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Laser Desorption Jet-Cooling Spectroscopy of the Benzoic Acid Monomer

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(Received: March 5, 1990)*

Laser desorption followed by jet cooling has been used to produce an intense beam of internally cooled benzoic acid monomers. As a result, the $S_1 \leftarrow S_0$ gas-phase absorption spectrum of the jet-cooled benzoic acid monomer could be identified for the first time. Delayed ionization out of a triplet state, populated by rapid $S_1 \rightarrow T$ intersystem crossing, followed by mass-selective detection of the parent ions is performed. The spectral lines have a Lorentzian shape with a line width of 6.5 cm^{-1}, corresponding to an intersystem crossing rate of 1.2×10^{12} s^{-1}.

Several years ago Poeltl and McVey,[1] and later Tomioka et al.,[2] reported the observation of the laser-induced fluorescence (LIF) spectrum of jet-cooled benzoic acid dimers. The monomer spectrum could not be detected when fluorescence detection was used. One reason for the failure to observe the monomer spectrum is the fact that, under normal conditions of jet cooling, a large proportion of benzoic acid will be present in the form of dimers. As will be shown below, laser desorption jet cooling can produce a beam with a large monomer concentration, which overcomes this problem. A second obstacle for studying the benzoic acid monomer spectrum is the short lifetime of the S_1 excited state, which strongly reduces the quantum yield of fluorescence. The fluorescence/phosphorescence properties of the benzoic acid monomer and dimer were explained with a simple energy level diagram proposed by Baba and Kitamura,[3] also shown in the paper of Baum.[4] Basically the idea is that in the benzoic acid monomer the first excited singlet state, the $^1(\pi,\pi^*)$ state, is nearly degenerate with a $^3(n,\pi^*)$ state, which makes the intersystem crossing from the $^1(\pi,\pi^*)$ state to the $^3(\pi,\pi^*)$ state via the $^3(n,\pi^*)$ state very efficient. In the dimer, on the other hand, the $^3(n,\pi^*)$ state is pushed up in energy whereas the $^1(\pi,\pi^*)$ state is pushed down in energy relative to the situation in the monomer. Although the $^3(\pi,\pi^*)$ state is still energetically available, the intersystem crossing rate is largely reduced for the dimer. Therefore, the dimer emits both fluorescence and phosphorescence whereas the monomer exhibits phosphorescence only. In 1985 Kamei et al.[5] claimed to have observed the $^1(\pi,\pi^*)$ state of the benzoic acid monomer using the sensitized phosphorescence excitation technique.[6] They concluded that electronic origins of two different rotational isomers of benzoic acid were located at 35 923 and 35 943 cm^{-1}, respectively. Their phosphorescence excitation spectrum (ref 5, Figure 4), however, contained a number of peaks due to the benzoic acid dimer and due to other clusters present in their beam, which made their assignment doubtful.

As stated, part of the difficulty for observing the spectrum of the monomer is its low concentration in the beam. Thermodynamic arguments predict that benzoic acid exists in the form of dimers at low temperatures,[7] and this is well documented experimentally by the work of Baum and McClure.[4,8-10] When benzoic acid is seeded in a beam by using a heated nozzle, dimers are also expected to form in the expansion region.

In a recent paper[11] we demonstrated that the technique of laser desorption followed by jet cooling can be applied to study the spectrum of monomers, dimers, and clusters of low vapor pressure organics. We now show that, with the use of a suitable matrix to desorb from, molecules with a higher vapor pressure can also be studied with this technique. In general, less clustering and dimer formation occurs when the molecules are entrained into the jet in the expansion region, compared to the approach in which the molecules are seeded in the beam. As a result, an intense pulsed beam of benzoic acid monomers could be produced.

