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Abstract

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THE EFFECT OF PRESSURE ON THE ABSORPTION SPECTRUM OF BENZENE IN THE NEAR INFRARED REGION*

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The present work continues the investigation of the effect of pressure (up to 25,000 kg/cm^2) on the absorption spectrum of benzene in the region 4300–6000 cm^{-1}. The general changes in the spectrum caused by pressure are identical to the changes observed for the longer-wavelength absorption bands of benzene in the preceding work (^{1}).

In the liquid state of the object, an increase in pressure leads to a shift of the bands toward lower frequencies. The transition to the solid state is accompanied by a sharp shift of the bands in the opposite direction and by their narrowing. Upon further compression of the sample, the bands also shift monotonically toward higher frequencies, while the half-width of the bands decreases only slightly

Table 1

No.	ν, cm^{-1}(p = 1 kg/cm^2)	Interpretation*	$\Delta\nu/\Delta$p $\cdot 10^3$ cm^{-1} $\cdot$ cm^2/kgliquid phase	$\Delta\nu/\Delta$p $\cdot 10^3$ cm^{-1} $\cdot$ cm^2/kgsolid phase
1	4022	ν_{15} (E$_2$g) + ν_6 (B$_1$u)	−2.3	1.2
2	4054	ν_{15} (E$_2$g) + ν_{14} (E$_1$u)	−0.7	0.8
3	4071	ν_{12} (E$_1$u) + ν_2 (A$_1$g)	–	1.3
4	4090	ν_{14} (E$_1$u) + ν_1 (A$_1$g)	–	1.3?
5	4152	ν_{15} (E$_2$g) + ν_{10} (B$_2$u)	−2.2	0.8?

No.	ν, cm^{-1}(p = 1 kg/cm^2)	Interpretation*	$\Delta\nu/\Delta p \cdot 10^3$ $cm^{-1} \cdot cm^2/kg$liquid phase	$\Delta\nu/\Delta p \cdot 10^3$ $cm^{-1} \cdot cm^2/kg$solid phase
6	4174	ν_{12} (E_1u) + ν_{10} (B_2u)	–	1.0**
7	4195	ν_{17} (E_2g) + ν_5 (B_1u)	–	1.3
8	4250	ν_{12} (E_1u) + ν_{17} (E_2g)	–	1.3
9	4509	ν_{13} (E_1u) + ν_5 (B_1u)	–	1.3 and 1.7***
10	4532	ν_{13} (E_1u) + ν_{15} (E_2g)	−0.9	0.9 and 1.1***
11	4568	ν_{12} (E_1u) + ν_{13} (E_1u)	−1.0	1.1
12	4608	ν_{16} (E_2g) + ν_5 (B_1u)	−1.5	1.1
13	4627	ν_{12} (E_1u) + ν_{16} (E_2g)	−1.1	1.0
14	4653	ν_{15} (E_2g) + ν_9 (B_2u)	−1.9	1.2 and 1.1***
15	5920	ν_{15} (E_2g) + ν_5 (B_1u)	–	1.0? ****
16	5988	ν_{12} (E_1u) + ν_1 (A_1g)	–	1.3? ****

* Notation of vibrations according to G. Herzberg ([10]).

** The value of $\Delta\nu/\Delta p$ is given as an average, since the band splits at high pressures into a triplet.

*** The data correspond to different phases of solid benzene.

**** The accuracy of the measurements is low because of the weakness of the bands.

slightly (Figs. 1 and 2). An improvement in the accuracy of the measurements was achieved owing to narrowing of the spectral slits to 0.08 mm. On the basis of general concepts developed for liquids under pressures up to $p \leq 10000$ kg/cm^2 by Drickamer ([2]), the shift of bands toward higher frequencies is explained by

* The content of the article was reported by the author at the XV Conference

Fig. 1

Figure 1: Fig. 1

on Spectroscopy in Minsk in July 1963.

with an increasing role of repulsive forces in the overall balance of intermolecular forces as the intermolecular distances decrease with increasing pressure.

When benzene is solidified under pressure, the intensity of many of its absorption bands increases in comparison with that observed under normal conditions. This makes it possible to detect bands that at $p = 1$ kg/cm^2 can be noticed only with a large thickness of the liquid layer. A special case is constituted by pressure-induced bands, for which the absorption intensity at the maxima of the bands increases as the pressure is raised.

Fig. 1. Spectrograms of mixtures of benzene + NaCl at pressures $p = 1$ kg/cm^2 (1), 4200 kg/cm^2 (2), and 20400 kg/cm^2 (3) (the recording was made at different gain factors)

It should be noted that the hysteresis, observed earlier when the pressure was decreased, in the shift $\Delta\nu$ (1) is a misunderstanding caused by an extremely slow recovery of the volume of the NaCl salt transmitting the pressure. In addition, it has been established that the dependences $\Delta\nu = \Delta\nu(p)$ for the bands 4532 and 4653 cm^{-1} undergo a discontinuity at $p \approx 13000$ kg/cm^2 (Fig. 2). It is accompanied by an anomalous increase in absorption. Apparently this is connected with a phase transition of benzene into the second modification of the solid state, found by Bridgman at $p = 12500$ kg/cm^2 (3) and not noticed by us in the previous work. The shift $\Delta\nu > 0$ during the transition indicates a decrease in the dimensions of the crystal cell of benzene.

