signatures of the dimer of benzene. Along with the red-shifted shoulders, two very weak bands, enlarged in Figure 2, are observed. The first one is observed at 3012.9 cm^{-1} and the second one has two components at 3056.8 and 3058.1 cm^{-1} close to the detection limit of our apparatus.

The strongest ν_{20} band displays two weak features at 3043.8 and 3043.1 cm^{-1} (see Figure 3), which were revealed by removing the monomer contribution from spectrum *b* using the monomer simulation at 10 K. The R-branch intensity in the simulated spectrum of the monomer is higher than that of the P-branch. However, the experimental spectrum shows approximately equal intensity for both P and R branches. This behavior has been earlier observed by Snavely et al.[25] who reported the monomer spectrum recorded in jet-cooled condition and also the simulated spectra at different temperatures. However, the peaks in both P- and R-branches from the simulation and experiment are in very good agreement. All the observed bands are listed in the Table 2.

The very weak band we observed at 3012.9 cm^{-1} was first observed by Page et al.[27] They interpreted it as a combination band involving intermolecular vibrations. However, Erlekam et al.,[21] who observed more recently the band at 3012.4 cm^{-1} in the $(C_6H_6)(C_6D_6)$ dimer, reassigned it to the ν_{13} C−H fundamental stretch. We believe that our observation corresponds to the first direct absorption observation of the ν_{13} band of the benzene homodimer. The assignment of this band to the benzene−He dimer is ruled out as the C_6 axis is still preserved in the benzene−He dimer and symmetry of the benzene is not reduced. Hence, the ν_{13} band still remains forbidden in the benzene−He dimer. The difference of 0.5 cm^{-1} between our observation and the one of Erlekam et al. may be induced by the change in the interaction between the two partners (C_6H_6 and C_6H_6 in the former case and C_6H_6 and C_6D_6 in the latter case).

Similarly, the very weak doublet at 3056.8 and 3058.1 cm^{-1} is in close agreement with the work of Erlekam et al. This band corresponds to the ν_7 band, which is IR forbidden in the benzene monomer, but allowed on dimerization by symmetry reduction. Its double degeneracy, lifted on dimerization, leads to the doubling of the band. The presence of these two latter forbidden transitions implies that at least one of the molecules forming the dimer is of lower symmetry compared to the monomer. We did not observe the ν_2 band reported on the study of Page et al.[26] and Erlekam et al.[21] We believe that this band is buried in the combination band $\nu_1 + \nu_6 + \nu_{19}$. However, we should mention that this band was observed by us in larger homobenzene clusters for which the red-shift is more pronounced.[27]

The two peaks characterizing the ν_{20} band are red-shifted by about 4.1 and 4.8 cm^{-1} from the monomer band. Page et al. had observed a smaller red-shift of about 1−2 cm^{-1},[26] while Erlekam et al.[27] had observed red-shifts between 1.9 and 4.3 cm^{-1}, depending on the site of the C_6H_6 molecule in the dimer (top or stem). Our observed values seem then globally consistent with

Table 2. Summary of the Observed Band Positions of the Monomer and the Dimer. [a]

vibrational mode (Wilson numbering)	vibrational frequencies of benzene monomer (cm^{-1})	vibrational frequencies of benzene dimer (cm^{-1})			
		$(C_6H_6)^S(C_6D_6)^T$, ref 21	$(C_6D_6)^S(C_6H_6)^T$, ref 21	$(C_6H_6)_2$, ref 26	$(C_6H_6)_2$, this work
$\nu_{13}(B_{1u})$[b]	3015	3012.4		3014	3012.9
$\nu_{20}(E_{1u})$	3047.9	3044	3043.6	3047	3043.8
		3045.6	3046		3043.1
$\nu_7(E_{2\,g})$[b]	3056.7	3056.2			3056.8
		3057.3			3058.1
$\nu_2(A_{1\,g})$[b]	3073.9	3070.9		3072	

[a] Modes marked by an asterisk are inactive in the infrared for the monomer. A hyphen represents an unobserved transition. (ref 21 is the work by Erlekam et al. and ref 26 is the work by Page *et al.*). [b] Represents the monomer frequencies which are forbidden and these are from ref 21 as well. In columns 3 and 4, S and T stand for stem and top.

