

CCA-1350

YU ISSN 0011-1643

UDC 541.1:547.58

Original Scientific Paper

Depolarization Ratio $\rho_{\perp}(\pi/2)$ of Raman Bands for Dissolved and Molten Benzoic Acid Dimers

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Received December 15, 1981

The first measurements of the depolarization ratios for vibrational bands of dissolved and molten benzoic acid, obtained by 90° Raman scattering, are reported. The number of observed depolarized bands is smaller than that expected for a planar structure. The results obtained in the present measurements and some steric considerations related to the benzoic acid dimer structure, support the assumption of a non-planar conformation.

INTRODUCTION

Although the X-ray analysis of solid benzoic acid (BAC) at room temperature is known since a long time,¹ the problem of the proton-pair ordering in hydrogen bonds and some details related to the dimer planarity remain still unsettled.

Anomalies in the low temperature IR^{2,3} and NMR⁴ spectra are also known. In order to explain them Hayashi et al. assumed²⁻⁴ that two possible dimer structures (two orderings of proton pairs with a slight energy difference) exist in the crystal.

In a most recent X-ray analysis⁵ at room temperature the proton-pair disorder was observed: a significant electron density peak on the difference Fourier map was situated in the middle of the O...H—O bond. A very small angle (1.5°) between mean planes of the carboxylic and benzene rings was determined.

In all studies of solid BAC performed so far, Hayashi's model²⁻⁵ was invariably used and the planarity of the dimer was assumed in order to explain the observed anomalies. The observed phenomena were, however, not satisfactorily reproduced using this model.

The temperature dependence of the BAC crystal Raman spectrum, in particular the doubling of some bands and their intensity variation with the temperature (our unpublished results) disagree with the predictions of the Hayashi's model. Actually, the features observed in the low-temperature Raman spectra could be explained in terms of the non-planar dimer conformation. Another indication of the dimer non-planarity arises from steric considerations: intramolecular non-bonded O...H distances inside the planar monomer as well as intermolecular O...H distances between neighbouring dimers, in the crystal [1,1,0] direction, are shorter than the corresponding sum of the van der Waals radii.

The main purpose of the present study is to verify the generally accepted assumption that the BAC dimer is planar. As a first step we shall consider the problem of the planarity of the dimers in the solution and in the melt. This could make it easier to draw further conclusions about the conformation in the solid state.

EXPERIMENTAL

All Raman spectra were recorded with a modified LOMO DFS-12 spectrometer using the 4880 Å excitation line from an Ar⁺ laser Spectra Physics 164-03. A lens of 50 mm focal length was used to focus the laser beam on the sample. The light scattered at 90° was collimated by a Minolta lens (aperture 1 : 1.2 and 58 mm focal length) and analyzed with a Polaroid film. A $\lambda/2$ plate in front of the entrance slit ensured the polarization to be always perpendicular to the grating's grooves. A cooled EMI 9558A photomultiplier was used to detect the spectrum and the anode pulses were amplified, discriminated and counted with a SSRI (PARC) 1120, 1110 system. The recorder Goertz, Servogor S, registered their analogue value.

The polarization of the incident beam was kept perpendicular to the scattering plane during all measurements. The depolarization ratio values determined in such conditions $\rho_{\perp}(\pi/2) = I_{\perp}/I_{\parallel}$ are in the range $0 \leq \rho_{\perp}(\pi/2) \leq 3/4$. The depolarization ratios of the bands corresponding to the totally symmetrical vibrations vary in the full range $0 \leq \rho_{\perp} < 3/4$ excluding the value $\rho_{\perp} = 3/4$. On the contrary, the ratios of bands corresponding to non-totally symmetrical vibrations have a single value $\rho_{\perp} = 3/4$ (see ref. 6, page 92). In the present study we shall concentrate our attention on the depolarized bands, $\rho_{\perp} = 3/4$.

BAC solution spectra were recorded with incident beam power of 200 mW. For the BAC melt spectra laser powers at the sample of 200 and 600 mW were used.

Merck p. a. grade substances were used without further purification. The samples were prepared by adding 10% of pure solvent to the saturated solution. Finally, all solutions were filtered to remove undissolved particles.

RESULTS

We found the signal-to-noise ratio to be satisfactory for the given experimental conditions. For example, the observed background spectrum counting rate of 25 counts per second (c/s) was found for pure CCl₄ with analyzer in the perpendicular position. The peak intensity counting rate of the band at 458 cm⁻¹ was 233000 c/s under identical conditions. The optical set-up for the depolarization measurements was checked by determination of the depolarization ratios for bands of pure CCl₄, benzene and formic acid. Results of these test-measurements agreed very well with those of other authors.