Table 1 gives the frequencies of the band maxima at normal pressure, as well as the values $\dfrac{\Delta\nu}{\Delta p} \cdot 10^3$, where $\Delta\nu$ is the shift of the maximum in cm^{-1} when the pressure is increased by Δp kg/cm^2. It includes data for bands studied earlier (1), with the value $\Delta\nu/\Delta p$ for band No. 1 in the solid phase and the value ν for band No. 5 being refined. The interpretation of the bands proposed by Keii (4) was checked by us and proved correct for all bands except Nos. 1 and 11.

Most of the bands investigated, in terms of the symmetry of the combination vibrations, belong to the class E_{1u}. The exceptions are bands Nos. 2, 10, and 13, for which the resulting symmetry is $B_{1u} + B_{2u} + E_{1u}$. It follows from the table that the indicated bands, in magnitude of $\Delta\nu/\Delta p$ in both aggregate states, are smaller than the others. Evidently, the deformations of the molecule caused by pressure affect vibrations of the same symmetry in the same way. On this basis, bands Nos. 1 and 11 are given in the table an interpretation different from that indicated by Keii.

In the entire spectral interval studied, the most noticeable pressure-induced

Fig. 2. Dependence of the shift $\Delta\nu$ of the maximum of the 4532 cm^{-1} band on pressure

Figure 2: Fig. 2. Dependence of the shift $\Delta\nu$ of the maximum of the 4532 cm^{-1} band on pressure

bands are 4071, 4174, 4509, and 4532 cm^{-1} (Table 1). The bands 4090 and 4195 cm^{-1}, previously noted as induced bands, are significantly weaker in intensity. The independence of the appearance of induced bands from the nature of the salt transmitting the pressure testifies to their "benzene" origin.* The coincidence of the frequencies of some of them with the data Keya at $p = 1$ kG/cm^2 makes it possible to suppose that their appearance is connected with a violation of the selection rules upon deformation of the molecules. A possible explanation of the induced bands is given in Table 1. The experimental relationship between $\Delta\nu/\Delta p$ and the symmetry of the vibration is thereby observed. On the other hand, the new bands may be caused by vibrations of molecules in the crystal relative to one another, combining with the strongest intramolecular vibrations with frequencies 4054, 4568, and 4653 cm^{-1}. The oscillator strengths of the last two vibrations are approximately the same. However, the frequency differences of the principal bands and their assumed satellites are respectively: +16, +120, −59, and −36 cm^{-1}, or, if measured from the band 4653 cm^{-1}, then for the last two induced bands −144 and −121 cm^{-1}. The values obtained do not coincide with the vibrational frequencies of crystalline benzene at low temperature (6), although they are close in order of magnitude. Without rejecting such an explanation, one may in addition propose another hypothesis, according to which the new bands are associated with the presence of discrete positions of benzene molecules on the surface of the salt (1), caused by the polarizing action of the latter (see below). For a critical assessment of each of the assumptions, the data are still insufficient.

Fig. 2. Dependence of the shift $\Delta\nu$ of the maximum of the 4532 cm^{-1} band on pressure

In the preceding measurements, the pressure-transmitting medium was NaCl. It is known that strong electric fields arise at the surface of an ionic salt (7,8), changing the spectrum of the adsorbate (9). In order to check the influence of the salt, benzene was studied under pressure in NaF, NaBr, and KCl media. The ratio of the frequency shifts in different salts at the same pressure is described fairly well by the inverse ratio of the constants a of their lattices, if compared with the results in NaCl (Table 2).

Table 2

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* This refutes the hypothesis of simultaneous transitions occurring in the molecule of the substance and in the surrounding salt, which was put forward earlier in work (5).

ν, cm^{-1} ($p = 1\ \text{kG/cm}^2$)	ν, cm^{-1} ($p = 1\ \text{kG/cm}^2$)	$\Delta\nu_i/\Delta\nu_{\text{NaCl}}$	$\Delta\nu_i/\Delta\nu_{\text{NaCl}}$	$\Delta\nu_i/\Delta\nu_{\text{NaCl}}$
liquid C_6H_6	mixture $C_6H_6 + \text{NaCl}$	$\frac{a_{\text{NaCl}}}{a_{\text{NaF}}} = 1.2$	$\frac{a_{\text{NaCl}}}{a_{\text{NaBr}}} = 0.95$	$\frac{a_{\text{NaCl}}}{a_{\text{KCl}}} = 0.89$
4052	4054	1.2	0.82	0.82
4533	4532	1.3	0.97	1.0
4571	4568	1.2	0.93	0.77
4652	4653	1.1	0.85	1.0

To explain this fact one may use Hückel' s theory (⁷), according to which the field strength F at a distance x from an ion with charge e is described by the formula

$$F(a,x) = A\frac{e}{a^2}\exp\left[-2\pi\sqrt{2}\,\frac{x}{a}\right],$$

where A is a constant. In this representation, the ratio $\Delta\nu_1/\Delta\nu_2$ in different media, denoted by the indices 1 and 2, can be compared with the ratio of the increments of energy acquired by the molecule in the electric fields of different salts. The experimental result satisfies this ratio at $x = a$. The different compressibility of the salts, affecting x, leads to a deviation of the observed ratio $\Delta\nu_1/\Delta\nu_2$ from the expected a_2/a_1. The polarizing influence of the salt manifests itself already under normal conditions. In Table 2

the frequencies of the bands of liquid benzene and of a benzene + NaCl mixture, equal in liquid-layer thickness, at $p = 1\ \text{kg/cm}^2$, were compared. The differences in frequencies are small, but they are revealed much more clearly in experiments under pressure, in which, with series measurements, the errors in determining $\Delta\nu$ are reduced.

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