Details of our experimental setup have been given elsewhere[11] and only a short description will be given here. Laser desorption is performed very close to the orifice of a pulsed supersonic jet. A KrF excimer laser is used for the desorption. The supersonic jet is formed by expanding Ar with 8 atm backing pressure through a 0.5 mm diameter nozzle. Benzoic acid was dissolved in methanol and the solution was put into a $2 \times 4 \times 1$ mm^3 piece of activated carbon. The activated carbon can contain a large amount of organics, and even benzoic acid, with a vapor pressure of approximately 5×10^{-4} Torr at room temperature, stays in this matrix for several days in 10^{-6}–10^{-7} Torr vacuum. During the measurements, we desorbed from the same spot on the activated carbon for several hours at 10 Hz, without a significant decrease in signal. The desorbed molecules are entrained into the jet and the internal degrees of freedom are cooled down by multiple collisions with the seeding gas. About 10 cm away from the nozzle, the molecular beam is crossed perpendicularly with both the doubled output of a Nd:YAG pumped dye laser and the output of an ArF (193 nm) excimer laser. Both laser beams have a 2 mm diameter cross section. The laser beams cross the molecular beam between the extraction plates of a linear time-of-flight (TOF) mass spectrometer, and mass-selective ion detection is performed. The ionization potential of both the monomer and the dimer is too high to make one-color (1 + 1)-resonance-enhanced multiphoton ionization (REMPI) via the S_1 state possible. Therefore, the ArF laser is used for ionization out of the intermediate state, after resonant excitation with the dye laser.

The spectra we obtained are shown in Figure 1. The upper panel shows the spectrum of the benzoic acid monomer. All major resonances are due to the $S_1 \leftarrow S_0$ transition, induced by the dye laser, which was scanned from 281 to 273 nm. Ions were detected at the parent mass (122 amu) after delayed ionization with the ArF laser out of the triplet state, which is populated via $S_1 \rightarrow T$ intersystem crossing, as discussed above. In this case the ArF laser was delayed by 130 ns with respect to the laser used for the resonant excitation, but identical spectra were obtained for delay times up to 2 μs. A reduction of the total ion signal for still longer delay times results from triplet-state benzoic acid monomers leaving the detection region. Above each peak in the spectrum the frequency distance to the electronic origin (in cm^{-1}) is indicated. The absolute vacuum frequency of the laser was calibrated

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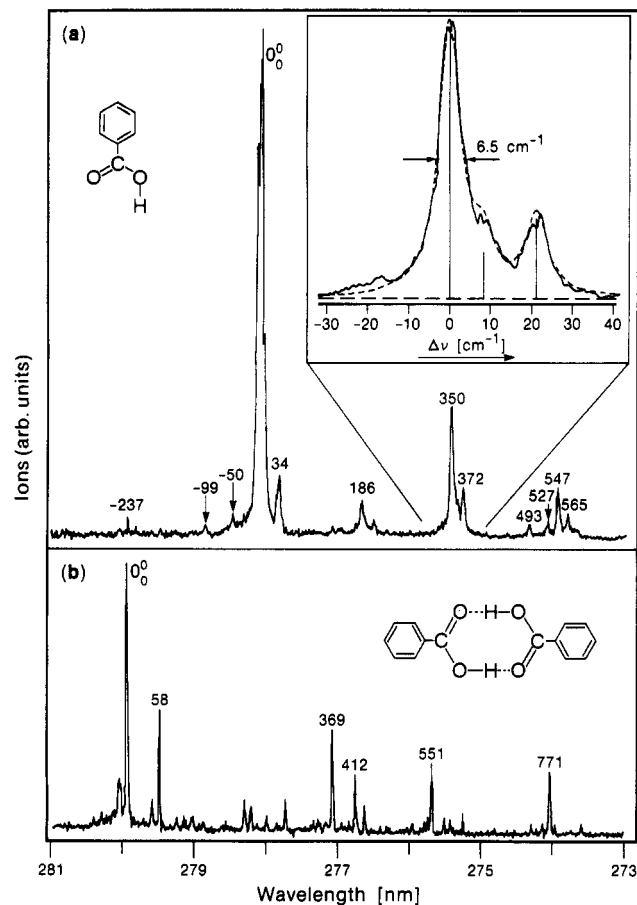(11) Meijer, G.; de Vries, M. S.; Wendt, H. R.; Hunziker, H. E. *J. Chem. Phys.*, in press.

