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Fig. 1. Absorption spectra of benzene at different pressures. Spectral slit width 0.08 mm. a –P = 1 kg/cm^2; –P = 4200 kg/cm^2; –P = 8300 kg/cm^2; –P = 12,500 kg/cm^2; –P = 18,700 kg/cm^2. The arrows beneath the spectra indicate the bands of the C_6H_6 molecule and the bands induced by pressure; the arrows above the spectra indicate absorption bands of atmospheric vapors and gases

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Abstract

Full Text

PHYSICS

Yu. A. KLYUEV, B. OKSENGORN

THE EFFECT OF PRESSURE ON THE INFRARED ABSORPTION SPECTRUM OF BENZENE

(Presented by Academician A. N. Terenin, January 3, 1963)

The effect of small pressures on the absorption spectrum of benzene in the near ultraviolet region of the spectrum was studied earlier by one of the authors (^{1}). It was established that, when the pressure was increased to 1500 kg/cm^2, the absorption bands A_n^0 shifted toward the red side of the spectrum. No changes in the band width or in the integral intensity were detected.

In the present article we give the results of studies of the effect of pressures up to 25,000 kg/cm^2 on the absorption spectrum of benzene in the overtone region of vibrational frequencies 4000–4300 cm^{-1}. Under such compressions, at room temperature benzene passes from the liquid state into the solid state, which leads to characteristic changes in the spectrum. The work was carried out on a monochromator from an IKS-12 spectrometer with a LiF prism and a lead sulfide detector. To obtain maximum illumination of the high-pressure cuvette, developed by one of the authors (^{2}), a special illuminator with a point zirconium lamp was used. The reduced thickness of the benzene layer was approximately 0.1 mm, and therefore weak absorption bands against the general background are barely noticeable.

Fig. 2. Dependence of the shift of the maximum of the benzene absorption band 4053 cm^{-1} on pressure. The arrows indicate the sequence of pressure change

Figure 2: Fig. 2. Dependence of the shift of the maximum of the benzene absorption band 4053 cm^{-1} on pressure. The arrows indicate the sequence of pressure change

Fig. 1. Absorption spectra of benzene at different pressures. Spectral slit width 0.08 mm.
a $-P = 1$ kg/cm^2; $-P = 4200$ kg/cm^2; $-P = 8300$ kg/cm^2; $-P = 12{,}500$ kg/cm^2; $-P = 18{,}700$ kg/cm^2. The arrows beneath the spectra indicate the bands of the C_6H_6 molecule and the bands induced by pressure; the arrows above the spectra indicate absorption bands of atmospheric vapors and gases.

At atmospheric pressure, in the spectrum of this layer of benzene the known absorption bands 4023, 4053, 4160, and 4195 cm^{-1} are observed (Fig. 1, *a*). Of these, the last two were clearly revealed only under pressure and, in contrast to ...

tion from the bands of atmospheric water vapor; upon compression they shifted and changed their shape. With the exception of the 4023 cm^{-1} band, the wave numbers of the band maxima agree well with the data of Key' s work (^{3}). According to his interpretation, verified by us, the most intense band

Fig. 2. Dependence of the shift of the maximum of the benzene absorption band 4053 cm^{-1} on pressure. The arrows indicate the sequence of pressure change

4053 cm^{-1} is due to a combination vibration with frequency $\nu_{15} + \nu_{14}$, the band 4160 cm^{-1} to the frequency $\nu_{15} + \nu_{10}$, and the band 4195 cm^{-1} to the frequency $\nu_{17} + \nu_5$. The frequencies of the component vibrations are given in Herzberg' s notation (^{4}) and therefore are not discussed in detail. The weak band 4023 cm^{-1}, not detected by Key, may be represented as one of the combinations of vibrations: $\nu_{15} + \nu_6$ or $\nu_{15} + \nu_2$.

