The infrared absorption spectrum of the gas phase neutral benzoic acid monomer and dimer

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The IR absorption spectrum of the jet-cooled benzoic acid monomer and dimer have been recorded throughout the 500–1900 cm^{-1} range via ion dip spectroscopy. Both spectra show a wealth of vibrational modes and the monomer spectrum is remarkably different from that of the dimer. Density functional theory calculations show quantitative agreement with the experimental data. The C–O–H out-of-plane bending vibration in the dimer is poorly reproduced in the theoretical calculations and a more accurate description of the doubly hydrogen bonded structure is therefore still needed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1622657]

I. INTRODUCTION

Over the last decade a substantial number of experiments have been performed to investigate the structure of isolated molecules of biological interest. These studies include the pioneering spectroscopic work of the Levy and Simons groups on, among others, amino acids in the gas phase[1–4] and of De Vries on gas phase nucleobases.[5] These studies are very important as they address the fundamental properties of isolated molecules by eliminating such influences as the aqueous environment in which they are usually found. In nature, molecules are frequently attached to other species (such as the water molecules mentioned before) by hydrogen and/or van der Waals bonding. The most notable example of this is the double stranded helix of DNA, which is bonded through numerous hydrogen bonds. It would now also be of interest to study the effects of bonding on the structure of individual subunits. It has been concluded that bonding solely by dispersive forces can result in almost no conformational changes to the different constituents.[6] For hydrogen bonded molecular systems, however, the structure of the individual monomer units might be significantly altered.

Studies involving (doubly) hydrogen bonded systems include investigations of the pairing configurations of nucleic acid base pairs[7–10] and some of their analogues[11–14] and of small acid dimer systems.[15–18] Some of these involve IR spectroscopy in the spectral region where the X–H (X=C,O,N, . . .) stretching fundamentals are found. A remarkable observation is the commonly found, broad, structured absorption around 3000 cm^{-1}, which is attributed to strong mixing between the X–H stretching fundamental and bending overtone modes.[11,15,16] Finally, Gerhards *et al.* probed the C=O stretching vibrations of a protected amino acid dimer system.[19]

To study other vibrational modes a tunable source of IR radiation that allows one to probe the lower vibrational energy region is required. Here we present IR absorption spectroscopic studies with a free electron laser of the smallest aromatic acid, benzoic acid (BA), and its dimer. The BA dimer is doubly hydrogen bonded through the carboxylic acid group; it has a double minimum potential in the O–H stretching coordinate in which the hydrogen atoms of the OH group can switch synchronously between monomer units. Its high symmetry makes the BA dimer a very interesting system that can serve as a prototype for doubly hydrogen bonding, and it has been studied quite extensively using various techniques.[20–23] From a direct measurement of the IR spectra, one can draw conclusions on possible changes in the vibrational structure upon dimerization of individual BA monomer units. In an earlier study, Stepanian *et al.* recorded the matrix isolation spectrum of BA and found substantial differences between the IR spectra of the monomer and dimer.[24] It is unclear, however, what the influence of the

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argon matrix is in such studies and gas phase experiments are highly desirable.

II. EXPERIMENT

The experiment is performed in a molecular beam setup as used in previous studies,[25–29] and only a brief description is given here. A sample of benzoic acid is heated to a temperature of 75 °C and seeded into argon (stagnation pressure ∼1 bar). This mixture is then expanded through a 0.5-mm-diameter nozzle into vacuum via a pulsed valve. Gas pulses of about 50 μs duration are released at a repetition rate of 10 Hz. In the adiabatic expansion the internal degrees of freedom in the molecules are cooled and rotational temperatures of about 5 K are reached. The expansion conditions enable the formation of benzoic acid dimer clusters, which are internally cooled as well. About 4 cm downstream from the source the molecular beam is skimmed and enters a differentially pumped Wiley–McLaren type linear time-of-flight (TOF) mass spectrometer.