Figure 1. (Panel a) Spectrum of the benzoic acid monomer. The spectrum is due to the $S_1 \leftarrow S_0$ absorption. The S_1 state undergoes rapid intersystem crossing to a lower lying triplet state. Mass-selective detection of the parent ions (122 amu) is performed after delayed one-photon ionization out of this triplet state. The electronic origin of this spectrum is at 35960 cm^{-1}. The lines have a Lorentzian shape, with a fwhm of 6.5 cm^{-1}, corresponding to an intersystem crossing rate of 1.2 $\times$ 10^{12} s^{-1}. The arrows indicate the origins of the benzoic acid–Ar and the benzoic acid–Ar$_2$ complexes. (Panel b) Spectrum of the benzoic acid dimer. This spectrum is due to the corresponding absorption band in the dimer. The intersystem crossing in the dimer is much slower, and direct ionization (no delay) out of the excited singlet state, followed by detection of the parent ions (244 amu) is performed. The origin of the dimer transition is at 35723.6 $\pm$ 1.0 cm^{-1}. The major peaks in the dimer spectrum can just be recognized in the upper spectrum as well.

on atomic lines of Mn, around 280 nm, and is accurate within 1 cm^{-1}. The lower panel shows the spectrum of the benzoic acid dimer, also detected at the mass of the parent (244 amu). To observe this spectrum the dye laser used for the resonant excitation and the ArF laser used for ionization have to be overlapped in time; on the dimer mass no spectrum could be recorded for delay times longer than the fluorescence lifetime of the excited singlet state. The spectrum of the dimer is the same as that observed in LIF experiments,[1,2] and the mass selection leaves no doubt about the origin of this spectrum. A minor difference between the LIF spectra and the two-color (1 + 1)-REMPI spectra is the appearance of two weak lines about 14 cm^{-1} blue-shifted from both the origin and the hydrogen-bond vibration of the dimer when the latter detection technique is used. At the moment we do not have an identification for these lines, but their absence from the LIF spectra suggests that they are from a short-lived complex.

It should be noted that we did not observe any sign of the $^1(n,\pi^*)$ state of the dimer, using two-color (1 + 1)-REMPI. This contradicts a report by Tomioka et al.,[2] who observed a spectrum with a long vibrational progression, and ascribed it to one-color (1 + 2)-REMPI via the $^1(n,\pi^*)$ state of the dimer. Such a process would have a very low ionization efficiency, and it seems possible that the spectrum reported by Tomioka et al.[2] was due to another species in the beam. The two-color (1 + 1)-REMPI that we

applied should be much more sensitive. Therefore, we believe that our failure to observe any other state indicates that the $^1(\pi,\pi^*)$ state should be regarded as the lowest lying singlet state.

When we take a closer look at the spectrum recorded at the monomer mass, the major peaks from the dimer are seen just above the noise level. This means that the excited-state dimer can fall apart and end up in an excited triplet monomer and a ground-state monomer, a situation similar to that found for the *p*-aminobenzoic acid (PABA) dimers.[11] This process is quite likely because the triplet dimer has more than enough internal energy to dissociate the hydrogen bonds. The excited triplet monomer is then detected with delayed ionization. The absolute intensity of the dimer resonances detected on the monomer mass (by ionization out of the monomer triplet state) is only slightly less than the dimer signal detected on the dimer mass (by ionization out of the dimer singlet state). The spectrum displayed in the upper panel of Figure 1 can be directly compared to the phosphorescence excitation spectrum shown by Kamei et al. (ref 5, Figure 4). In both cases triplet-state monomers are detected (with some delay), after resonantly exciting the species in the molecular beam. A comparison of both spectra shows that the monomer/dimer ratio in our beam is larger by about a factor of 50 compared to the monomer/dimer ratio in the experiment of Kamei et al.[5] Furthermore, the two strong peaks at 35923 and at 35943 cm^{-1}, assigned by Kamei et al.[5] to origins of two different isomers of benzoic acid, are absent from our spectra. Instead we see two very weak peaks (indicated by arrows), which we ascribe to origins of the benzoic acid–Ar (at 35910 cm^{-1}) and the benzoic acid–Ar$_2$ (at 35861 cm^{-1}) vdW complexes. These origins are red-shifted by about 50 and 99 cm^{-1}, respectively, from the origin of the benzoic acid monomer. Higher order vdW clusters are less likely to be formed as the preferential sites are occupied by the first two Ar atoms. Kamei et al.[5] used He as a seeding gas, and the two strong peaks that they assigned to different isomers of the benzoic acid might have been due to the corresponding benzoic acid–He vdW complexes. A smaller red shift is expected for the He complexes than for the Ar complexes.[12] This identification is also in agreement with the fact that Kamei et al.[5] see far more clusters (dimers, vdW clusters, and hydrogen-bonded complexes) than are seen in our spectrum.

