The Ultraviolet Transitions of Benzoic Acid. 1. Interpretation of the Singlet Absorption Spectrum

J. Clayton Baum[†] **and Donald S. McClure***

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received June 19, 1978*

Abstract: The ultraviolet absorption spectrum of benzoic acid at 77 K and higher temperatures is reexamined. The previous assignment of some of the vibronic peaks of benzoic acid in hydrocarbon glasses to the monomer species is shown to be incorrect. Experimental data and semiempirical molecular orbital calculations show how the electrons are redistributed in the various electronic states of benzoic acid. The charge-transfer component, though small, does influence the transition energy and oscillator strength of the benzenoid states; however, the polarization data for benzoic acid do not justify the assignment of the 230-nm band as primarily a charge-transfer band.

I. Introduction

Benzoic acid is the simplest aromatic carboxylic acid. As such, this molecule possesses a number of properties that make a detailed examination of its electronic states worthwhile. Our interest in benzoic acid is in its ability to act as both a proton donor and a proton acceptor in hydrogen bonding and its tendency to dimerize via these hydrogen bonds. It will be seen that these characteristics of benzoic acid produce a variety of differences in the electronic and vibrational spectra when compared to other monosubstituted benzenes. The carboxyl substituent also introduces a series of $n\pi^*$ electronic states and their location and interaction with the benzenoid $\pi\pi^*$ states is important, especially in view of the extensive research[1] on other carbonyl-containing molecules.

The changes in the hydrogen bonds upon excitation should be relatively small since the electronic reorganization occurs mainly in the aromatic ring and is only transmitted to the hydrogen bonds through the carboxyl group. Nevertheless, the acid ionization constant of benzoic acid (as a complex with water in aqueous solution) is markedly changed in its first excited singlet state.[2] We believed that it should be possible to understand how this change comes about and to learn considerably more about the changes in the hydrogen bonds by doing a careful study of the spectroscopy of benzoic acid. From the experimental and theoretical data, we, indeed, develop a quite detailed picture of the hydrogen-bond changes.

These studies of benzoic acid required both low-resolution solution spectra at 77 K and high-resolution mixed-crystal experiments at liquid helium temperatures. In order to guide the spectroscopic interpretation a complete vibrational assignment of benzoic acid dimer in the ground state was made. In addition the electronic spectral data were interpreted and extended with the help of various semiempirical quantum mechanical calculations. This project was carried out cooperatively by groups at Princeton and Rutgers Universities.

In the present paper, the first of the series, it seems appropriate to begin with the low-resolution absorption spectrum of benzoic acid in order to resolve the problems at this level of interpretation which still have not been settled in the published literature. The ultraviolet absorption spectrum of benzoic acid consists of three bands centered near 280, 230, and 190 nm (Figure 1). These bands have been labeled C, B, and A, respectively.[3] There is general agreement that the C band of benzoic acid is analogous to the $B_{2u} \leftarrow A_{1g}$ (^1L_b) transition in benzene.[4-6] However, the B band has been assigned as an intramolecular charge-transfer band on the basis of localized orbital calculations[7] and polarized absorption[8] while recent CNDO/S-CI molecular orbital computations[4,5] indicate very little charge transfer associated with either the B or C bands. We have obtained new experimental and computational data which aid in the correct assignment.

A second problem that needs clarification is the interpretation of the increased number of peaks in the C band at low temperature in hydrocarbon solutions as being due to the presence of both monomer and dimer species of benzoic acid.[9,10] It is hard to rationalize the existence of monomers at low temperature because thermodynamic data[11] strongly favor complete dimerization. In addition, we have found the structure of the C band in the crystal at 77 K to be remarkably similar to the low-temperature spectrum of benzoic acid dissolved in hydrocarbon solvent.[9] Since it is known that crystalline benzoic acid exists entirely as dimers,[12] the previous assignment of certain bands in the solution spectrum at 77 K to the monomer species seemed even more doubtful. To resolve this conflict we have examined the room temperature and liquid nitrogen temperature spectra of benzoic acid and methyl benzoate in a variety of solvents. The results of this study and an explanation compatible with Ito's data and our own are presented.[13] In the following papers[14,15] the hydrogen bonding of benzoic acid in its ground and excited states is discussed in detail on the basis of both experimental data and molecular orbital calculations.

