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

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(Received 6 August 2003; accepted 8 September 2003)

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
The temporal output of this 10 Hz, pulsed laser is 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-\(\mu\)s 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.
monomer will exhibit IVR at energies below 1000 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 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

\[ a(n) + (1 - a(n)) \exp(-\sigma(n) l(n)) = \exp(-\sigma(n) l(n)) + a(n) \left[ 1 - \exp(-\sigma(n) l(n)) \right] \]

in which \(\sigma\) is the cross section, \(l\) the laser intensity and \(a\) the fractional population that remains in the ground state, all functions of frequency \(n\). 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 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 measure 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 cm\(^{-1}\) at the low frequency end of the spectrum, gradually deteriorating to 12 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 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 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 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 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 cm\(^{-1}\). The second discrepancy between

![FIG. 2. Observed IR absorption spectrum of the benzoic acid monomer, compared to the calculated IR spectrum (lower curve; stick spectrum).](image-url)
as 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 \textit{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.

\textbf{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

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|}
\hline
\textbf{Observed} & \textbf{Theory} & \\
Material & Line position & Intensity & Reference 24 \\
\hline
\textbf{Monomer} & & & Mode description \\
571 & 583 & 71 & 568 Out-of-plane C–O–H bend \\
587 & 617 & 50 & 628 In-plane 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–H bend, ring deformation \\
1591 & 1595 & 5 & 1590 C–C–H bend, ring deformation \\
1609 & 1615 & 18 & 1606 C–C–H bend, ring deformation \\
1752 & 1767 & 350 & 1752 C=O stretch, C–O–H bend \\
\hline
\textbf{Dimer} & & & \\
510 & 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 & & & \\
\hline
\end{tabular}
\caption{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.}
\end{table}
data are therefore directly presented in the form of relative cross sections. They are derived from the ion dip spectrum in the same 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 (~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 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 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.

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.

ACKNOWLEDGMENTS

This work is part of the research program of “Stichting voor Fundamenteel Onderzoek der Materie (FOM),” and it is in part financially supported by the Council for Chemical Sciences (CW) both of which are financially supported by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek” (NWO).