The real origin of the benzoic acid monomer is the large, broad peak at 35960 cm^{-1}, not assigned but also observable in the spectrum of Kamei et al.[5] Several vibronic transitions in the monomer, which are reflected in the spectrum of the dimer,[1,2] are clearly seen. The vibration at 547 cm^{-1} is most likely the mode 6b, an analogue of the Herzberg–Teller active mode in benzene, found in the dimer spectrum at 551 cm^{-1}.[1,2] The vibration at 350 cm^{-1} in the monomer cannot correspond to the 369-cm^{-1} vibration of the dimer if the interpretation of Tomioka et al.[2] for this vibration is correct; they assign this vibration in the dimer to the second overtone of a hydrogen-bond vibration, which would of course not show up in the monomer spectrum. When the interpretation of the dimer spectrum according to Poeltl and McVey[1] is accepted, the 350-cm^{-1} vibration in the monomer would be the 6a mode. Another possibility would be to assign this vibronic transition to the 16a mode.[10] It is interesting to note that the benzoic acid monomer spectrum has a reasonably strong vibration around 186 cm^{-1}. Most likely this vibration is due to the out-of-plane or in-plane bend of the COOH group. It is this vibration that also shows up in the PABA spectrum, and that shows anomalous behavior in the case of the PABA dimer.[11]

The vibration around 350 cm^{-1} is shown enlarged in the inset, together with a best fit of the line profile (dashed curve). Assuming that the actual Lorentzian line width of each individual rotational line is much larger than the width of the rotational envelope in the absence of broadening, the line shape is fitted to a Lorentzian profile around the indicated stick spectrum. The best fit is obtained when a line width (fwhm) of 6.5 cm^{-1} is assumed. Compared with this width, the 0.5-cm^{-1} line width of the dye laser can be neglected. Via the relation $\Delta\nu = 1/2\pi\tau$, in

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which $\Delta\nu$ is the line width associated with a lifetime τ, a lifetime of 0.8 ± 0.1 ps is found for the excited singlet state of the benzoic acid monomer. This confirms that rapid intersystem crossing causes a low fluorescence quantum yield and makes detection of the benzoic acid monomer by LIF hard to perform.

It seems that the origin of the benzoic acid spectrum consists of at least three closely spaced lines, partly overlapped within the Lorentzian line width. This complicated line shape might well be due to the expected near-degeneracy of the excited singlet state with the $^3(n,\pi^*)$ state. This near-degeneracy is indirectly demonstrated by the large singlet-triplet intersystem crossing rate. To the blue side of the major peaks in the spectrum (shift 20-40

cm^{-1}) an extra peak appears. One could speculate that these peaks are due to isomers, such as two possible conformations for the OH group.

In conclusion, we have demonstrated that the technique of laser desorption followed by jet cooling can be used to advantage even for molecules that have a vapor pressure that is high enough such that they could also be seeded in a beam. In that case the laser desorption technique produces less clusters. In the case of benzoic acid, it enabled us to identify the $S_1 \leftarrow S_0$ gas-phase absorption spectrum of the jet-cooled monomer for the first time. From the observed width of the peaks an intersystem crossing rate of 1.2×10^{12} s^{-1} is deduced.