II. Experimental Section

The absorption spectra were measured with a Cary Model 14 spectrophotometer whose wavelength readout was calibrated with a mercury penlamp. The temperature-dependence study of the absorption spectrum was carried out with the sample placed in a glass double Dewar with Suprasil windows. The sample was suspended in the inner Dewar, separated by a vacuum space from the liquid nitrogen. The temperature was monitored with a thermocouple attached to the sample cell. The other spectra at 77 K were taken with the sample either immersed in liquid nitrogen or with the liquid-nitrogen level kept just below the windows in contact with the bottom of the cell holder. In the latter case the temperature was below 85 K. Fast cooling (30–45 s) was achieved by plunging the sample into the coolant. Slow cooling involved cooling the sample to 77 K over a period of at least 15 min.

The benzoic acid was Baker "Analyzed" Primary Standard, further purified by zone refining. Methyl benzoate was obtained from Matheson Coleman and Bell. Mallinckrodt absolute ethyl ether and Gold Seal absolute ethanol (Commercial Solvents Corp.) were used. The benzin (petroleum ether) was a 30–60 °C fraction of hydrocarbons obtained from AMSCO. All other solvents were Matheson Coleman and Bell "spectroquality". Spectroscopic tests of the purity of all chemicals were made. The growth of oriented crystals of benzoic acid from the melt between Suprasil flats is described elsewhere.[16] The orientation of a crystal of submicron thickness was confirmed by comparing its optic-axis figure under convergent light with the optic-axis figure of a larger crystal cleaved along its (001) plane.

[†] Bowdoin College, Brunswick, Maine 04011.

0002-7863/79/1501-2335$01.00/0

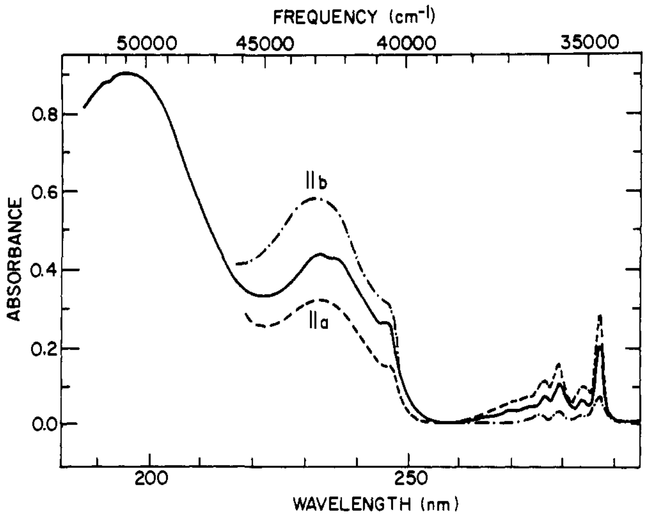


Figure 1. Absorption spectrum of crystalline benzoic acid (~0.1-μm path length) at 77 K. Absorption was observed through the (001) plane of the crystal. (——), unpolarized spectrum; (---), polarized parallel to *a* axis; (-·-), polarized parallel to *b* axis.