The molecules in the beam interact with incoming UV laser beams as well as with an IR laser beam at the crossing point of the mutually perpendicular molecular beam axis, laser beam axis, and TOF axis. Ions are produced in this region and accelerated toward a micro channel plate (MCP) detector, yielding mass spectra with a resolution of $M/\Delta M \approx 200$. The signal from the MCP detector is amplified and fed into a 10 bit, 100 Ms/s digital oscilloscope that is read out by a PC. Two digital delay/pulse generators are used to synchronize the molecular beam to the various laser sources.

For the measurement of the IR absorption spectra of the jet-cooled neutral benzoic acid monomer and dimer, IR ion dip spectroscopy (IR-IDS) is employed. Ions are produced from ground state molecules using a two-color ionization scheme. For this, the molecules are first excited to the vibrational ground state in the first electronically excited singlet state S_1 using a frequency doubled, Nd:YAG pumped pulsed dye laser (Rhodamine 6G, 5 ns pulses, spectral width around 0.4 cm^{-1}). The molecules are then ionized by the light from an ArF excimer laser (193 nm). A few microseconds before the excitation laser is fired, the IR laser interacts with the molecular beam. If a vibrational transition is induced by the IR light, molecular population is transferred from the ground state into an excited vibrational state, leading to a depletion of ground state molecules. This results in a dip in the number of produced benzoic acid ions. By measuring the ion yield of benzoic acid ions, while varying the wavelength of the IR laser, the ion-dip spectrum is obtained.

The IR radiation is produced at the Free Electron Laser for Infrared Experiments (FELIX) user facility at our institute.[30] The temporal output of this 10 Hz, pulsed laser system consists of a few-μs long burst (macropulse) of micropulses. The micropulse spacing within the burst is set to 1 ns. The micropulse duration is set to about 100 optical cycles, which results in a spectral bandwidth of approximately 0.5% (full width at half maximum) of the central frequency. The frequency range that can be covered extends from 40 to 2000 cm^{-1}, although only the range from 500 to 1900 cm^{-1} is used in the present study. Typically, energies of up to 100 mJ are reached in the macropulse.
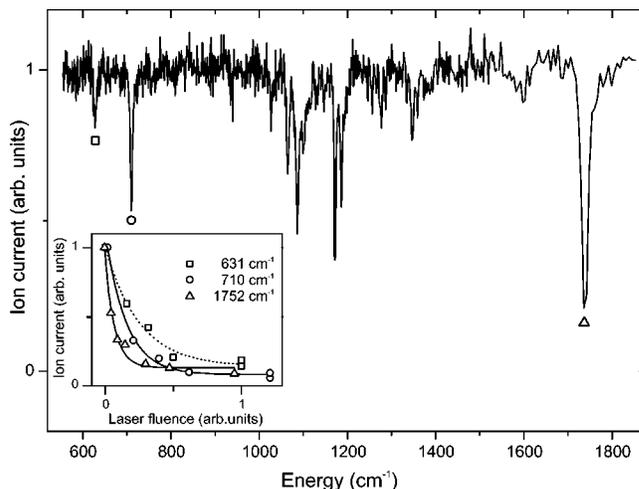

FIG. 1. Observed IR ion-dip spectrum of the benzoic acid monomer. In the inset the laser fluence dependence of the depletion of the resonances marked with symbols is shown.

For the monomer, the transition to the S_1 state has been reported at 35 955 cm^{-1}. The BA monomer undergoes a fast intersystem crossing from the S_1 state into the lowest electronically excited triplet state, T_1, a process that takes place on a sub-ps time scale.[22] The lifetime of the triplet state is rather long, presumably many microseconds. The ArF laser is fired some 100 ns after the excitation laser and thus ionizes all molecules from T_1. For the benzoic acid dimer, the $S_1 \leftarrow S_0$ transition is redshifted by 200 cm^{-1}. Interestingly, the benzoic acid dimer does therefore not exhibit the fast intersystem crossing to the triplet state that is so characteristic for the monomer and the benzoic acid dimers can be directly ionized out of the S_1 state. As the lifetime of the S_1 state of the BA dimer is only 9 ns, the ionizing laser is now fired almost simultaneously with the excitation laser.

