

Low Energy Modes of the Hydrogen-Bonded Dimer of Benzoic Acid

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Hydrogen bonding in isolated, cooled dimers of benzoic acid is explored following preparation in a free jet expansion. Analysis of the laser excitation spectrum in the low energy region allows for the identification of the modes involved in hydrogen bonding in the excited state of the dimer, and cluster formation is noted between the ground state dimers. Van der Waals complexes of the dimer with rare gas atoms are also identified. Assignments of the observed dimer modes have been made and the results are compared with previous studies in solution and matrices and with normal mode analyses.

INTRODUCTION

Intermolecular hydrogen bonding has been previously examined using a wide variety of spectroscopic techniques.^{1–6} Complexation in the gas phase, in solution, in glassy matrices and in single crystals has been considered. The spectral resolution of the vibronic structure has, except in studies of single crystals at low temperatures,⁴ been rather limited. Solvent effects and matrix packing effects have often resulted in appreciable spectral shifts and in subtle specific perturbations. Comparison of these studies with calculations³ has proven difficult. To avoid such complications we have recently applied the technologies of free jet expansions^{6–9} and tunable lasers to explore the high resolution excitation spectrum of cooled dimers of hydrogen-bonded benzoic acid.⁶ In this report we will now present information on the low energy region of the spectrum, $\approx 150\text{ cm}^{-1}$ to the higher

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and lower energy of the 0-0 transition. In these new studies we have varied the nature of the cooling process to help distinguish the character of vibronic hot bands, van der Waals complexes with rare gas atoms and the true hydrogen bonding modes of the dimer.

In previous studies⁶ we surveyed the excitation spectrum to 1800 cm^{-1} and considered the assignments of the principal features of the d_0-d_0 (non-deuterated) dimer, the d_0-d_1 and d_1-d_1 (carboxy deuterated) dimer, and the d_5-d_5 (ring deuterated) species. In these excitation studies we obtain information on the excited state of the dimer. The free jet expansion of benzoic acid results in ground state dimer formation, in agreement with solution, matrix and single crystal studies.⁴ The formation of two strong hydrogen bonds results in a stabilization energy of approximately 16 kcal/mol ^{10,11} and this is sufficient to ensure production of the dimer at low temperature. In the free jet expansion we observe cooling of the rotational energies to several degrees Kelvin and vibrational cooling to 10-50 K, depending on the expansion gas partner and operating conditions. At these low temperatures the dimer is quite stable and we have not identified any features due to monomers. Given the strong directional character of the hydrogen bonds, a single planar configuration (C_{2h} symmetry) is formed and this is consistent with the available X-ray crystallographic¹² and spectroscopic data.^{4,6} The best evidence for dimer formation comes from studies of mixed isotopes of benzoic acid.^{4,6} Such studies will be presented in the Results section. The excitation spectrum of the cooled dimer corresponds to that of the perturbed monomer of benzoic acid. Excitation of the lowest electronic band at 280 nm, the so-called C band, corresponds to the $\pi^* \leftarrow \pi$ transition, similar to the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition in benzene.⁴

Our primary interest here is in the hydrogen bonding modes and low energy features of the dimer spectrum. Although strongly bound by the two hydrogen bonds, the monomers are only weakly electronically coupled. The interaction of the dipoles is severely limited by the orientation and separation of the benzenoid rings. The coupling is on the order of 0.3 cm^{-1} , as verified in simple calculations and by the observed splittings of the spectral features.⁴ Although many attempts have been made to resolve the low energy components in Raman and far-IR measurements,^{13,14} broadening and shifting in solution or in matrices present serious problems which may be easily overcome with the use of free jet expansion techniques.