Wavenumbers of the characteristic dimer and monomer bands are known from earlier Raman measurements (e. g. refs. 7, 8). In our spectra only weak monomer bands are observed and, owing to their significant separation, these bands do not disturb the determination of the depolarization ratio for the dimer bands. For isolated Raman bands of the BAC dimer the depolarization ratio was determined by taking into account values of the peak intensity. The same results were obtained assuming a triangular band shape.

During the course of this work a large number of spectra has been recorded and we chose only the most representative ones. Figure 1. shows the spectrum of BAC dissolved in CCl₄ in the frequency range 1100—1350 cm⁻¹ with the analyzer in both positions. The three bands of lower frequency are assigned to the characteristic vibrations of the monosubstituted benzene derivatives, while the remaining two are assigned to vibrations of the carboxylic ring predominantly of C—O stretching and C—O—H bending character. Actually, in the crystal spectrum at low temperatures, these bands split into

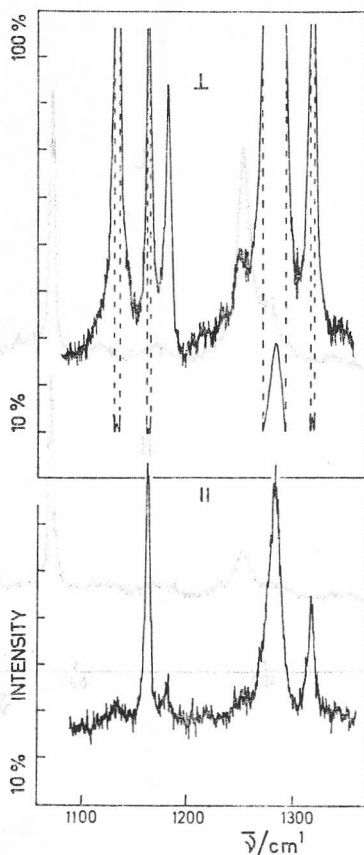


Figure 1. Raman spectra I \perp and II \parallel of benzoic acid dissolved in CCl $_4$.

two components, which at very low temperatures exhibit a well determined shoulder. Therefore, each of the two bands observed at room temperature is apparently due to a coincidence of the carboxylic- and aromatic-ring vibrations. The spectrum of molten BAC, shown in Figures 2a and b, has been recorded at $T = (132 \pm 2)^\circ\text{C}$. The complete sets of depolarization ratios for various BAC solutions at room temperature and those for BAC melt at 132°C are listed in Table I. The error in the depolarization ratio is estimated to be $\pm 10\%$ (if not stated otherwise). The depolarization ratio has been determined even in cases where the intensity I_{\parallel} was extremely weak or in cases of bands which are close to a strong band of the solvent. The error has been estimated to be $\pm 30\%$ and ρ_{\perp} is marked in Table I by an asterisk.

The depolarization ratio has been determined for 17 of the 22 observed bands presented in Table I. The bands at 190, 610, 810, 1162 and 1602 cm^{-1} exhibit a high degree of depolarization but only the band at 190 cm^{-1} can be considered to have $\rho_{\perp} = 3/4$. In previously mentioned measurements, performed on benzene and formic acid, the values of the measured depolarization ratio of known non-totally symmetric vibrations are always higher or equal