the work of Erlekam et al. It may be noted that the ν_{20} band is IR allowed in the monomer and it is doubly degenerate. Considering the T-shaped dimer, the degeneracy is lifted in the stem molecule producing the splitting of the ν_{20} band in to two components. On the other hand, in the top molecule, the C_6 symmetry is still preserved and the degeneracy is not lifted. Hence, on the whole, for T-shaped homodimers, one should observe three bands. This has not been observed in our spectra due to the limited experimental resolution of 0.5 cm^{-1} used in the present work. We tentatively assigned the band at 3043.8 cm^{-1} to the top molecule and the band at 3043.1 cm^{-1} to the stem molecule (this assignment was already proposed by Erlekam[28]). Indeed, it is well-known that the hydrogen bond donor is associated with a more pronounced red-shift. For the T-shaped benzene dimer, the stem molecule can be considered as the hydrogen bond donor and the π electron cloud of the top molecule can be considered as the hydrogen bond acceptor. Earlier, a blue shifting hydrogen bond was proposed for the T-shaped benzene dimer by Hobza and co-workers.[11,12] Following the work by Erlekam et al., Hobza's group has shown that the T-shaped structure that shows blue-shift is really a saddle point. The real minimum, which is slightly tilted, does show red-shift.[13] However, the energy difference between the T-shaped structure and the tilted minima, occurring on both sides, is rather small (0.16 kcal mol^{-1}) and the experiment may only reveal an average. In our work, we did not observe any blue shift of the ν_{20} band caused by such "antihydrogen bonding". However, Hobza's observation of a blue-shift in benzene dimer resulted in widespread interest in blue-shifting hydrogen bond and many real examples have since been found.[29]

The recording of a higher resolution spectrum (0.015 cm^{-1}) in the ν_{20} band region was attempted to observe some rotational features of the dimer. The resulting spectrum is shown on Figure 4. All the partially resolved rotational features could be attributed to the monomer on the basis of a simulation performed using the spectroscopic constants given by Domenech et al.[23] Unfortunately, the dimer spectrum remains unresolved, forming a dip in the observed spectrum indicated by the encircled part in the Figure 4.

As mentioned earlier, ab initio calculation performed by the on-the-fly molecular dynamics simulation based on DFT-D method indicates that at 10 K, which is our experimentally observed temperature, both the PD and TS structures exist and at higher temperatures the TS structure is dominant.[14] To verify, if any of the existing peaks in the observed infrared spectrum could result from the PD structure, it was decided to calculate the infrared

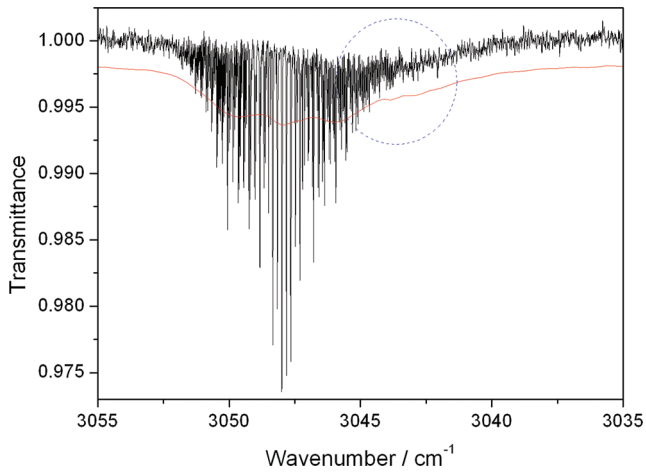

Figure 4. Comparison of high resolution and low resolution spectra of the benzene dimer recorded at same experimental conditions (conditions *c*) optimizing the dimer formation. The encircled part denotes the unresolved dimer absorption. The observed spectrum corresponds to the minimum redshift observed for the ν_{20} band, obtained by tuning the jet conditions very carefully.

spectrum for both TS and PD structures. The infrared intensities for the various C−H stretching modes of the two benzene dimers (TS and PD) as well as of the monomer presented in Table 3 have been determined by one of us following a Density Functional Theory methodology consisting of DFT calculations corrected by a nonscaled empirical dispersion term (DFT-D).[30,31] This methodology has been used combined[31] with a revised version of the PBE correlation functional, a LYP exchange functional, and a Dunning's correlation consistent cc-pVTZ basis set to both optimize the geometries of the two dimers and the monomer and to calculate their IR vibrational spectra. More details concerning these calculations and the associated references can be found in.[31] The frequencies are harmonic and unscaled and so these are primarily used for comparison of the monomer and the TS/PD values.