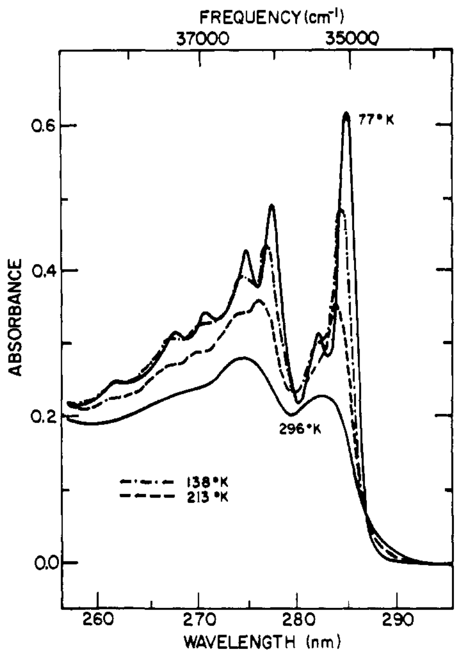


Figure 2. Effect of temperature on the C-band absorption of 2.1 × 10^{-4} M benzoic acid in methylcyclohexane–isopentane (1:6) (10-mm path length).

III. Results

Absorption at Room Temperature. Pronounced environmental effects on the absorption spectrum of benzoic acid (and methyl benzoate) can be observed even at room temperature. Our observations, which are in general agreement with those reported in the literature, are summarized below. Included are several new results. In hydrocarbon solvents there is an intensity increase and red shift of the B and C bands of benzoic acid upon dimerization.[17,18] The spectral data in carbon tetrachloride and chloroform at solute concentrations similar to those in the hydrocarbon solutions show that the equilibrium is shifted toward the monomer as the result of weak hydrogen bonding to the solvent.[16] Larger wavelength and intensity *decreases* of the benzoic acid absorption occur in solvents (ethanol, ethyl ether, water) capable of forming strong hydrogen bonds with benzoic acid.[17,19] The further spectral changes that take place upon dilution of benzoic acid in water[19] and ethanol[16] can be attributed to ionization of the acid.

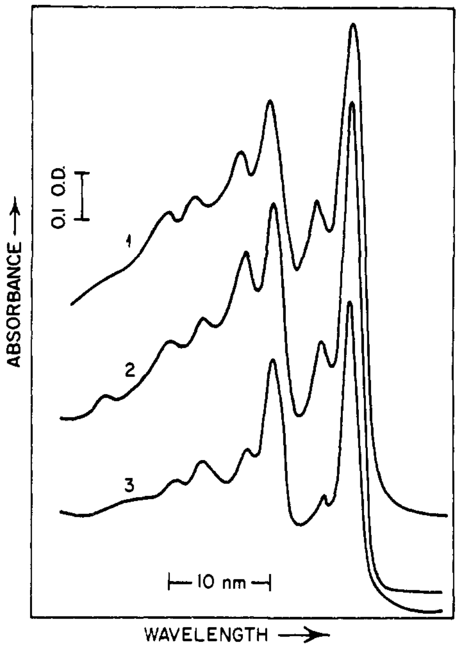


Figure 3. Comparison of the monomer and dimer C-band absorption at 77 K: (1) benzoic acid neat crystal (~0.3-μm path length); (2) 2.1 × 10^{-4} M benzoic acid in methylcyclohexane (10-mm path length); (3) 4.0 × 10^{-3} M methyl benzoate in methylcyclohexane (1-mm path length and vertical scale reduced by 0.5). Each spectrum has been shifted horizontally so that their absorption origins coincide.

The spectral properties of methyl benzoate in all the solvents mentioned above are not affected by changes in concentration.[16-18] In ether and ethanol the positions of the methyl benzoate bands remain unchanged from their positions in hydrocarbon solvents but there is some broadening in both solvents compared to the spectrum in hydrocarbon solutions.[19] The broadening in ethanol is "complexity" broadening caused by the presence of different (H-bonded and non-H-bonded) absorbing species in solution. The broadening in ether indicates non-hydrogen-bonding interaction between ether and the chromophore.[19]

Absorption at Low Temperature. Much more information can be obtained from spectra in organic glasses at 77 K than from room temperature solution spectra. Figure 2 shows the sharpening of the C band of benzoic acid in methylcyclohexane–isopentane as the temperature is lowered to 77 K. Ito et al.[9] labeled the first, third, and fifth peaks at low temperature "dimer bands" and the second, fourth, and sixth peaks "monomer bands". However, as noted in the Introduction, this interpretation is questionable.