III. RESULTS

A. The benzoic acid monomer

In Fig. 1 a typical ion dip spectrum of the BA monomer as recorded with FELIX is displayed. The trace shows the ion current signal due to BA monomers, corrected for source and UV laser intensity fluctuations. The signal is proportional to the population remaining in the vibrational ground state after interaction with the IR light. One can identify a number of resonances, of which a few show a population decrease of more than 50%. In particular, the resonance at 1752 cm^{-1} can result in a depletion as high as 80%. This is quite an interesting observation, as in the interaction of an isolated, nondegenerate two-level system with electromagnetic radiation population transfer is limited to 50% (in the non-Rabi limit). Apparently, there is an extra channel into which population is transferred after excitation to this vibrational state. One possibility is the occurrence of intramolecular vibrational redistribution (IVR), by which vibrational energy is redistributed over "dark" states that are iso-energetic with the excited vibrational state. Through this coupling, a more than 50% depletion of the ground state population is possible. Although it appears to be quite unlikely that the BA

monomer will exhibit IVR at energies below $1000\,\text{cm}^{-1}$ as molecules of this (still rather limited) size simply lack the required density of states that allows for IVR to take place, depletions of over 50% are reached even here. To be able to convert the observed ion-dip spectra to IR absorption spectra, one needs to know the maximum possible depletion signal at each frequency, i.e., one needs to know where the baseline of the spectrum is. In addition, one needs to verify that the observed depletion signals are single-photon events. In order to test whether the resonances are due to single-photon absorptions, the population decrease as a function of laser fluence is measured for a few selected resonances. This is done by varying the laser fluence with a set of fixed-value attenuators. The results of these measurements are displayed in the inset in Fig. 1, where the population decrease for the resonances at 631, 710, and $1752\,\text{cm}^{-1}$ is plotted as a function of laser fluence. In a single-photon excitation process the remaining population in the ground state is described by

$$a(\nu)+(1-a(\nu))\exp(-\sigma(\nu)I(\nu))=\exp(-\sigma(\nu)I(\nu))+a(\nu)[1-\exp(-\sigma(\nu)I(\nu))]$$

in which σ is the cross section, I the laser intensity and a the fractional population that remains in the ground state, all functions of frequency ν. As the observed curves are well described by this functional dependence it is concluded that we indeed deal with single-photon absorptions. In the high laser power limit, the population for all resonances converges to about 0.1. This could be intrinsic to the BA molecule, i.e., $a=0.1$, but is more likely explained by a slight misalignment of the laser beams, i.e., a nonperfect overlap of the FELIX beam with the UV laser beams.

To rule out a possible scheme where the vibrationally excited, electronic ground state molecule is resonantly ionized via a vibrationally excited level in the S_1 state, which could lead to a wrong IR intensity or to an altogether absence of a particular resonance, the experiment is also performed with a slightly different detection scheme. The IR-IDS spectra that are measured with the first UV laser tuned to a vibrationally excited level in the S_1 state (at $350\,\text{cm}^{-1}$ from the S_1 origin) show identical depletions, suggesting that such an alternative detection scheme is highly unlikely.

We can now directly interpret the IR-IDS data as a measurement of the IR absorption cross section. In the following we present results as relative cross sections, as this allows for a direct comparison to theoretical calculations. To obtain relative cross sections from the ion dip spectra, the ion signal is corrected for source and UV laser fluctuations to obtain a (nearly) constant baseline ion signal, and subsequently the natural logarithm from these data is taken, and normalized to the (relative) FELIX fluence. In Fig. 2, the IR absorption spectrum of the BA monomer obtained in this manner is shown. The observed frequencies of a total of nineteen spectral lines are indicated in the figure and are also listed in Table I. The absolute frequency accuracy is about $3\,\text{cm}^{-1}$ at the low frequency end of the spectrum, gradually deteriorating to $12\,\text{cm}^{-1}$ at the high frequency end. The linewidth observed in the spectrum is almost exclusively determined by the bandwidth of the laser, and is some 0.5% of the FELIX frequency.

