Infrared Spectra of Crystalline Chloroform at High Pressure

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Infrared absorption spectra of polycrystalline chloroform were measured at 100°K and the results were discussed in comparison with the X-ray diffraction data.[1] In order to justify the previous analysis and to determine the assignment of components of internal mode splittings in the crystal field, measurements of spectra of single crystals or oriented crystals are most desirable.

In the present work, single crystals of chloroform have been produced in a diamond high-pressure cell at room temperature. Sample crystals were grown from liquid chloroform sealed between a molybdenum gasket and diamond anvils in a high-pressure cell (High Press. Optics, Co.). Pressure was increased up to about 30 kbar on the sample until solidification to a polycrystal occurred (the pressure in the cell was roughly estimated by counting the rotations of the screw as shown in its catalogue). The pressure was then decreased gradually until the crystal melted, and the pressure was again increased rapidly until single crystals were grown. By repeating the procedure, the single crystals as shown in Fig. 1 were obtained. Although the crystals grown in the cell consisted not of one block but of several blocks, the polarization effect on the spectra was observed, indicating some orientation of the single crystals.

Infrared spectra were recorded on a modified Jasco DS-301 prism (triple-pass) spectrometer, whose beam was first focussed on the sample using a mirror of long focal length. An AgBr grid wire polarizer was employed. No polarization effect from the diamond cell was detected at 1 atm and also at high pressures.

Spectra of samples 1 and 2 are shown in Figs. 2 and 3, respectively. Sample 1 shows two peaks at 3053 and 3008 cm^{-1} in the ν_1 region and three peaks at 1226, 1207 and 1198 cm^{-1} in the ν_4 region, while sample 2 has two peaks at 3048 and 3008 cm^{-1} in the ν_1 region as well as two peaks at 1225 and 1210 cm^{-1} in the ν_4 region without the lowest frequency peak. In these figures the dotted lines represent the spectra in ploarized light. The polarizer was used in such a way that the most significant spectral changes from the unpolarized spectra might be observed. For polycrystals the spectra obtained at high pressures are very similar to those reported for the polycrystalline film at 100°K, though the crystal field splittings for the ν_4 vibration are somewhat larger for the crystals at high pressures than for that at 100°K. The peak at 3050 cm^{-1} was not reported for the polycrystalline film, but we have observed it by making a thicker film at 100°K.

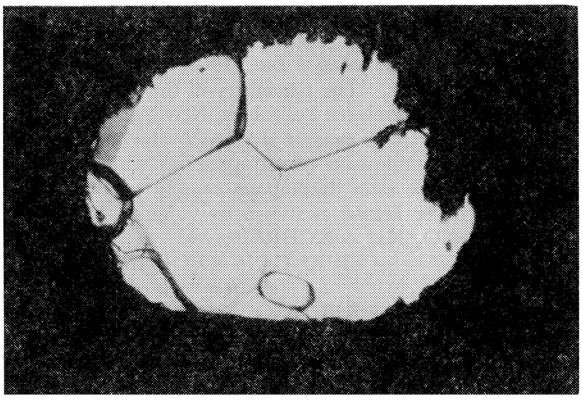

Fig. 1. CHCl$_3$ single crystals grown in diamond cell at *ca.* 30 kbar (sample 2).

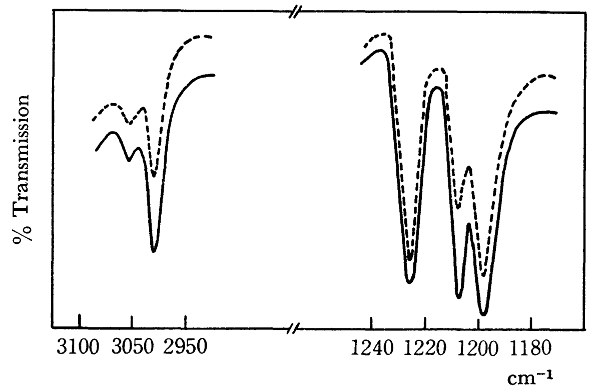

Fig. 2. ν_1 and ν_4 bands of CHCl$_3$ for sample 1.
—— unpolarized, ------ polarized

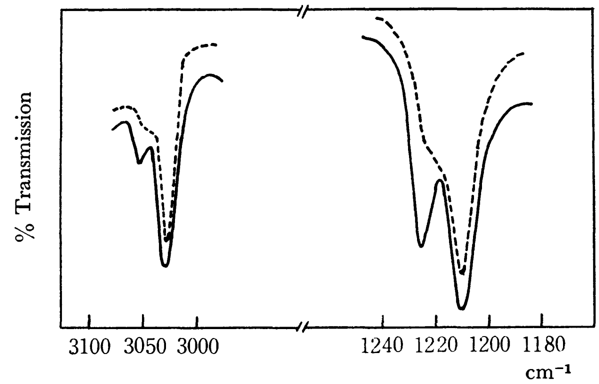

Fig. 3. ν_1 and ν_4 bands of CHCl$_3$ for sample 2.
—— unpolarized, ------ polarized

As can be seen from Figs. 2 and 3, the central peak at 1207 cm^{-1} in the ν_4 band and the peak at 3008 cm^{-1} in the ν_1 band are ascribed to one crystal axis component while the peaks at 1225 cm^{-1} and at 3050 cm^{-1} are assigned to another crystal axis component. Since the chloroform crystal belongs to D_{2h}^{16} and the CH bonds lie on the ac plane, making an angle of 14° with the *a* axis, the peak at 3008 cm^{-1} is assigned to the *a* axis component. The three peaks in the ν_4 band can then be assigned to the *c*, *a*, and *b* axis components, respectively, from high to low frequencies, supporting the previous analysis.

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1) A. Kimoto and H. Yamada, This Bulletin, **41**, 1096 (1968).