The C band of benzoic acid in methylcyclohexane (MCH) is compared in Figure 3 with the spectra of crystalline benzoic acid (curve 1) and of methyl benzoate in MCH (curve 3). (The latter two spectra have been *shifted* horizontally in Figure 3 so that the three absorption origins coincide.) In the crystalline state, benzoic acid exists entirely as one species (dimer).[12] Methyl benzoate is incapable of self-association and likewise exists entirely as one species (monomer) in MCH at 77 K. Yet, it is apparent in Figure 3 that all three samples exhibit the same structure in the C-band region when cooled to 77 K. The conclusion consistent with these facts is that only one species (dimer) need be present to explain all the peaks that appear in the C band of benzoic acid in MCH at 77 K. This conclusion agrees with the prediction from thermodynamic data[11] that complete benzoic acid dimerization occurs at low temperature in non-H-bonding solvents.

Table I. Assignment of C-Band and B-Band Vibrational Structure of Benzoic Acid and Methyl Benzoate at 77 K

	λ, nm ± 0.2	C Band ν, cm^{-1} ± 25	$\Delta\nu$, cm^{-1} ± 50	assignment
BA[a]/MCH[b]	284.7	35 114	0	origin
	282.0	35 451	335	ν_{6a}
	277.3	36 051	937	ν_{12}
	274.4	36 419	1305	$\nu_{12} + \nu_{6a}$
	270.5	36 958	1844	$2 \times \nu_{12}$
	267.6	37 358	2244	$2 \times \nu_{12} + \nu_{6a}$
	261.0	38 303	3189	$3 \times \nu_{12} + \nu_{6a}$
MB[c]/MCH	280.9	35 589	0	origin
	278.5	35 896	307	ν_{6a}
	273.7	36 526	937	ν_{12}
	271.3	36 849	1260	$\nu_{12} + \nu_{6a}$
	267.0	37 442	1853	$2 \times \nu_{12}$
	264.7	37 767	2178	$2 \times \nu_{12} + \nu_{6a}$
	260.3	38 406	2817	$3 \times \nu_{12}$
	258.4	38 688	3099	$3 \times \nu_{12} + \nu_{6a}$
BA (crystal)	287.2	34 809	0	origin
	284.0	35 201	392	ν_{6a}
	279.5	35 768	959	ν_{12}
	276.5	36 156	1347	$\nu_{12} + \nu_{6a}$
	272.1	36 740	1931	$2 \times \nu_{12}$
	269.3	37 122	2313	$2 \times \nu_{12} + \nu_{6a}$

	λ, nm ± 0.3	B Band ν, cm^{-1} ± 40	$\Delta\nu$, cm^{-1} ± 80	assignment
BA[a]/MCH[b]	243.3	41 089	0	origin
	238.4	41 934	845	ν_{12}
	234.8	42 576	1487	ν_{8a}
MB[c]/MCH	238.0	42 004	0	origin
	233.3	42 850	846	ν_{12}
	229.7	43 521	1518	ν_{8a}
	225.7	44 293	2289	$\nu_{12} + \nu_{8a}$

[a] Benzoic acid. [b] Methylcyclohexane. [c] Methyl benzoate.

All of the peaks in the C band of benzoic acid in MCH can be assigned as vibrations of the dimer species with the help of the high-resolution mixed-crystal spectra to be discussed in later papers.[20,21] The assignments for the spectra of benzoic acid and methyl benzoate in MCH and of crystalline benzoic acid are given in Table I. The two modes—ν_{12} and ν_{6a}—involve in-plane distortion of the aromatic-ring skeleton. Both the intensity and frequency of the latter mode are sensitive to the substituent and hence to the interactions of the substituent with its environment.

