Far Infrared Spectra of Solid 1,2-Dihalogenoethane

Jiro HIRAISHI

National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151

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Far infrared spectra are measured for solid 1,2-dichloro-, dibromo-, and diiodoethane at several temperatures. The translational lattice vibrations of the crystals are observed for both high and low temperature phases. The observed frequencies of the low temperature phase of 1,2-dichloroethane agreed with the frequencies calculated by Mizushima *et al.* (Ref. 5). The nature of the phase transition is discussed on the basis of the temperature dependence of the spectra. The low frequency Raman spectrum of 1,2-diiodoethane is also reported.

Solid 1,2-dichloroethane and 1,2-dibromoethane undergo phase transitions at 177.0 and 249.49 K, respectively.[1] Lipscomb *et al.*[2] studied the X-ray diffraction of the high temperature phase (α phase) as well as the low temperature phase (β phase) of 1,2-dichloroethane and concluded that in the α phase either the molecule rotates freely or the orientation of the molecule around its Cl–Cl axis is disordered. The nature of the phase transition has been discussed in terms of Raman spectroscopy by several investigators.[3-6] For 1,2-dichloroethane, Ozora, *et al.* observed the low frequency Raman bands at several temperatures and concluded that the molecule rotates freely in the α phase.

For 1,2-dibromoethane, we reported the temperature dependence of the low frequeycy Raman bands due to the rotational lattice vibrations and showed that the nature of its phase transition is similar to that of 1,2-dichloroethane, although the crystal structure of its α phase is probably different from that of the β phase of 1,2-dichloroethane.[6]

The space group of the β phase of 1,2-dichloroethane is $C_{2h}{}^5$—$P2_1/c$; a unit cell contains two molecules.[2] The lattice vibrations at the center of the Brillouin zone are classified into $3a_g+3b_g+2a_u+b_u$. The vibrations of the a_g and b_g species are rotational modes and are Raman active, while those of the a_u and b_u species are translational modes and are infrared active. Ozora *et al.*[4] and Mizushima *et al.*[5] calculated the optically active lattice vibrations on the basis of Buckingham-type potentials between intermolecular atoms. They used the frequencies of the rotational lattice vibrations. No infrared study of the translational modes has been made in detail. Durig *et al.*[3] reported a very weak band at 50 cm^{-1} for 1,2-dichloroethane in the far infrared spectrum.

Hassel and Hveding[7] reported that solid 1,2-diiodoethane undergoes a rotational phase transition at 25.8 °C. However, no vibrational spectroscopic study has been made of the lattice vibrations of the crystal. In the present paper the far infrared spectra of solid 1,2-dichloroethane, 1,2-dibromoethane, their deuterated compounds, and 1,2-diiodoethane were studied at several temperatures in order to obtain information about the relation between translational lattice vibrations and the phase transition.

Experimental

Far infrared spectra were measured by use of a Hitachi model 070 interferometer. A cryostat equipped with a small refrigerator, Cryomech model GB03, was used for the measurements at low temperatures. Liquid samples were sealed into polyethylene cells of about 1 mm thickness. The translational lattice vibrations are very weak in the infrared spectra, because 1,2-dihalogenoethane molecules have a *trans* form in the solid state and have no dipole moment. For this cell thickness the bands due to intramolecular vibrations were completely saturated. The resolution used for the measurements was 0.65, 1.3, or 2.6 cm^{-1}, depending on the width of the bands. The temperature at the polyethylene cell was measured by use of an Au (with 0.07 atomic % Fe) chromel thermocouple obtained from Osaka Sanso Inc., which was calibrated by the calibrated GaAs thermometer of Lake Shore Cryogenics Inc. The temperature was kept constant within 0.5 K during the measurement of one interferogram. Although it reached approximately 13 K at the sample holder (made of copper), the temperature at the cell was about 65 K, because of the low thermal conductivity of the polyethylene plates.

The spectra of 1,2-diiodoethane was measured by use of a silicon plate with the cell thickness of about 0.5 mm. Commercially available 1,2-diiodoethane powder was used for the measurements, after subliming several times.

Results and Discussion

1,2-Dibromoethane. Figure 1 shows the far infrared spectra of 1,2-dibromoethane at several temperatures. At 69 K three bands at 51.1, 42.8, and 37.0 cm^{-1} were observed. The crystal structure of 1,2-dibromoethane has not yet been studied in detail. Reeds and and Lipscomb[2b] quoted the work by Meerman and

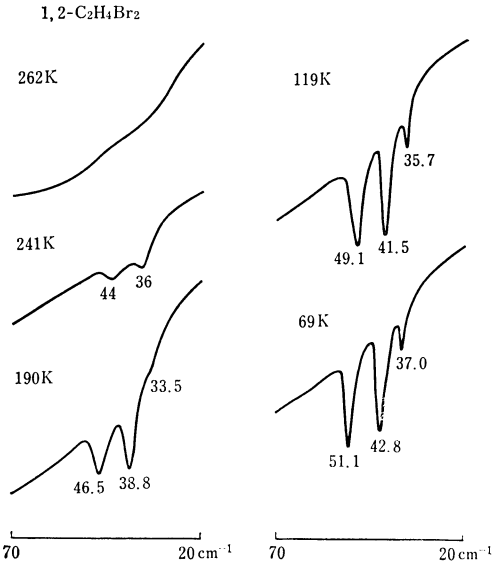

Fig. 1. Far infrared spectra of solid 1,2-$C_2H_4Br_2$.