EXPERIMENTAL

The free jet apparatus is described in more detail elsewhere.⁶ In brief, a $28 \times 44 \times 60$ cm chamber is evacuated using a 6 in diffusion pump backed by a 1000 l/minute mechanical pump. A pulsed valve (General Valve Corporation) with a 0.8 mm orifice is cycled at a repetition rate of 10-20 Hz and is held at a temperature of 100°C. Benzoic acid (Aldrich, 99.9% zone refined) or carboxy-deuterated benzoic acid (d_1), prepared as described elsewhere,⁶ are contained in a heated U-tube. Rare gases were passed through this tube into a heated transfer line and to the pulsed valve. Helium (99.997%, MG Scientific), neon (99.99%, Matheson), and argon (99.998%, Matheson) are used in these studies.

A Moletron DL II dye laser is pumped by a UV-24 nitrogen laser and the output is frequency doubled with a KHP angle-tuned crystal. Tunable UV radiation from 285 to 265 nm with a pulsewidth of ≈ 4 ns and linewidth of ≈ 1.5 cm^{-1} was obtained. The laser is mildly focused into the chamber through light baffles and crosses the pulsed free jet at a distance of ≈ 2.5 cm (30–40 nozzle diameters) from the expansion orifice. Laser induced fluorescence is viewed at the third right angle by a telescope using a 38 mm diameter, f/1, S1 quartz lens. For total fluorescence a Corning 0–53 cutoff filter is inserted before the EMI 9635QB photomultiplier.

A three channel boxcar integrator samples the total fluorescence signal, the excitation laser energy and a signal from a wavelength calibration etalon. Scanning of the dye laser and doubling crystal, collection of the data from the boxcar, and manipulation and storage of the data are handled by an HP9825A computer interfaced to a MINC and VAX computer. Absolute wavelengths are determined with a Cary 81 1-meter monochromator. Further details on the design and operation of our pulsed free jet are published elsewhere.⁶

RESULTS

The low energy spectral region of the jet-cooled benzoic acid dimer in He is presented in Figure 1. The first 150 cm^{-1} region of excitation above the electronic origin corresponds to the region where absorbance features due to the hydrogen bonding modes of the benzoic acid

dimer are expected to appear. In addition to a number of weaker features, the spectrum of Figure 1 is dominated by a large absorption band appearing at 58 cm^{-1} above the 0-0 band. Also apparent in Figure 1 are spectral features lying to the red of the electronic origin. These are due to formation of clusters of dimers and are not due to hot bands. The nature of these bands is considered further in the Discussion section.

Figure 2 depicts the low energy region of the spectrum for expansions in He, Ne, and Ar diluent gases. The degree to which a polyatomic is cooled depends directly on the choice of the diluent, with the efficiency of cooling increasing in the order $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$.⁹ These trends are appropriate for rotational cooling due to the low energies and close spacing of the levels. Vibrational cooling is more complex and depends on the nature of the mode and the

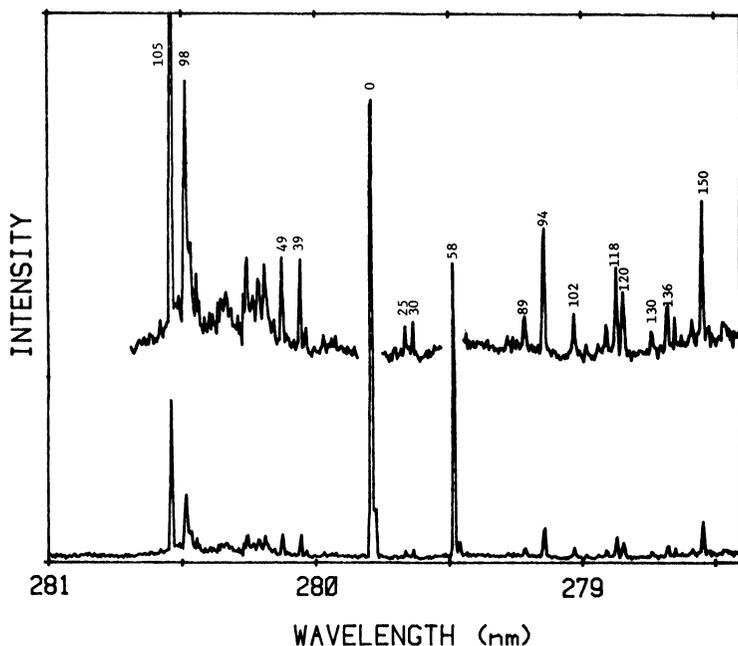


FIGURE 1 Low energy region of the excitation spectrum of the jet-cooled dimer of benzoic acid in 2300 torr He. The numbers above individual peaks show the position in cm^{-1} versus the 0-0 component and are taken from calibration with an etalon and are $\pm 2\text{ cm}^{-1}$. Upper spectrum is $4\times$ expansion.

