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Abstract

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THE EFFECT OF PRESSURE ON THE VIBRATIONAL ABSORPTION SPECTRUM OF CHLOROFORM

When liquid chloroform was compressed with hydrogen (up to 2200 kg/cm^2), one of the authors found a slight shift of the maximum of the band $4\nu_1$, the third overtone of the stretching vibration of the C—H bond, toward longer wavelengths, and a strong broadening of the band $3\nu_1 + \nu_4$, where ν_4 is the frequency of the deformation vibration corresponding to bending of the C—H bond relative to the rest of the molecule (^{1}). The shift toward the red side of the spectrum was explained by an increase in the mutual attraction of the molecules due to dispersion forces, and the broadening of the band by the effect of dissolution of the gas in the liquid.

Drickamer and co-workers studied the effect of pressure on the shift of the fundamental absorption band of chloroform, ν_1. They investigated, up to 10,000 kg/cm^2, solutions of chloroform in polar and nonpolar solvents (^{2}), and, up to 50,000 kg/cm^2, pure chloroform (^{3}). In the second work, upon freezing of the liquid, a sharp shift of the band toward longer wavelengths was observed. According to Bridgman' s data, upon the transition of chloroform to the solid state under pressure the polar volume of chloroform decreases strongly (^{4}); therefore it is natural to expect an increase in the role of repulsive forces in the overall balance of intermolecular interaction forces, and consequently a shift of the band toward shorter wavelengths.

The present work was undertaken in order to clarify the question of the shift of the absorption bands of chloroform when it passes from the liquid to the solid state under compression. Concerning the vibrational spectra of substances at high pressures, only the works of Lippincott and co-workers are known (^{5}).

The high-pressure chamber and the optical method of its calibration by phase transitions of several salts are described in (^{6}). The light flux from a point zirconium lamp DAts-50, after passing through the chamber and the monochromator of an IKS-12 spectrometer with a LiF prism, was detected by an uncooled lead sulfide photoresistor.

Chloroform, placed in a NaCl matrix, at normal pressure gave a spectrum whose band shapes and positions of their maxima were identical with the spectrum of the pure liquid. In the work the strongest absorption bands were investigated:

Fig. 1. Shift of the maximum of the $2\nu_1$ absorption band of chloroform with pressure

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$2\nu_1$, the first overtone of the stretching vibration of the C—H bond, with a maximum at 5909 cm^{-1}, and the combination band $\nu_1 + \nu_4$, with a maximum at 4203 cm^{-1}. The frequencies of the band maxima agree well with the results of a number of authors (7,8). The refractive index of the liquid investigated was 1.448.

With increasing pressure p, a shift $\Delta\nu$ of the band maxima was observed relative to their positions at 1 atm. The changes undergone by both bands during the raising and release of pressure (direct and reverse experiments) were qualitatively identical. The observed hysteresis of $\Delta\nu$ was not specially studied. In the liquid phase the bands shifted toward lower frequencies. Upon freezing, which occurred at 8000 kg/cm^2, they shifted toward higher frequencies; with further increase in pressure the bands shifted monotonically toward higher frequencies. Below the freezing point, an increase in pressure caused a noticeable broadening of the bands; above it, no broadening was observed. On transition to the solid phase the bands narrowed almost twofold and the absorption increased. No changes in the intensity of the bands as a function of pressure in the different phases were detected.

In Fig. 1, the solid curves show our results for the $2\nu_1$ band, obtained in direct and reverse experiments (indicated by arrows). For comparison, Drickamer' s data are given (dash-dotted lines); the dependence represented by lines 1 was calculated from the results for the fundamental-frequency band ν_1 (3), while curve 2 is taken from (2). All three dependences of $\Delta\nu$ on pressure for the liquid phase correlate rather well with one another. Upon freezing, the shift of the band is opposite in sign to the shift noted earlier by Drickamer, and in magnitude it reached 6 cm^{-1}. Compression of solid chloroform caused the band to shift toward the blue side of the spectrum; an increase in pressure by 10 000 kg/cm^2 was accompanied by a shift equal to +8.8 cm^{-1}. The curvature of the experimental lines near the freezing point is due to the gradual change in the aggregate state of the sample. We consider that the true dependence is represented by the dashed line.