In the lower part of Fig. 2 a calculated IR spectrum is shown (stick spectrum). Frequencies and intensities of IR
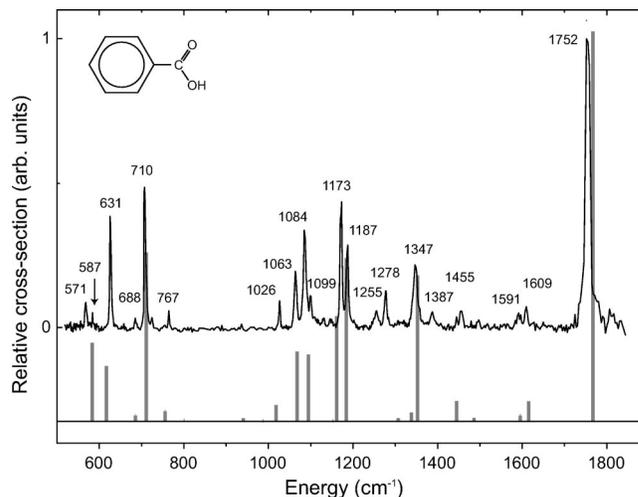

FIG. 2. Observed IR absorption spectrum of the benzoic acid monomer, compared to the calculated IR spectrum (lower curve; stick spectrum).

active modes are determined from density functional calculations using the Becke3LYP functional with Dunning's D95(d,p) basis set, as implemented in GAUSSIAN 98.[31] The frequencies in the calculated spectra are scaled by a factor of 0.98 to show best agreement with experimental data. The calculated vibrational modes are visually inspected using viewing software. Both (scaled) theoretical line positions and a short description (where possible) of the fundamental IR active vibrations are given in Table I.

The theoretical and experimental spectra agree very well, both in line positions and intensities. In particular for the line intensities this might be considered rather remarkable. After all, different vibrational modes are expected to exhibit different IVR rates. These different IVR rates would then seriously influence the extracted relative cross sections. The good agreement between the theoretical and experimentally obtained spectra suggests that such influences are minimal, however. This is most likely explained by efficient vibrational redistribution, i.e., rapid IVR, on our experimental time scale.

The dominant mode in both spectra is the one experimentally found at $1752\,\text{cm}^{-1}$ which is readily assigned to the $C=O$ stretching vibration. Most of the other resonances are also unambiguously assigned to fundamental vibrations. There are still two spectral regions where the agreement between theory and experiment is less than perfect. The first region is that between 550 and $650\,\text{cm}^{-1}$, where three distinct resonances are found whereas only two fundamentals are expected. It is interesting to note that the two strongest observed modes have line positions that are considerably further apart than predicted. Such behavior could be the signature of a Fermi resonance, however, the two strong theoretical modes are of different symmetry, which rules out a Fermi coupling between the two of them.[32] The weak but clearly observable resonance at $588\,\text{cm}^{-1}$ could nevertheless still be the result of a Fermi resonance with one of the fundamentals. A possible set of fundamentals that may combine to serve as a partner in the Fermi interaction are calculated fundamentals at 157 and $424\,\text{cm}^{-1}$. The second discrepancy between

TABLE I. Observed and theoretical values for the IR active modes of the benzoic acid monomer and dimer (in cm^{-1}). Lines observed and attributed to either monomer or dimer from matrix isolation studies (Ref. 24) are listed as well.