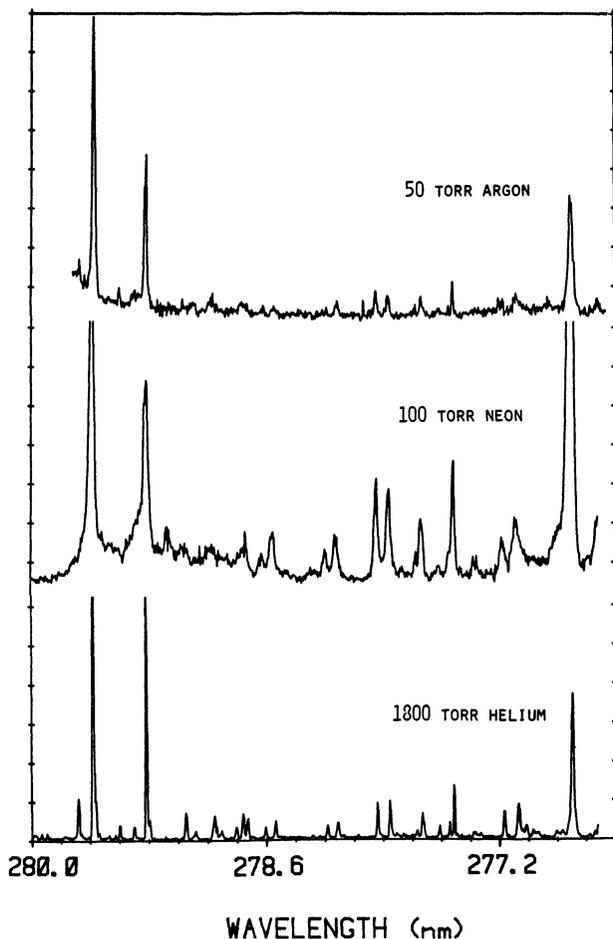


FIGURE 2 Low energy region of the excitation spectrum of the jet-cooled dimer of benzoic acid using 50 torr argon, 100 torr neon and 1800 torr helium.

expansion conditions.^{9,15} Although complexation of the benzoic acid dimer with a rare gas atom should be minimized with He as the carrier gas, the use of other diluents permits identification of these van der Waals complexes. Spectral features which are independent of the diluent gas must be considered as resulting from transitions of

the benzoic acid dimer itself, while those features dependent on the diluent gas can be systematically identified as being due to van der Waals complexes. From Figure 2 it is evident that virtually all of the low energy features of the benzoic acid spectrum are due to inherent molecular transitions and not to van der Waals complexes. Table I gives a listing of spectral features and the suggested assignments.

The spectrum of a mixture of 75% undeuterated (d_0) and 25% carboxy deuterated (d_1) benzoic acid is shown in Figure 3. The features to the red of the 0-0 transition are believed to be due to a dimer weakly bound to a second dimer. The structure is similar to that of the dimer and the four bands at -107 , -105 , -91 and -89 cm^{-1} are due to the $d_0^*-d_1$, $d_0^*-d_0$, $d_1^*-d_1$ and $d_1^*-d_0$ electronic species, respectively. Here the star indicates the member of the dimer that is excited. In the mixed dimer of d_1 and d_0 , either component can be excited and, due to the weak nature of the electronic coupling, the electronic energy exchange is slow on the timescale of the experiment. The relative intensities of these four peaks in Figure 3 do not appear to scale