Fig. 1. Shift of the maximum of the $2\nu_1$ absorption band of chloroform with pressure

The difference between the direction of the shift of the $2\nu_1$ band according to our data and according to Drickamer' s data is apparently explained by the transition of chloroform into close, but different, solid-state phases. This may be caused by different experimental conditions. The absence of a phase p—T diagram for chloroform does not allow this assumption to be verified.

Fig. 2. Dependences of the shift of the maxima of the $\nu_1 + \nu_4$ absorption bands and of the pressure-induced band on pressure

Figure 2: Fig. 2. Dependences of the shift of the maxima of the $\nu_1 + \nu_4$ absorption bands and of the pressure-induced band on pressure

Fig. 3

Figure 3: Fig. 3

In Fig. 2, the shift of the $\nu_1 + \nu_4$ band at different pressures is presented. Using Buckingham' s conclusions (9), verified under normal-pressure conditions by Price (10), the change in the frequency of the maximum of the combination band can be represented in the following form:
$\Delta(\nu_1 + \nu_4) = \Delta\nu_1 + \Delta\nu_4$.

Fig. 2. Dependences of the shift of the maxima of the $\nu_1 + \nu_4$ absorption bands and of the pressure-induced band on pressure

For the calculated dependence of the shift $\Delta\nu_4$ as a function of pressure, a slight change in frequency in both states of the substance and a sharp red shift upon its solidification are characteristic (Fig. 3). In Drickamer' s work, the red shift upon freezing was explained by a reorientation of molecules relative to one another, with the final mutual arrangement of the molecules corresponding to the minimum potential energy of repulsion (2). Chloroform molecules must be arranged so that the C—H bonds of different molecules lie on one line and each H atom has 3 Cl atoms as its nearest neighbors.

In studying the $\nu_1 + \nu_4$ band, a new absorption band was found with a maximum frequency of 4193 cm^{-1}, induced by pressure (Fig. 4). But—

band immediately after freezing appeared first in violation of the symmetry of the main band. The peaks of the bands were clearly resolved at pressures above 12,850 kg/cm^2. With increasing pressure the indicated band shifted to the blue side, as shown in Fig. 2 by the dotted line.

For explaining the origin of the new band it may be assumed that, with increasing pressure, the probability increases of excitation of a triple simultaneous transition of the type $\nu_1 + \nu_5 + \nu_3$, where ν_5 and ν_3 are the frequencies of the deformation vibrations of the C—Cl and C—Cl$_3$ bonds, respectively. However, according to Kaye' s data (^{7}), the sum of the indicated frequencies is 4165 cm^{-1}, the frequency values being taken at atmospheric pressure; therefore this assumption requires additional confirmation.

Fig. 3. Shift of the maximum of the ν_4 absorption band with pressure

The theory of Ketelaar and Hooge (^{11}) may be taken as the basis of another interpretation, according to which, as the density of solutions increases, new absorption bands arise, $\nu_x = \nu_1 + \nu_2$, where ν_1 and ν_2 are the vibrational

Fig. 4

Figure 4: Fig. 4

frequencies of the object and of the solvent. In the present work the solvent was the medium consisting of NaCl salt, the frequency of optically active vibrations of which is 16.4 cm^{-1} (^{12}), i.e., of the same order as the difference between the frequencies of the bands $\nu_1 + \nu_4$ and 4193 cm^{-1}. The absence of a sum-frequency band, which in intensity should be greater than the observed difference combination of frequencies, as well as the absence of similar satellite bands near the $2\nu_1$ band, casts doubt on the correctness of the proposed assumption; it is possibly caused by the small dispersion of the instrument and by the presence of interfering absorption bands of atmospheric water vapor. Investigations in this direction are continuing.

Fig. 4. Change in the absorption spectrum of chloroform under pressure in the region of the $\nu_1 + \nu_4$ band (S –spectral slit width).
a –$p = 1$ kg/cm^2, b –7100, c –12,900, e –17,000, d –21,300 kg/cm^2

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