Observed	Theory Line position intensity		Reference 24	Mode description
Monomer				
571	583	71	568	Out-of-plane C–O–H bend
587				
631	617	50	628	In-plane ring C–C–C bend
688	685	6	687	Out-of-plane ring C–C–H bend
710	711	152	711	Out-of-plane ring C–C–H bend (umbrella mode)
767	755	9	767	In-plane C–O–H bend, ring deformation
1026	1018	15	1027	In-plane ring C–C–H bend
1063	1068	63	1066	In-plane ring C–C–H bend
1084	1094	60	1086	In-plane ring C–C–H bend
1099			1100	
1173	1162	94	1169	C–C–H bend, C–O–H bend, both in-plane
1187	1183	147	1185	C–C–H bend, C–O–H bend, both in-plane
1255			1251	
1278			1275	
1347	1353	131	1347	C–C–H bend, C–O–H bend, both in-plane
1387			1383	
1455	1444	18	1456	C–C stretch, ring deformation
1591	1595	5	1590	C–C stretch, ring deformation
1609	1615	18	1606	C–C stretch, ring deformation
1752	1767	350	1752	C=O stretch, C–O–H bend
Dimer				
510				
540	543	130	547	Acid groups asymmetric rocking
664	659	45	670	Acid groups asymmetric scissor
682	681	15		Out-of-plane ring C–C–H bend
708	706	163		Out-of-plane ring C–C–H bend
797	799	22		Acid groups scissor, ring deformation
810	803	17		Out-of-plane ring C–C–H bend
962	1028	221	960	Out-of-plane acid group C–O–H bend
1022	1018	24		In-plane ring C–C–H bend
1066	1073	24		In-plane ring C–C–H bend
1126	1126	8		In-plane ring C–C–H bend
1176	1166	48		In-plane ring C–C–H bend
1243				
1269				
1297	1300	140	1297	C–C–H bend, C–O–H bend, both in-plane
1322	1324	687	1322	C–C–H bend, C–O–H bend, both in-plane
1432	1440	76	1430	C–C–H bend, C–O–H bend, both in-plane
1453	1446	199		C–C–H bend, C–O–H bend, both in-plane
1498	1490	50		C–C–H bend, C–O–H bend, both in-plane
1591	1593	51		C–C stretch, ring deformation
1618	1615	60		C–C stretch, ring deformation
1709	1710	956	1699	C=O stretch, in-plane C–O–H bend
1824				

theory and experiment is found between 1200 and 1300 cm^{-1}. As no fundamentals are expected in this region it is very likely that the resonances observed here are combination modes. A possible assignment for the resonance at 1278 cm^{-1} is the combination between the fundamental at 710 cm^{-1} and one of the modes participating in the (possible) Fermi resonance around 600 cm^{-1}. For the resonance at 1255 cm^{-1} various combinations between strong IR active modes and calculated low-lying vibrations could be responsible. As the latter have never been observed, a definite assignment is not possible.

It is noted that most resonances that are found in this work have been identified by Stepanian *et al.* in a matrix isolation (MI) spectroscopy experiment as well.[24] The MI

intensities differ somewhat from the present data, but in general good agreement is found. For completeness, the values determined via MI spectroscopy have been included in Table I.

B. The benzoic acid dimer

As in the case of the BA monomer, the ion dip spectrum of the BA dimer (not shown here) exhibits resonances that show depletions of up to 100%. The density of states for the dimer is considerably larger than that of the BA monomer, so that already at 500 cm^{-1} it seems feasible that rapid IVR can occur. It has been verified that the observed depletion signals result from a one-photon absorption process and the dimer
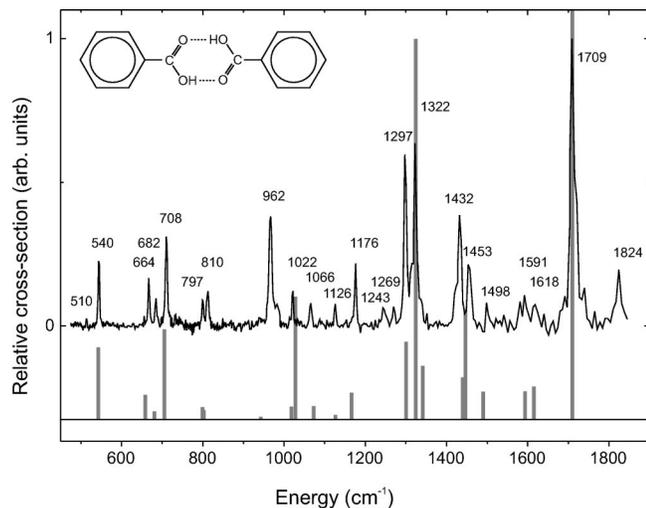
FIG. 3. Observed IR absorption spectrum of the benzoic acid dimer, together with the calculated IR spectrum (lower curve; stick spectrum).

data are therefore directly presented in the form of relative cross sections. They are derived from the ion dip spectrum in the same way way as for the BA monomer, as described in the previous section.