stated that the crystal structure of the β phase of 1,2-dibromoethane was similar to that of 1,2-dichloroethane. Three bands owing to the translational lattice vibrations are expected to appear in the infrared spectra in the space group of C_{2h}^5 with two molecules in a unit cell. The present result does not contradict the statement by Reeds and Lipscomb. The spectra of 1,2-$C_2D_4Br_2$ were also measured and three bands at 50.8, 42.6, and 37.0 cm^{-1} were observed at 70 K. The small isotopic shifts are consistent with the assignments of the bands to translational lattice vibrations. The spectra of 1,2-dichloroethane show only two bands below 100 cm^{-1}, as will be seen later. The very weak band at 37.0 cm^{-1} may be assigned to an impurity. However, it did not decrease in intensity after the sample was purified by means of a spinning band fractional distillation column made by Tokyo Kagakuseiki Co., Ltd.

1,2-Dichloroethane. Two bands at 62.8 and 51.1 cm^{-1} were observed for 1,2-dichloroethane at 67 K (62.3 and 50.3 cm^{-1} for 1,2-$C_2D_4Cl_2$), as shown in Fig. 2, although three bands were expected, as noted above. Since the band of the lowest frequency of 1,2-dibromoethane is very much weaker than the others, it can be assumed, in the case of 1,2-dichloroethane, that the lowest frequency band is too weak to be observed.

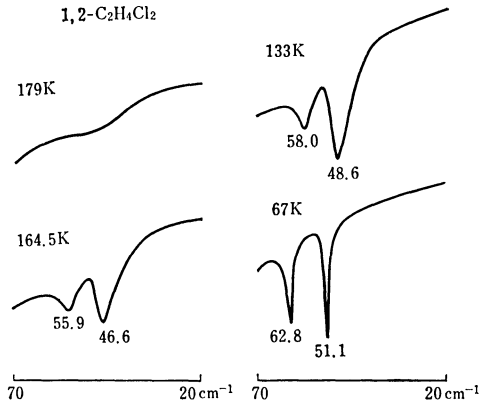

Fig. 2. Far infrared spectra of solid 1,2-$C_2H_4Cl_2$.

Ozora, *et al.*,[4] and Mizushima *et al.*[5] calculated the optically active lattice vibrations of 1,2-dichloroethane on the basis of the crystal structure at 133 K. According to their calculations, the third missing band may appear in the frequency region higher than 70 cm^{-1}. We could not detect the band in the frequency region lower than 150 cm^{-1}; here silicon plates were used instead of polyethylene sheets for the cell and windows, with the cell thickness of about 2 mm, to eliminate the interference of the band at 72 cm^{-1} from the polyethylene plates. In these calculations, the first derivatives of potential functions are neglected. Pomposiello *et al.* calculated the effect of the first derivatives on lattice vibrations of several molecular crystals including *trans*-1,2-dichloroethane.[8] Their result indicates that the frequencies of the translational lattice vibrations are not affected significantly by the first derivatives in the case of 1,2-dichloroethane and thus cannot eliminate the apparent discrepancy between the two possibilities concerning the assignment of the third missing band. In Table 1 the observed frequencies are assigned, tentatively, according to the calculation by Mizushima *et al.*

Table 1. Observed and calculated frequencies (cm^{-1}) of the β phase of 1,2-$C_2H_4Cl_2$

	Obsd	Calcd	
		a)	b)
a_g	117	109	111.6
	79	87	79.2
	55	58	50.4
b_g	—	99	97.0
	73	77	73.0
	(55)	60	49.9
a_u	—	98	83.8
	48.6	71	47.4
b_u	58.0	53	51.3

a) From Ref. 4. b) From Ref. 5.

1,2-Diiodoethane. Four bands (176, 136, 41.5, and 33.5 cm^{-1}) were observed below 200 cm^{-1} at 288.5 K. The bands at 176 and 136 cm^{-1} are assigned to the CCl bending (b_u species) and the torsional vibrations (a_u species), respectively. The other bands are very weak and are assigned to the intermolecular vibrations. The space group of solid 1,2-diiodoethane is C_{2h}^5 [7,9] and three translational lattice vibrations are infrared active. The spectra at various temperatures are shown in Fig. 3. Only two bands were observed