TABLE I
Low energy spectral features of the d_0 benzoic acid dimer

Peak (cm^{-1}) ^a	Intensity	Assignment
-105	<i>s</i>	tetramer
-98	<i>m</i>	tetramer
-49	<i>w</i>	tetramer
-39	<i>w</i>	tetramer
2	<i>vs</i>	0-0 band
25	<i>vw</i>	van der Waals (He)
30	<i>vw</i>	H-bond
58	<i>s</i>	ν_2^{H} H-bond
61	<i>vw</i>	H-bond?
89	<i>vw</i>	H-bond?
94	<i>w</i>	H-bond
102	<i>vw</i>	H-bond
118	<i>w</i>	$2\nu_2^{\text{H}}$
120	<i>w</i>	Ph-COOH torsion
130	<i>vw</i>	ring torsion
136	<i>vw</i>	ring torsion
150	<i>w</i>	d_5 0-0 band (impurity)

^a Accuracy of wavenumbers relative to the electronic origin is ± 2 cm^{-1} .

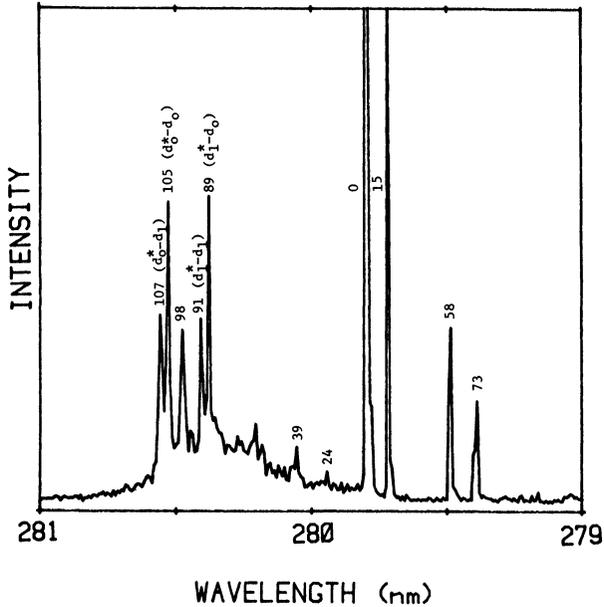


FIGURE 3 Low energy region of the excitation spectrum of a mixed sample of approximately 75% d_0 and 25% d_1 isotopic species of benzoic acid in 2300 torr He. See discussion in text.

properly, due largely to error introduced by normalizing spectral features to laser power. Due to doubling crystal tracking error, the signal/reference ratio is overestimated in regions of very small reference values, as evidenced by the hump in the baseline of Figure 3. The other regions of this spectrum, where doubling is more efficient, relative peak heights are exactly as would be expected for a 75% d_0 and 25% d_1 benzoic acid mixture (19:56:6:19 or roughly 3:9:1:3).⁶

DISCUSSION

To a good approximation, the vibrational modes of the benzoic acid dimer may be divided into essentially two types—internal modes

(monomer modes) and external modes (H-bonding modes). Due to the fact that the electronic coupling of the monomer units is weak, the electronic excitation may be regarded as primarily localized on one monomer unit of the dimer⁴. Hence, the internal modes of the dimer are essentially perturbed monomer modes. When two monomers bond to form a dimer, however, six new (external) vibrational modes are also created from the three rotations and three translations which are lost upon complexation. These six new external modes involve relative motions of one monomer with respect to the other and are therefore called the hydrogen bonding modes. The three Raman active hydrogen bonding modes may be thought of as being relative *translations* of the monomer units. They are the ν_1'' (O \cdots H stretch), ν_2'' (O—H \cdots O in-plane bend) and ν_6'' (O—H \cdots O out-of-plane bend). The three infrared active hydrogen bonding modes, which may be considered as being relative *rotations* of the monomer units, are the ν_3'' (O \cdots H stretch + O—H \cdots O in-plane bend), ν_4'' (O—H \cdots O out-of-plane bend) and ν_5'' (ring torsion). We have considered the vibrational assignments of the higher energy internal modes in a previous paper⁶, and now wish to consider the low energy hydrogen bonding modes in more detail.