In Fig. 3 the IR absorption spectrum of the BA dimer is displayed. Below the experimental data, the corresponding theoretical spectrum is shown as a stick spectrum. The line positions are scaled with the scaling factor that gave the best match between theoretical and experimental spectra for the monomer, i.e., a factor of 0.98. It is clear from looking at the experimental data that the signal-to-noise ratio for the dimer spectrum is somewhat worse than for the monomer spectrum, which is solely due to the lower abundance of the dimer in the beam ($\sim 10\%$ relative to the monomer abundance).

The agreement between experimental and theoretical spectra is rather good. From a visual inspection of the modes, it is clear that most vibrations in the dimer are best described as either a symmetric or an antisymmetric combination of two monomer vibrations. Of these, only the latter have any significant IR intensity. As in the IR absorption spectrum of the BA monomer, most resonances are readily assigned to fundamental vibrations. The spectrum is dominated by a strong mode at 1709 cm^{-1} which matches the theoretical calculations very well, and which is assigned to the asymmetric C=O stretching vibration. Here, it is interesting to note that Gerhards *et al.* observed a considerably smaller shift of a C=O stretching vibration frequency upon dimerization, in an experiment involving a protected amino acid dimer system.[19] In the low energy region the agreement between theory and experiment is striking: with a single exception—the resonance at 962 cm^{-1}—all resonances between 500 and 1200 cm^{-1} are very well predicted, both in line positions and intensities. At higher energies, in the region between 1200 and 1700 cm^{-1}, line positions still match quite well, but intensities seem somewhat off. In the whole spectrum, two modes show clear discrepancies. One of these is the fairly strong resonance at 962 cm^{-1}. It seems quite likely that this resonance has to be assigned to the strong

mode in the theoretical spectrum at 1028 cm^{-1}. This mode is the asymmetric out-of-plane bending vibration of the O–H groups. As the hydrogen atoms are directly involved in the double hydrogen bond, it is not surprising that the theoretical calculated frequency is overestimated, as the harmonic approach that is used may no longer be valid. It also shows that the theoretical model has to be adjusted if one wants to reproduce hydrogen bonding interactions correctly. The second discrepancy is for the resonance at 1824 cm^{-1}. This resonance might result from a combination band of the C=O stretching vibration at 1709 cm^{-1} with a low frequency intermolecular stretching vibration, e.g., the one predicted at 120 cm^{-1}.

One can compare the data presented to here the ones obtained by Stepanian *et al.* in absorption spectroscopy of matrix-isolated BA.[24] In general, good agreement is found although more lines are found and unambiguously identified in the present study than in the MI experiment. In cases where BA monomer and BA dimer vibrational modes overlap, the dimer modes often escape observation in the MI experiments. This is avoided in the present gas-phase, mass-selective technique. The observed line positions are tabulated in Table I and a description of the modes is given. The MI data of Stepanian *et al.* are added for completeness.[24]

IV. CONCLUSIONS

The IR absorption spectra of the jet-cooled benzoic acid monomer and dimer have been recorded in the 500–1900 cm^{-1} region. These spectra were obtained using the method of IR ion dip spectroscopy. Due to the mass-selected detection scheme, one can directly compare the vibrational structure of the monomer to that of the dimer, and it is seen that dimerization leads to a dramatic change in the vibrational structure. The theoretical methods used to calculate the IR absorption spectrum proved to be very accurate in this mid-IR spectral region, in contrast to earlier studies in the O–H stretching region. The fact that theoretical calculations clearly fail in the prediction of hydrogen bond affected vibrations, in this study demonstrated for the O–H out-of-plane bending vibration in the dimer, leads to conclude that some fine-tuning in the methods to describe hydrogen-bonded systems is imperative.

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