If any monomer of benzoic acid were present at 77 K, the origin of its absorption would be expected to lie in the same spectral region as the ν_{6a} vibronic band of the dimer.[9] In this case, the integrated intensity of the ν_{6a} region relative to the intensity of the dimer origin should depend on the concentration of benzoic acid. We have found that this intensity ratio is *independent* of the concentration at low temperature and is also independent of the rate of cooling.

In poor solvents or slowly cooled solutions a new absorption band appears near 288 nm which turns out to be that of benzoic acid crystallites.

The B and A bands of benzoic acid and methyl benzoate in MCH at 77 K are shown in Figure 4. The B-band origin of benzoic acid is 900 cm^{-1} to the red of the methyl benzoate origin; this difference is nearly twice that in their C-band origins (474 cm^{-1}) and can be ascribed to the exciton-type dipolar interaction within the dimer.[18] The structure of the B band is assigned in Table I. The normal mode ν_{12} is a radial skeletal vibration of the aromatic ring while mode ν_{8a} represents a quinoidal distortion of the carbon skeleton. The A-band structure may be due to vibronic components and/or a mixture of electronic states (see below).

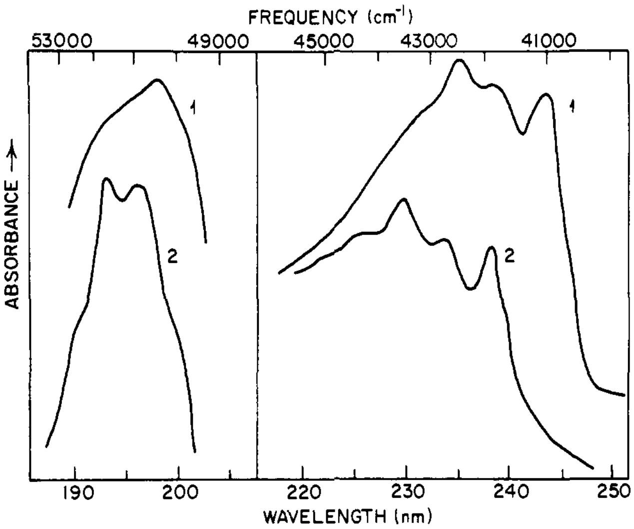
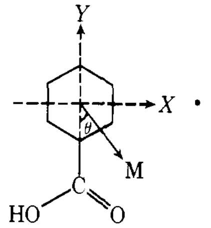


Figure 4. Absorption spectra of A and B bands of 3×10^{-4} M benzoic acid (1) and 3×10^{-3} M methyl benzoate (2) in methylcyclohexane at 77 K (1-mm path lengths).

No evidence of $^1n\pi^*$ absorption to the red of the C band of benzoic acid was found. High-resolution fluorescence experiments[20,21] give convincing proof that the lowest singlet transition is $\pi\pi^*$.

Polarization of the Absorption Bands. A primary justification for the charge-transfer assignment of the B band of benzoic acid has been polarization data.[8] The polarization ratio for a transition can be determined by relating the transition moment to the molecular axes which are in turn related to the crystal axes from crystallographic data. The in-plane molecular axes used by both Sim et al.[12] (X-ray crystallographic study) and Tanaka[8] (polarized absorption study) are shown below.



The transition moment (M) is at an angle (θ) to the Y axis. An angle of 90° (short-axis polarized, ^1L_b) gives an a:b crystal-axes ratio of 12:1 using the oriented-gas model, while angles of 0 (long-axis polarized, ^1L_a) and 6.5° (the angle calculated by Tanaka[8] for a charge-transfer transition) give ratios of 1:11.5 and 1:6, respectively. (Tanaka's calculated ratio of 1:30 is for an angle of −6.5°.)

Our polarization ratios (Figure 1) are lower than predicted for both the C band (a:b 6:1) and B band (a:b 1:3). These results were not too surprising because each of our samples consisted of several crystals only approximately oriented in the same direction. Strain introduced during the growth and cooling of our samples between quartz flats might have also contributed to the lower ratios.