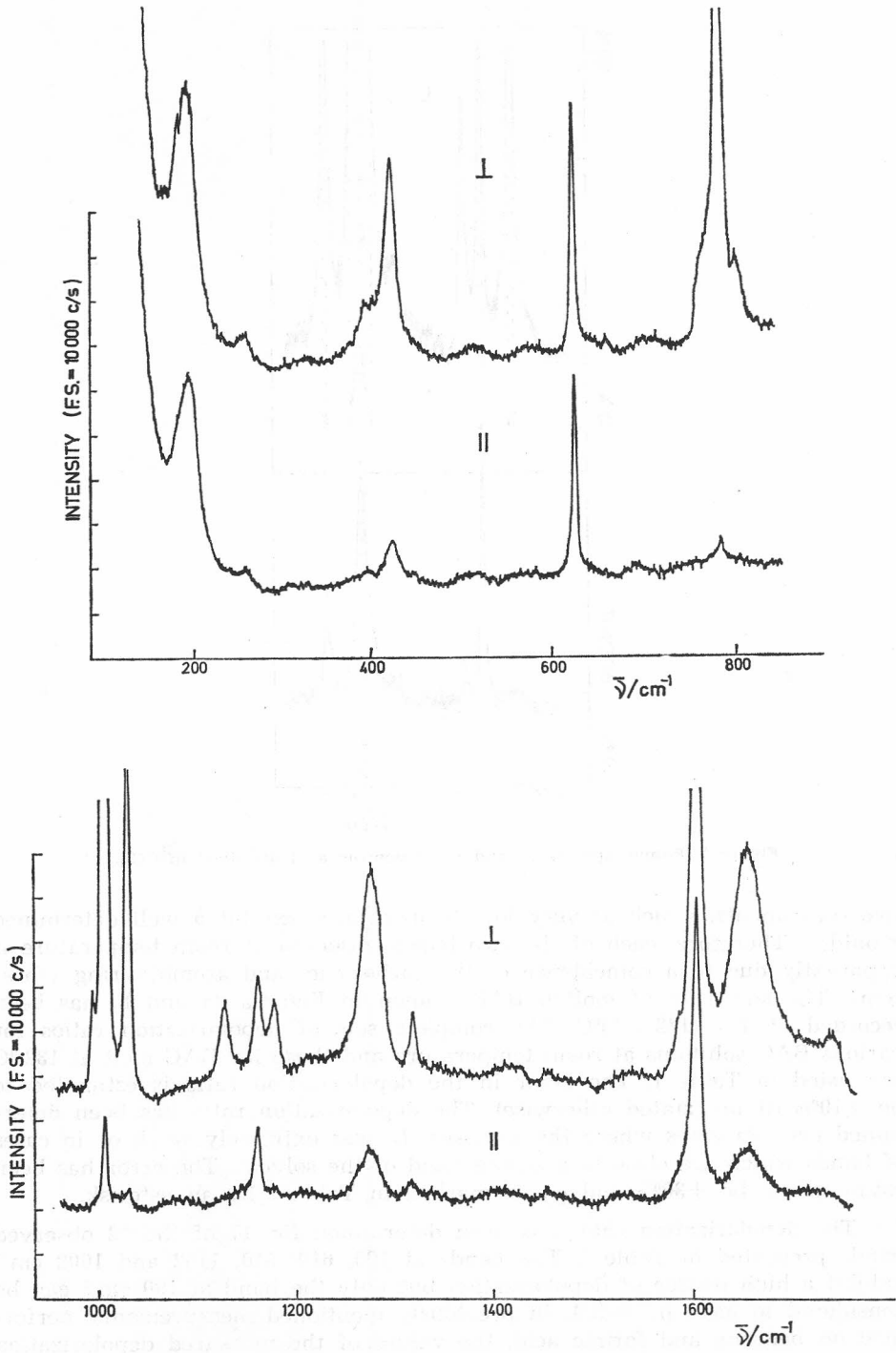


Figure 2a) and b). Raman spectra I_⊥ and I_∥ of molten benzoic acid.

TABLE I

Depolarization Ratio of Raman Bands for Dissolved and Molten Benzoic Acid Dimers

| Frequency (cm ⁻¹) | Depolarization ratio ρ_{\perp} ($\pi/2$) | | | | | Polarization ^a |
|----------------------------------|---|--|-------------------|-----------------|-------------|---------------------------|
| | CCl ₄ | Solution in CH ₂ Cl ₂ | CHCl ₃ | CS ₂ | BAC melt | |
| 1653 | 0.22 | 0.24 | 0.15 | 0.17 | 0.23 | P |
| 1602 | 0.46 | 0.50 | 0.37 | 0.53 | 0.52 | P |
| 1586 | | | | | | P ^b |
| 1460 | | | | | | P ^b |
| 1440 | | | | | | P ^b |
| 1320 | 0.27 | 0.27 | 0.16 | 0.21 | 0.28 | P |
| 1285 | 0.20 | 0.21 | 0.14 | 0.19 | 0.23 | P |
| 1180 | 0.11* | 0.10* | 0.15* | | 0.11* | P |
| 1162 | 0.72 | | 0.43 | 0.55 | 0.66 | P |
| 1130 | 0.04* | 0.02* | 0.08* | | 0.13* | P |
| 1025 | 0.02 | 0.02 | 0.02 | | 0.02 | P |
| 1000 | 0.02 | 0.03 | 0.02 | 0.03 | 0.03 | P |
| 990 | 0.05* | 0.07* | 0.03* | | 0.10* | P |
| 930 | | | | | | |
| 810 | | 0.60* | | | 0.43* | P |
| 785 | | 0.03 | 0.04* | | 0.02 | P |
| 660 | 0.27* | | | | | P |
| 610 | 0.46 | 0.75 | 0.55 | | 0.75 | P |
| 505 | | 0.45* | | | | P |
| 410 | 0.51 | | | | 0.23 | P |
| 250 | | | | | | |
| 190 | | 0.70* | 0.50* | | 0.75* | D |