In Figure 1, one low energy vibrational feature located at 58 cm^{-1} to the blue of the 0-0 band is particularly strong. We feel that this band is associated with the ν_3'' hydrogen bonding mode for essentially three reasons. It has been shown that the localization of electronic excitation on one monomer unit within the dimer serves to strengthen the acceptor hydrogen bond while weakening the donor hydrogen bond.^{4,15} The resulting deformation of the molecule—a compression of one hydrogen bond and a stretching of the other—is best described as a ν_3'' dimer mode vibration. It is not unreasonable, then, to suspect that the ν_3'' dimer mode might be important in the spectrum. Secondly, the 58 cm^{-1} band tends to appear in combination bands with many of the observed monomer modes, and particularly with those modes which involve substantial in-plane motion of the carboxyl group. From a physical viewpoint, a ν_3'' type dimer mode should be easily capable of combining with internal modes involving a similar carboxyl group motion.

Our final reason for associating the 58 cm^{-1} band with the ν_3'' dimer vibration is that it appears as the most prominent low-energy feature. Our recent work on the resolved fluorescence emission from the

dimer¹⁶ also shows a prominent low-energy feature that occurs at 114 cm^{-1} . It is therefore quite probable that this 114 cm^{-1} band is due to the same dimer vibration (in the ground state) as is the 58 cm^{-1} band (in the excited state), since vibrational overlap factors would not be expected to be terribly different for electronic absorption versus emission. Normal mode calculations by Meshitsuka *et al.*¹³ and, more recently, by Klausberger, Furic and Columbo¹⁴ support this assignment. Our observed value compares most favourably with the predicted values of Meshitsuka, who calculated the ν_3'' vibrations of benzoic single crystals to be 108 and 110 cm^{-1} , and compared these with bands observed in the infrared at 104 and 106 cm^{-1} , respectively. (The dimer exists in two orientations in the benzoic crystal lattice giving rise to two symmetries and, hence, two frequencies.) Agreement with our gas phase value is extremely good, and implies a very small lattice effect on the ν_3'' vibration, an implication which might be reasonable for an in-plane vibrational mode. It is also not unreasonable for the ν_3'' vibration to change from 114 cm^{-1} in the ground state to 58 cm^{-1} in the excited state since this mode would be most affected upon electronic excitation.

We would now like to consider some of the weaker spectral features in Figure 1. Although these are subject to much greater uncertainties, studies in different diluent gases (Figure 2) at different stagnation pressures allow for identification of these weak features as due to dimer vibrations or van der Waals complexes.

Blue shifted bands relative to the electronic origin at 30 cm^{-1} , 94 cm^{-1} and 102 cm^{-1} may be attributed to the benzoic acid dimer hydrogen bonding modes of the excited state. It is also probable that a 61 cm^{-1} mode, which appears as a sideband on the 58 cm^{-1} mode, is also a hydrogen bonding mode. Assignment of these bands to specific hydrogen bonding modes is not feasible at present.

The spectrum of Figure 3 reveals spectral splittings of the red-shifted bands resulting from the dimers formed from 75% undeuterated (d_0) and 25% carboxydeuterated (d_1) benzoic acid. This splitting was previously noted for the electronic origin of benzoic acid⁴ and, more recently, for vibrational modes in the excited state.⁶ As before, the carboxyl group deuterium produces an anomalous isotope shift. In Figure 3 we observe two doublets to the red of the 0-0 band at $107, 105\text{ cm}^{-1}$ and $91, 89\text{ cm}^{-1}$ which are due to excitation to the $d_0^*-d_1$, $d_0^*-d_0$ and $d_1^*-d_1$, $d_1^*-d_0$ electronic species, respectively,