Tanaka[8] published a polarized absorption spectrum of a single crystal of benzoic acid grown by sublimation. He found the a-axis:b-axis integrated intensity ratio for the C band to be (10 ± 2):1, which is in good agreement with the ^1L_b assignment of the band. The a-axis:b-axis intensity ratio measured by Tanaka for the B band was 1:(31 ± 3). This ratio, however, was based on the subtraction of a new band at 210 nm which Tanaka said was responsible for most of the ab-

Table II. Input Parameters for Pariser–Parr–Pople Calculations

center	z^a	h^b	IP,[d] eV	γ_{AA},[e] eV	bond	k^c	β,[f] eV
-CH-	1.0	0.00	11.16	11.13	CH—CH	1.00	−2.39
-C(OOH)	1.0	0.19	11.16	11.13	Ph—COOH	0.86	−1.70
=O	1.0	1.28	17.70	15.23	C=O	1.10	−2.70
-OH	2.0	1.21	34.12	18.82	C—OH	0.84	−1.80

[a] π-electron contribution: H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, 1967. [b] Hückel h: ref a. [c] Hückel k: ref a. [d] Valence-state ionization potential: D. L. Beveridge and J. Hinze, *J. Am. Chem. Soc.*, **93**, 3107 (1971). [e] One-center coulomb integral: ref d. [f] Resonance integral: Y. G. Smeyers and C. Sieiro, *Theor. Chim. Acta*, **28**, 355 (1973).

Table III. Singlet States of Benzoic Acid (Monomer)

	wavelength, nm			oscillator strength			polarization[b]			charge transfer[d]	
	obsd[a]	CNDO	PPP	obsd[a]	CNDO	PPP	obsd	CNDO	state[c]	CNDO	PPP
C band	278	270	265	0.014	0.003	0.011	Y	Y	^1L_b	0.05	0.18
B band	230	220	227	0.19	0.12	0.21	Z	Z	^1L_a	0.06	0.26
A band	196	193	198	0.9	0.41	0.54		Z	^1B_a	0.02	0.12
	193	191	193		0.51	0.90		Y	^1B_b	0.00	0.06

[a] See text. [b] Y = short axis; Z = long axis of molecule. [c] Platt notation; assigned on the basis of the polarization and CI composition. [d] The fractional transfer of an electron from the aromatic ring to the carboxyl group is predicted to be 0.10 in the ground state by CNDO (0.04 by PPP). The amount of charge transfer shown in the table is the fractional number of electrons above the value for the ground state transferred from ring to carboxyl.

Table IV. Correlation of Energy and Intensity Changes with Charge-Transfer Character, Relative to Fluorobenzene[a]

	^1L_b		^1L_a		charge transfer[c]		
	$\Delta\Delta\nu$, cm^{-1} [b]	f	$\Delta\Delta\nu$, cm^{-1} [b]	f	S_0	^1L_b	^1L_a
fluorobenzene	0000	0.003	0000	0.150			
toluene	600	0.003	1400	0.168	0.06	−0.01	−0.01
phenol	1700	0.020	4100	0.132	0.28	−0.07	−0.06
benzoic acid	1800	0.014	6100	0.20	0.10	+0.05	+0.06
aniline	3800	0.028	7500	0.144	0.26	−0.17	−0.15

[a] All experimental data except benzoic acid are from ref 4, Table 9. [b] Frequency shift (to lower energy) relative to fluorobenzene. [c] Fraction of an electron; positive means increased electron density on the substituent; from CNDO/S-CI computations.

sorption in the B-band region along the a-axis direction. In a later communication[22] Tanaka implied that the 210-nm band is actually b-axis polarized. This new band, which is not present in solutions containing benzoic acid, was said to appear because of crystalline effects. We have found no evidence for Tanaka's 210-nm band in either polarized or unpolarized absorption spectra of crystalline benzoic acid (Figure 1).