Table 1

Absorption band ν, cm^{-1}	Interpretation of bands	$\frac{\Delta\nu}{\Delta p} \cdot 10^3$, $cm^{-1} \cdot cm^2/kg$, liquid phase	$\frac{\Delta\nu}{\Delta p} \cdot 10^3$, $cm^{-1} \cdot cm^2/kg$, solid phase
4023	$\nu_{15}(E_{2g}) + \nu_6(B_{1u})$	−2.3	0.9
4053	$\nu_{15}(E_{2g}) + \nu_{14}(E_{1u})$	−0.7	0.8

Graph: dependence of the displacement $\Delta\nu$ of the pressure-induced benzene band at 4071 cm^{-1} on pressure $p \cdot 10^3$, with axes labeled $\Delta\nu$ in cm^{-1} and pressure in kg/cm^2.

Figure 3: Graph: dependence of the displacement $\Delta\nu$ of the pressure-induced benzene band at 4071 cm^{-1} on pressure $p \cdot 10^3$, with axes labeled $\Delta\nu$ in cm^{-1} and pressure in kg/cm^2.

Absorption band ν, cm^{-1}	Interpretation of bands	$\frac{\Delta\nu}{\Delta p} \cdot 10^3$, cm^{-1}·cm^2/kg, liquid phase	$\frac{\Delta\nu}{\Delta p} \cdot 10^3$, cm^{-1}·cm^2/kg, solid phase
4160	$\nu_{15}(E_{2g}) + \nu_{10}(B_{2u})$	−2.2	–
4195	$\nu_{17}(E_{2g}) + \nu_5(B_{1u})$	–	1.3

Upon compression of the sample up to the onset of benzene solidification (^{5}), which under the conditions of our experiments occurs at 1900 kg/cm^2, all bands shift toward lower frequencies (Figs. 1 and 2). The half-width of the 4053 cm^{-1} band, which can be measured more accurately, does not change in this process. At the moment of crystallization a sharp shift of the bands toward higher frequencies is observed (Fig. 2). Above the point of phase change, a further increase in pressure promotes a subsequent monotonic shift of the bands in the same direction and the development of new bands absent from the spectrum of liquid benzene. The new, pressure-induced bands also shift toward higher frequencies as the sample is compressed further (Fig. 3). When the pressure is lowered, hysteresis is observed (Fig. 2). The phase transition $C_6H_6I \rightarrow C_6H_6II$, which Bridgman found at 12,500 kg/cm^2 (^{5}), was not observed by us.

In Table 1 each band is characterized by the value $\Delta\nu/\Delta p$, where $\Delta\nu$ is the displacement of the band maximum in cm^{-1} relative to its position at normal pressure, and Δp is the corresponding change in pressure in kg/cm^2. In each combination of vibrations determining the bands 4023, 4053, and 4160 cm^{-1}, the vibration ν_{15} is involved; therefore the difference in $\Delta\nu/\Delta p$ is determined by the nature of the other component vibrations. The symmetry of each vibration is indicated in the table. In the liquid phase the bands 4023 and 4160 cm^{-1} behave identically. Therefore the band 4023 cm^{-1} should be interpreted as $\nu_{15} + \nu_6$, and not $\nu_{15} + \nu_2$, since the vibrations ν_6 and ν_{10} belong to the same symmetry type B_u, whereas ν_2 belongs to the type A_{1g}. It also follows from the table that in the liquid phase the bands that experience the