* The error of depolarization ratios is estimated to be $\pm 30\%$.^a The conclusion on the bands polarization is derived from present measurements.^b The conclusion on the polarization of these bands is derived from their position in the spectrum.

to 0.7. Therefore, the lower values obtained for BAC melt can not be caused by an experimental error. From the 17 bands, whose depolarization ratio has been determined, only one is depolarized while the other 16 bands are polarized.

DISCUSSION AND CONCLUSIONS

Assuming that in the considered experimental conditions the structure of the BAC dimer is planar (C_{2h} symmetry) we expect in the Raman spectrum:

29 polarized bands of species A_g ($0 \leq \rho_{\perp} < 3/4$) and

13 depolarized bands of species B_g ($\rho_{\perp} = 3/4$).

In the spectral region from 160 to 1700 cm⁻¹, in which we are able to observe well resolved BAC bands, we expect 21 bands from the first and 12 from the second group. However, from the 33 expected bands, only 22 were observed and for 17 of these bands the depolarization ratio could be measured.

Besides, the bands at 1440, 1460 and 1586 cm⁻¹ could certainly be considered also as polarized, even if their depolarization ratios were not determined. These bands correspond to well-known in-plane vibrations of the monosubstituted benzenes which, for the C_{2h} symmetry, are totally symmetric. Therefore, assuming a planar structure for the dimer, instead of the 21 polarized and 12 depolarized expected bands we observe 19 polarized and 1 depolarized.

The number of observed depolarized bands (only 1) is too small compared to the expected number from the C_{2h} symmetry group. It is, of course, well

known that depolarized bands are generally weaker, and often cannot be observed in the Raman spectrum. However, in our spectra there are bands at 810 and 990 cm^{-1} which certainly correspond to out-of-plane vibrations of monosubstituted benzenes⁹ and as can be seen from Table I, they are not depolarized.

The present results on the number of depolarized bands in the Raman spectra of the free dimer as well as the steric considerations point out that the assumption of the planar structure should be revised. Consequently, the dimer symmetry is lower than C_{2h} . Two symmetry groups are possible: C_1 or C_i . The first one can be excluded since the separation of the IR and Raman active vibrations is conserved in all spectroscopic investigations performed so far. Thus, the symmetry of the dimer is C_i .

From measurements of this kind it is impossible to extract the angle between the two planes. However, the angle between the planes of the carboxylic and of the benzene rings for substituted benzoic acids in solid is usually between 5° and 30° . Most probably, the carboxylic ring of the benzoic acid departs from the mean plane of the benzene rings by a similar angle.

After this work was completed, a paper by R. Feld et al.¹⁰ appeared with new results on the solid BAC structure obtained by X-ray and neutron diffraction at room and low temperature. The slight non-planarity and a disorder of the proton pairs are here confirmed. An attempt is made to interpret the results obtained at low temperature by the model of proton-pair disorder proposed by Hayashi, but the agreement is apparently poor. The dimer non-planarity (e. g. double minimum potential for a coordinate describing a torsion) might be much more useful in explaining the crystal structure and the anomalous temperature dependence of solid BAC spectra.

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SAŽETAK

Omjer depolarizacije $\rho_{\perp}(\pi/2)$ Ramanovih vrpca dimera benzojeve kiseline u otopinama i talini

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Po prvi puta je određen omjer depolarizacije $\rho_{\perp}(\pi/2)$ vibracijskih vrpca otopina i taline benzojeve kiseline, s pomoću Ramanova raspršenja na 90° . Broj opaženih depolariziranih vrpca premalen je u usporedbi s brojem koji proizlazi iz pretpostavke o planarnoj konformaciji. Na temelju mjerenja i steričkih razmatranja izveden je zaključak o neplanarnosti dimera.