Even without the interference of the 210-nm band the determination of the B-band polarization ratio is difficult because the tail of the A band extends into the B-band region (Figure 1). Nevertheless, it is hard to believe that this ratio could be as high as that measured by Tanaka. Our opinion is that, although the polarization data do permit a determination of the symmetry, they do not permit an accurate analysis of the amount of charge-transfer character in the B band. We therefore turned to the predictions of semiempirical molecular orbital calculations, discussed in the next section.

Semiempirical Molecular Orbital Calculations. The Del Bene and Jaffe[23] CNDO/S-CI valence electron program[24] and a Pariser-Parr-Pople (PPP) π-electron program[25] were used for the molecular orbital calculations on benzoic acid. The PPP program was modified to calculate the two-center repulsion integrals using the Beveridge-Hinze method.[26] Standard[27] bond lengths and bond angles were adopted for benzoic acid instead of the experimental geometry[12] because the molecular orbital calculations are for the isolated monomer rather than the dimer in a crystalline environment. In addition, there is evidence[28] that the carbon-oxygen distances measured in the crystal are not the true values even for the dimer. We did select the experimental value of the Ph-COOH bond length since this distance depends on the substituent. The other input parameters chosen for the PPP program after many trial variations are listed in Table II. The first 60 monoexcited configurations were included in the CNDO configuration interaction and complete (20) monoexcited configuration interaction was performed in the PPP computations.

The computed energies and intensities are in general agreement with previous calculations[4,5,29] and with the experimental results (Table III). Since the calculated results are for the isolated monomer of benzoic acid, the experimental energies shown in Table III were taken from the vapor spectrum of benzoic acid[16] (C band) and from the solution spectrum of the monomer corrected to the vapor (B and A bands).[30] Note that the vertical-transition energies are computed at a fixed geometry and therefore correspond to the Franck-Condon maxima, not the 0-0 bands. The experimental oscillator strengths are those of the monomer in solution.

Examination of the molecular orbitals involved in the configuration interaction composition of each state shows that the C, B, and A bands are associated with the ^1L_b, ^1L_a, and ^1B_a + ^1B_b states, respectively. The ^1L_a state is *predicted* to undergo a quinoidal distortion, which is consistent with the strong appearance of ν_{8a} in the spectrum of the B band (Table I). The CNDO method indicates very little charge transfer in these bands. Although the π-electron calculations indicate more charge-transfer character, the amount in the B band is not significantly greater than that in the C band. As mentioned earlier, the experimental data show that there is no $^1n\pi^*$ state below ^1L_b. From other results,[20,21] we conclude that the lowest $^1n\pi^*$ state lies between ^1L_b and ^1L_a.

IV. Discussion

Nature of the Excited States. The good agreement of both types of semiempirical MO calculation with the experimental results shown in Table III is taken as evidence that the nature of the charge distribution given by these calculations should be approximately correct. The extent of charge transfer given in Table III shows that there is no band in the near UV which should properly be called a "charge-transfer band", even though each of the bands A, B, and C does contain an appreciable portion of charge-transfer configurations. The true charge-transfer band is in the vacuum ultraviolet, according to these results. This charge-transfer contribution in each state represents the main interaction between the ring and the carboxyl group and is therefore important in helping to understand solvent effects, in particular H-bonding effects, to be discussed in the following paper.[14]

In order to compare the charge transfer in benzoic acid to that in other monosubstituted benzene compounds, Table IV was prepared, showing CNDO results for ^1L_b and ^1L_a. (The parameters were chosen in the standard way.) Benzoic acid is not exceptional, according to these results.

The data in Table IV demonstrate that, as the charge-transfer character of the ^1L_b and ^1L_a states increases, there is a decrease in the transition energy and increase in the oscillator strength. (The ^1L_a intensity does not exhibit this latter effect because the transition is more allowed.) Furthermore, these changes are independent of the direction of charge transfer between the substituent and the ring.