These calculations do confirm the small red-shift predicted for ν_{13} for the TS, slightly tilted. They reveal for the PD structure very low intensity for the ν_{13} band, preventing its detection in our experiment even if it is formed in the supersonic expansion. Our results indicate that the observed spectrum positively identifies the T-shaped structure of the benzene dimer, in complete agreement with the work of Erlekam et al. However from the low

Table 3. Summary of the DFT-D Calculated Infrared Band Positions and Intensities for the Benzene Monomer and the TS and PD Dimers[a]

			T-shaped dimer					
	benzene monomer		stem		top		PD dimer	
vibrational mode (Wilson numbering)	frequency	intensity	frequency	intensity	frequency	intensity	frequency	intensity
$\nu_{13}(B_{1u})^*$	3071.1	0.0	3069.6	1.7	3072.1	0.1	3069.9	0.2
							3070.6	0.0
							3095.2	0.6
$\nu_{20}(E_{1u})$	3095.4	54.0	3097.7	55.3	3095.2	28.3	3095.5	90.3
	3095.7	54.0	3103.2	17.8	3096.6	45.0	3096.6	76.9
							3096.9	7.8
							3078.4	0.4
$\nu_7(E_{2\,g})^*$	3079.0	0.0	3076.9	2.2	3080.5	0.0	3078.7	2.8
	3079.4	0.0	3085.6	31.4	3081.3	0.2	3081.6	4.0
							3082.0	2.4
$\nu_2(A_{1\,g})^*$	3105.8	0.0	3130.0	3.8	3107.0	0.4	3107.7	0.2
							3108.2	7.1

[a] Modes marked by an asterisk are inactive in the infrared for the monomer. The frequencies are in cm^{-1} and the intensities are in km/mol.

resolution spectrum, we cannot confirm or rule out the presence of PD structure. The high resolution spectrum attempted did not have enough sensitivity to resolve the dimer transitions. Hence, the sensitivity of the present technique is not sufficient to observe the PD structure, even if it exists. We are planning experiments at SOLEIL (French Infrared Synchrotron Radiation Facility) to record the high-resolution rotationally resolved IR spectrum, which should be able to identify the PD structure should it exist.

IV. CONCLUSION

The direct absorption infrared spectrum of the benzene dimer formed in a free-jet expansion was recorded in the 3.3 μm region. Using direct absorption technique, for the first time, the C−H stretching fundamental modes ν_{13} and ν_7 corresponding to the IR forbidden modes in the bare benzene are observed along with the IR allowed ν_{20} mode. All three of these observed modes are found to be red-shifted. The presence of the ν_{13} mode indicates that the symmetry is reduced in one of the benzene molecules in the dimer, thus, supporting a T-shaped structure, in agreement with the previous work of Erlekam et al.

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ACKNOWLEDGMENT

The authors would like to acknowledge funding from the Indo-French Centre for the Promotion of Advanced Research (Project Number 3405-3, implemented by Dr. B. Rowe and Prof. E. Arunan). The DFT-D calculations were done using HPC resources from GENCI-[CCRT/CINES/IDRIS] (Grant 20010-[x2010085116]). Prof. K. P. J. Reddy, Dr. B. Rowe, Dr. Gopalkrishna Hegde, and Prof. G. Jagadeesh are warmly acknowledged for helpful discussions on the experimental methods.

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NOTE ADDED IN PROOF

Though Hobza's initial prediction of a blue-shift for benzene dimer has not been experimentally found, his prediction led to the observation of blue-shift in several hydrogen bonded systems. This has significantly contributed to a new definition of hydrogen bond formulated by an IUPAC task group recently.[32]