Fig. 3. Dependence of the displacement of the pressure-induced benzene band at 4071 cm^{-1} on pressure

greater perturbation from pressure are those which, in addition to the vibration ν_{15}, distinguished by the lowest symmetry among the vibrations studied, include the vibrations ν_6 and ν_{10}, which are more symmetric than ν_{14}. In our case, the pair consisting of the less symmetric vibrations $\nu_{15} + \nu_{14}$ shifts with increasing pressure more slowly than, for example, $\nu_{15} + \nu_6$. In earlier experiments with chloroform the same regularity was observed [6]. Indeed, in liquid chloroform $(\Delta\nu/\Delta p)_{2\nu_1} = -0.9 \cdot 10^{-3}$ and $(\Delta\nu/\Delta p)_{\nu_1+\nu_4} = -0.6 \cdot 10^{-3}$ cm^{-1}cm^2/kg, where the subscripts indicate the origin of the bands, ν_1 is the stretching vibration, and ν_4 is the deformation vibration of the C–H bond. Obviously, when estimating the influence of pressure on combination absorption bands, one should consider the symmetry properties of the component vibrations; moreover, pairs of less symmetric vibrations undergo a smaller perturbation upon compression.

In the solid state of benzene, the differences in the slope of the $\Delta\nu/\Delta p$ curves for the four bands are insignificant (Table 1). This indicates that the molecules are fixed in such mutual positions in which each pair of vibrations symmetrical to the same degree.* However, despite the fact that the 4195 cm^{-1} band is, in symmetry, completely identical with the 4023 cm^{-1} band, $\Delta\nu/\Delta p$ for them differ substantially. Apparently, the data given refer to a new band, induced by pressure, which masks the principal 4195 cm^{-1} band and whose shift is more significant. This is also indicated by the strong dependence of the intensity of the 4195 cm^{-1} band on pressure.

When benzene under pressure passes into the solid phase, induced bands appear in the spectrum at 4071, 4090, and 4195 cm^{-1} (Fig. 1, *b*–*d*). (In the present case and below, the 4195 cm^{-1} band is regarded as induced.) Compression of the sample leads to their shift toward higher frequencies at rates of $1.2 \cdot 10^{-3}$, $2.0 \cdot 10^{-3}$, and $1.3 \cdot 10^{-3}$ cm^{-1}·cm^2/kg. If it is assumed that these bands can be caused by fundamental vibrations of the benzene molecule, then for the first two bands the most probable combinations are the vibrations $\nu_{12}(E_{1u}) + \nu_2(A_{1g})$ and $\nu_{14}(E_{1u}) + \nu_1(A_{1g})$, respectively (3). With such identical symmetry both bands should shift with the same slope $\Delta\nu/\Delta p$, which is contradicted by experiment. In addition, the 4071 cm^{-1} band, as the pressure increases, grows in relative intensity just like the 4195 cm^{-1} band, which cannot be noted for the 4090 cm^{-1} band. We showed above that the first of these cannot be represented by a combination of the fundamental vibrations of benzene. Apparently, this conclusion should be extended to all the induced bands, and another explanation should be sought for them.

The induced bands, which have the appearance of satellites, are located on the high-frequency side of the strongest benzene band, 4053 cm^{-1}, at 18, 37, and 142 cm^{-1}, respectively. In work with chloroform (6) a pressure-induced band was found, situated on the low-frequency wing of the principal $\nu_1 + \nu_4$ band of chloroform, 15 cm^{-1} from its maximum.

A possible interpretation is that the new bands induced by pressure belong to benzene molecules introduced into the NaCl lattice in certain different positions, creating the observed discrete shifts of the vibrational frequencies.

In conclusion, we note that in the solid phase the dependence of the band shift on pressure, obtained on samples that had previously been subjected to strong compression (above 1900 kg/cm^2), differs from that obtained with fresh samples (dashed lines in Figs. 2 and 3). The induced bands arise at lower pressures than usual. This indicates the formation under pressure, as a result of the molding process, of a closer mutual penetration of benzene molecules into the salt medium.

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[*] It is interesting to note that, for chloroform in the solid state, $(\Delta\nu/\Delta p)_{2\nu_1} = 0.8 \cdot 10^{-3}$ and $(\Delta\nu/\Delta p)_{\nu_1+\nu_4} = 0.6 \cdot 10^{-3}$ cm^{-1}·cm^2/kg, i.e., they are close in magnitude to those observed in benzene.

Note: Figure translations are in progress. See original paper for figures.

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