V. Conclusion

In summary, there is no longer confusion about the appearance of "monomer bands" in the low-temperature spectra of benzoic acid, and there does not seem to be any good evidence for a predominant charge-transfer component to the B band. The semiempirical calculations give reasonable, though approximate, estimates of the distribution of electrons in the excited states and will be useful in our subsequent studies of the effects of electron excitation on the hydrogen bonds.

Acknowledgment. This research was supported by the National Science Foundation, Grant MP571-03266.

References and Notes

(1) A. Duben, L. Goodman, and M. Koyanagi in "Excited States", Vol. I, E. C. Lim, Ed., Academic Press, New York, 1974.
(2) E. L. Wehry and L. B. Rodgers, *J. Am. Chem. Soc.*, **88**, 351 (1966).
(3) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).
(4) C. J. Seliskar, O. S. Khalil, and S. P. McGlynn in ref 1.
(5) C. Sieiro and J. I. Fernandez-Alonso, *Chem. Phys. Lett.*, **19**, 557 (1973).
(6) J. Tanaka, S. Nagakura, and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).
(7) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).
(8) J. Tanaka, *Nippon Kagaku Zasshi*, **79**, 1379 (1958); J. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 833 (1963).
(9) M. Ito, M. Tsukioka, and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1559 (1960).
(10) H. Baba and M. Kitamura, *J. Mol. Spectrosc.*, **41**, 302 (1972).
(11) G. Allen, J. G. Watkinson, and K. H. Webb, *Spectrochim. Acta*, **22**, 807 (1966).
(12) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Crystallogr.*, **8**, 157 (1955).
(13) A recent study by Baba and Kitamura (ref 10) of the monomer-dimer emission properties of benzoic acid was based on the assignments of Ito et al. (ref 9). Their results and conclusions will be critically examined in a following paper (ref 15).
(14) Part 2: J. C. Baum and D. S. McClure, *J. Am. Chem. Soc.*, following paper in this issue.
(15) Part 3: J. C. Baum, to be published.
(16) J. C. Baum, Ph.D. Thesis, Princeton University, Princeton, N.J., 1974.
(17) M. Ito, *J. Mol. Spectrosc.*, **4**, 144 (1960).
(18) M. Hosoya, J. Tanaka, and S. Nagakura, *J. Mol. Spectrosc.*, **8**, 257 (1962).
(19) H. E. Ungnade and R. W. Lamb, *J. Am. Chem. Soc.*, **74**, 3789 (1952).
(20) Part 4: J. C. Baum and D. S. McClure, to be published.
(21) J. C. Baum, W. L. Cleveland, L. Goodman, and D. S. McClure, to be published.
(22) M. Vala, Jr., and J. Tanaka, *J. Mol. Spectrosc.*, **32**, 169 (1969).
(23) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807 (1968).
(24) J. Del Bene, H. H. Jaffe, R. L. Ellis, and G. Kuehnlenz, "CNDO/S-CI Molecular Orbital Calculations with the Complete Neglect of Differential Overlap and Configuration Interaction", Program 174, Quantum Chemistry Program Exchange, Indiana University, 1968.
(25) U. Mueller-Westerhoff, "PEP-Pi Electron Program", Program 167, Quantum Chemistry Program Exchange, Indiana University.
(26) D. L. Beveridge and J. Hinze, *J. Am. Chem. Soc.*, **93**, 3107 (1971).
(27) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970, pp 110–111.
(28) S. Hayashi and N. Kimura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 335 (1966); S. Hayashi and J. Umemura, *J. Chem. Phys.*, **60**, 2630 (1974).
(29) Y. G. Smeyers and C. Sieiro, *Theor. Chim. Acta*, **28**, 355 (1973).
(30) The solvent shift was determined using the empirical formula of N. S. Bayliss and L. Hulme, *Aust. J. Chem.*, **6**, 257 (1953).