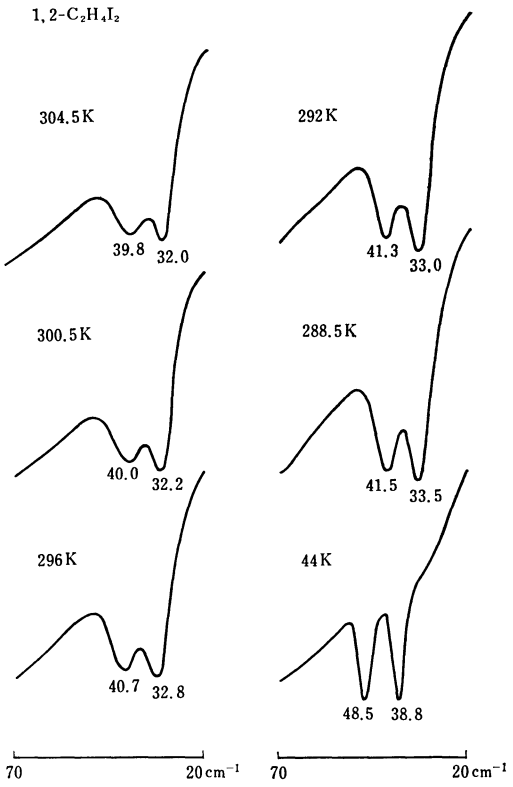

Fig. 3. Far infrared spectra of solid 1,2-$C_2H_4I_2$.

Table 2. Temperature dependence of the lattice vibrational frequencies (cm^{-1}) of 1,2-$C_2H_4Br_2$

Translational (in Far IR)			
69K	119K	190K	241K
51.1	49.1	46.5	44
42.8	41.5	38.8	36
37.0	35.7	33.5	—
Rotational (in Raman)[7]			
70K	116K	191K	245K
124.2	118.2	105.8	91.5
56.0	54.5	51.3	47
44.1	42.9	39.4	36
27.3	—	—	—

at the low temperature phase, as in the case of 1,2-dichloroethane.

Phase Transition and Translational Lattice Vibrations. Table 2 shows the frequencies of the lattice vibrations of 1,2-dibromoethane at several temperatures. The frequencies of the translational lattice vibrations in the β phase decrease upon approaching the transition temperature. Their behavior is similar to that of the lower frequency rotational modes. The highest frequency rotational mode is the libration around the Br–Br axis; this is the most unharmonic among the observed optically active lattice vibrations.

Above the transition temperature the absorption band is very broad for 1,2-dichloroethane as well as for 1,2-dibromoethane. As the crystal structure of the α phase of 1,2-dichloroethane is similar to that of the β phase, three translational lattice vibrations are also expected in the infrared spectra for the α phase, if the molecules rotate freely in the α phase. Figure 1 indicates that the spectra are not continuous at the transition temperature, which can be explained more plausibly in terms of the orientational disorder in the α phase. As Bertie and Whally discussed,[10] the $k=0$ selection rule is not applicable to an orientationally disordered crystal. Schwartz and Ron reported a similar discontinuity in the far infrared spectra at the transition temperature for acetylene[11] and cyclohexane crystals.[12] Chlorocyclopentane crystal also exhibits a very broad band in the disordered phase.[13]

1,2-diiodoethane crystal shows a continuous spectral change near the transition temperature, as given in Fig. 3. The transition temperature was confirmed to be 298.6 K, using DTA equipment from Rigaku Denki Co., Ltd.; this agreed well with the value reported by Hassel and Hveding.[7] The result of Fig. 3 is different from those of other crystals near the order-disorder transition, as discussed above; this can be explained in terms of free rotation of molecules in the high temperature phase of 1,2-diiodoethane.

Raman Spectrum of 1,2-Diiodoethane. The Raman spectrum of 1,2-diiodoethane was also measured by use of a Cary 82 spectrophotometer, with the 647.1 nm line of a Kr^+ laser as a source. Three bands at 43.5, 36.7, and 17 cm^{-1} were observed at approximately 290 K, as is shown in Fig. 4. 1,2-Dibromoethane and 1,2-dichloroethane[4] crystals show three rotational

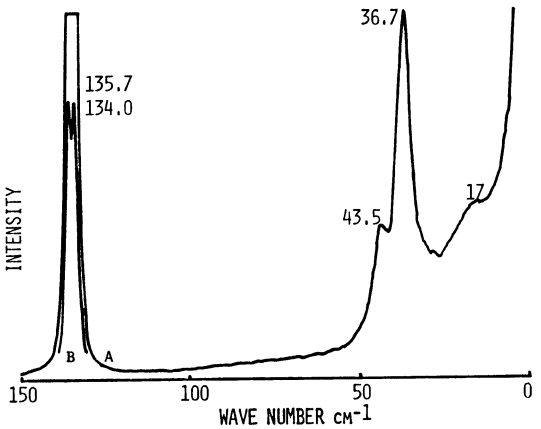

Fig. 4. Raman spectra of solid 1,2-$C_2H_4I_2$.
(A) $\Delta\nu=0.5\ cm^{-1}$. 5000 counts/full scale. (B) $\Delta\nu=0.2\ cm^{-1}$. 1000 counts/full scale. 134.0 and 135.7 cm^{-1} bands are assigned to the intramolecular CCI deformation vibrations (a_g and b_g species).

lattice vibrations in the Raman spectra, except for the rotational band around the halogen–halogen axis. Considering the results of 1,2-dichloro- and 1,2-dibromoethane crystals, the rotational band around the I–I axis is expected to be too weak and too broad to be observed at this temperature.

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