of the benzoic acid dimer complexed to one or more additional dimers. These features can be induced at high stagnation pressures regardless of the diluent and are not hot bands. Their location is independent of the rare gas component and therefore they are not due to van der Waals complexes with rare gases. The $d_1^*-d_0$ feature exhibits the normal blue shift from the $d_0^*-d_0$ feature due to the O—D bond. Note, however, that the $d_0^*-d_1$ and $d_1^*-d_1$ features are red-shifted by about 2 cm^{-1} with respect to the $d_0^*-d_0$ and $d_1^*-d_0$ features, respectively. This small red shift related to the fact that in the electronically excited state, the hydrogen bond to the carbonyl oxygen of the excited half of the dimer becomes stronger. The contribution of the O \cdots D acceptor hydrogen bond to the zero point energy is therefore greater in the excited state than in the ground state and a red shift is thus observed.

Although most of the other spectral features of Figure 3 reveal the normal $15 \pm 2\text{ cm}^{-1}$ blue shift (note pairs at $[-39, -24]$, $[0, 15]$, and $[58, 73]\text{ cm}^{-1}$) only the features associated with the higher order complex, probably the tetramer, exhibit the red shifted character as well. The features associated with the tetramer are particularly interesting. These features mirror similar bands in the free dimer and show that the basic nature of the dimer transition is only slightly perturbed by the presence of the weakly bound second dimer. Given the high population of dimers in the expansion zone and the relative absence of the monomer, one would expect dimer-dimer condensation. Higher resolution studies are currently being planned to examine these effects more fully.

CONCLUSIONS

In this paper, we have presented information on the low energy modes of the jet-cooled dimer of benzoic acid and the carboxy-deuterated analogue. Using various rare gas partners and stagnation pressure studies we have explored the role of hot bands and van der Waals complexes. Several of the low energy components of the spectrum of the cooled dimer have been associated with the hydrogen bonding modes. Information on both the electronically excited dimer and on the ground state dimer has been provided.

References

1. M. D. Joeston and L. J. Schaad, *Hydrogen Bonding* (Marcel Dekker, New York, 1974).
2. P. Schuster, G. Zundel and C. Sandorfy, eds., *The Hydrogen Bond, Recent Developments in Theory and Experiments* (North-Holland Publishing Company, New York, 1976).
3. S. Bratos, J. Lascombe and A. Novak, *Molecular Interactions*, eds., H. Ratajczak and W. J. Orville-Thomas (Wiley, New York, 1980) pp. 301–346.
4. J. C. Baum and D. S. McClure, *J. Am. Chem. Soc.* **102**, 720 (1980).
5. H. Aboe, N. Mikami, M. Ito and Y. Udagawa, *Chem. Phys. Lett.* **93**, 217 (1982); *J. Phys. Chem.* **86**, 2567 (1982).
6. D. E. Poeltl and J. K. McVey, *J. Chem. Phys.* **78** (1983).
7. R. Smalley, L. Wharton and D. H. Levy, *Acc. Chem. Res.* **10**, 139 (1977).
8. D. H. Levy, *Ann. Rev. Phys. Chem.* **31**, 197 (1980).
9. A. Amirav, U. Evan and J. Jortner, *Chem. Phys.* **51**, 31 (1980).
10. G. Allen, J. G. Watkinson and K. H. Webb, *Spectrochim. Acta* **22**, 807 (1966).
11. S. Nagaoka, N. Hirota, T. Matsushita and K. Nishimoto, *Chem. Phys. Lett.* **92**, 498 (1982).
12. G. A. Sim, J. M. Robertson and T. H. Goodwin, *Acta Cryst.* **8**, 157 (1955).
13. S. Meshitasuka, H. Takahashi, K. Higasi and B. Schrader, *Bull. Chem. Soc. Japan* **45**, 1664 (1972).
14. G. Klausberger, K. Furic and L. Colombo, *J. Raman Spectros.* **6**, 277 (1977).
15. J. C. Baum and D. S. McClure, *J. Am. Chem. Soc.* **101**, 2340 (1979).
16. D. E. Poeltl and J. K. McVey, submitted to *J. Chem. Phys.*