Heat of Formation of HO₂. A Direct Determination from Guided Ion Beam Studies of $O_2^+(^2II_g, v=0) + CH_4$

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The heat of formation of the hydroperoxyl radical, HO₂, and the ionization energy of methane, IE(CH₄), are measured directly, by using guided ion beam mass spectrometry to study the reaction of $O_2^+(^2II_g, v=0) + CH_4$. The O_2^+ ions are produced in a flow tube source and are shown to be completely thermalized. The thermodynamic values derived are IE(CH₄) = 12.54 $\pm$ 0.07 eV, $\Delta_f H_{298}°$(HO₂) = 3.8 $\pm$ 1.2 kcal/mol, $D_{298}°$(H-OO) = 48.3 $\pm$ 1.2 kcal/mol, and $D_{298}°$(H-OOH) = 88.4 $\pm$ 1.2 kcal/mol (where the uncertainties represent our 95% confidence limits). The present values are compared to prior experimental and theoretical values.

The hydroperoxyl radical, HO₂, plays an important role as an intermediate in many atmospheric reactions, combustion processes, and oxidation systems.[1] In addition, the HO₂ radical is thought to be a likely constituent of interstellar clouds[2] and to participate in many tropospheric and stratospheric photochemical reactions due to its possible participation in catalytic cycles for removing ozone.[3] The thermochemistry of this pivotal species is thus a critical factor in evaluating possible atmospheric reactions as well as initiation mechanisms, branching ratios, and equilibrium constants in combustion-oxidation chain reactions and modeling of all of these systems.

The heat of formation for the hydroperoxyl radical has been measured by many different methods and has a rugged history which dates back to 1955.[4,5] Both experimental and theoretical values are available, ranging between −6.9 and 5.75 kcal/mol, as shown in Table I. The widely used JANAF tables cite a value of 0.5 $\pm$ 2.0 kcal/mol, which is based on a review of the data by Wagman, Cohen, and Westburg, and has not been revised since 1978.[6] Recent experimental data of Howard,[7,8] Benson,[9,10] and others[11] suggest that this value is low. Shum and Benson (SB) critically reviewed the available literature values for $\Delta_f H_{298}$(HO₂) in 1983.[12] On the basis of what SB considered to be the most reliable values, they arrived at a *mean* value of $\Delta_f H$(HO₂) = $3.5^{+1.0}_{-0.5}$ kcal/mol.[13]

More recent values for $\Delta_f H$(HO₂) come from ab initio theoretical calculations. Calculations of the heat of reaction for HO₂ + H → H₂ + O₂ indirectly indicate that $\Delta_f H$(HO₂) = 5.3 kcal/mol.[14] A similar value of 5.75 kcal/mol is directly obtained by Sana et al.[15] These values are in close agreement with only the highest experimental value in Table I, that of Foner and Hudson.[4,16] The most recent experimental value is derived from Sawyer's evaluation of standard reduction potential data for

TABLE I: Literature Values for the Heat of Formation of HO₂ at 298 K

method	$\Delta_f H$(HO₂), kcal/mol	ref (year)
mass spectrometry	5 $\pm$ 2	4, 16 (1955/1962)
spectrophotometry	≤2.5	5 (1959)
gas chromatography	0.9	a (1974)
DF-LMR[b]	2.5 $\pm$ 0.6	7 (1980)
electron spin resonance	1.6 $\pm$ 2.5	11 (1982)
DF-LMR[b]	3.3 $\pm$ 0.6	8 (1982)
JANAF tables	0.5 $\pm$ 2	6 (1978/1985)
spectrophotometry	>3.0 $\pm$ 1.0	9 (1983)
VLPR[c]	4.6 $\pm$ 0.2	10a (1983)
VLPR[c]	≥3.4	10b (1983)
suggested average	$3.5^{+1.0}_{-0.5}$	12 (1983)
theory	5.3	14 (1986)
theory	5.75	15 (1987)
redox potentials	−6.9	17 (1989)
GIBMS[d]	3.8 $\pm$ 1.2	present results

[a] Kochubei, V. F.; Moin, F. B. *Dokl. Akad. Nauk SSSR* **1974**, *219*, 141. [b] Discharge flow-laser magnetic resonance. [c] Very low pressure reactor. [d] Guided ion beam mass spectrometry.

protons, water, and oxygen species.[17] He finds that the bond dissociation energy, $D°$(H-OO), is 59 kcal/mol, which implies

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