# The Raman Spectra and the Phase Transition of 1,2-Dibromoethane

Jiro HIRAISHI and Takako SHINODA

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

(Received May 13, 1975)

The lattice vibrations of 1,2-$C_2H_4Br_2$ and 1,2-$C_2D_4Br_2$ were measured by means of Raman spectroscopy. The temperature dependence of the frequencies and the half widths of the lattice vibrations indicates that the phase transition of the crystal is associated with the rotation of the molecule around the Br–Br axis.

The solids 1,2-dichloroethane and 1,2-dibromoethane, undergo a phase transition at 177 and 249.49 K, respectively.[1] According to the X ray diffraction studies by Lipscomb *et al.*,[2-4] the crystal of both the high ($\alpha$-phase) and the low temperature phase ($\beta$-phase) of 1,2-dichloroethane is monoclinic and belongs to the space group $C_{2h}^5$-$P2_1/c$. A unit cell consists of two molecules. Ozora, Nakagawa, and Ito[5] studied the temperature dependence of the low frequency Raman bands of 1,2-dichloroethane and concluded that the phase transition is associated with the free rotation of the molecule about the Cl–Cl axis, which agrees with the result by Reeds and Lipscomb.[3]

On the other hand, the crystal structure and the nature of the phase transition of 1,2-dibromoethane have not been studied in detail. Pitzer[1] measured the heat capacity of the crystal and suggested that the structure of the $\alpha$-phase of 1,2-dibromoethane was different from that of the $\beta$-phase. Reeds and Lipscomb[3] quoted the work by Meerman and stated that the $\beta$-phase of 1,2-dibromoethane has the same structure as that of the $\beta$-phase of 1,2-dichloroethane. In the present paper we report the temperature dependence of the low frequency Raman bands of 1,2-$C_2H_4Br_2$ and 1,2-$C_2D_4Br_2$ and discuss the nature of the phase transition of the crystal.

## Experimental

A chemically pure grade reagent of 1,2-$C_2H_4Br_2$ obtained from Tokyo Kasei Co. Ltd. was further purified by means of a spinning band fractional distillation column made by Tokyo Kagaku Seiki Co. Ltd. 1,2-$C_2D_4Br_2$ purchased from Merk Darmstadt Germany was used for the measurement without further purification.

The Raman spectra were measured by use of a laser Raman spectrometer, Kawaguchi Electric Works model RL-62. The 514.5 nm line of a NEC argon ion laser model GLG2003 was used as an exciting source.

Figure 1 shows the cryostat designed in our laboratory for the measurement of the Raman spectra of liquid or solid samples in the range from liquid helium temperature to about 150 °C. About one litre of liquid helium can be contained in D. A thermal station C has an volume of about 100 ml. For measurements below 90 K the cryostat is covered by a glass vessel which contains liquid nitrogen. A sample cell, shown in Fig. 2, is made of quartz glass. The cell is hung by means of nylon cords within the adiabatic shield. The temperature was measured by use of a chlomel p-constantan thermocouple, the calibration of which was reported elsewhere.[6] A germanium resistance thermometer, which was calibrated by Cryocal. Inc., was used in the temperature range below 30 K. The temperature of the sample was held constant within $\pm 0.05$ K during a measurement of a band.

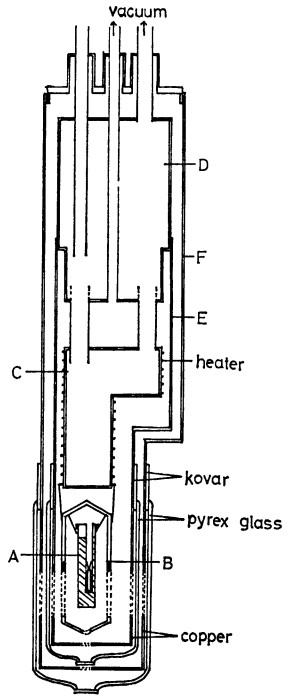


Fig. 1. A cross-section of the cryostat. A: sample vessel, B: adiabatic shield, C: thermal station, D: coolant container, E: inside jacket, and F: outside jacket.

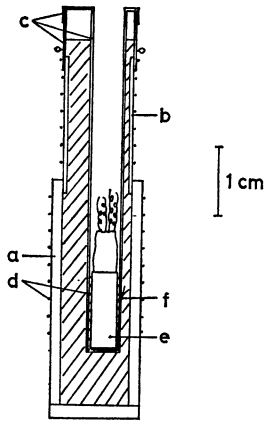


Fig. 2. A cross-section of the sample vessel. a: quartz glass, b: Kovar tube, c: silver-plated copper, d: manganin heater, e: germanium thermometer, and f: thermocouple.

## Result and Discussions

*Assignment of the Low Frequency Raman Bands of the β-Phase.* Four bands at 27.7, 44.9, 56.9, and 126.5 $cm^{-1}$ were observed for 1,2-$C_2H_4Br_2$ at 40.0 K in the frequency region below 150 $cm^{-1}$. 1,2-dibromoethane has two rotational isomers, the *trans* and *gauche* forms. As the molecule has a *trans* form in the crystalline state[7] and the lowest frequency[8] of the Raman active intramolecular vibrations of the *trans* form is 190 $cm^{-1}$, the bands observed below 150 $cm^{-1}$ are definitely attributable to the lattice vibrations. According to Ozora, Nakagawa, and Ito,[5] the β-phase of 1,2-$C_2H_4Cl_2$ also exhibits four bands in the Raman spectra below 150 $cm^{-1}$. This result does not contradict the suggestion by Pitzer[1] that the crystal structure of the β-phase of 1,2-$C_2H_4Br_2$ is the same as that of the β-phase of 1,2-$C_2H_4Cl_2$.

Six rotational lattice vibrations ($3a_g+3b_g$) are expected to appear in the Raman spectrum of the β-phase. Ozora, Nakagawa, and Ito assigned the highest frequency band of the four of the β-phase of 1,2-$C_2H_4Cl_2$ to the rotational mode about the Cl–Cl axis. In order to confirm the assignments we also observed the Raman spectrum of 1,2-$C_2D_4Br_2$. The observed frequencies of 1,2-$C_2H_4Br_2$ and 1,2-$C_2D_4Br_2$ near 95 K are shown in Table 1. The transition temperature, $T_c$, of 1,2-$C_2D_4Br_2$ crystal was found to be about 256.0 K, from the total thermal analysis, by using the cryostat described above. As the $T_c$ of 1,2-$C_2D_4Br_2$ is higher by about 6.5 K than that of 1,2-$C_2H_4Br_2$, the temperature for 1,2-$C_2D_4Br_2$ in Table 1 is a little higher than that for 1,2-$C_2H_4Br_2$. $\nu_D/\nu_H$ and $I_D(A)/I_H(A)$ in the table represent the values of the ratios of the frequencies and the principal moment of inertia around the A axis, respectively, of 1,2-$C_2D_4Br_2$ to those of 1,2-$C_2H_4Br_2$. The values of the moment of inertia of the molecules were calculated by assuming that all of the valence angles were 109°28′ and the interatomic distances were $r_{CH}=r_{CD}=1.09$, $r_{CC}=1.54$, and $r_{CBr}=1.91$ Å.[9] The lowest frequency band observed at 27.7 $cm^{-1}$ for 1,2-$C_2H_4Br_2$ at 40.0 K was not observed above 80 K, as the tail of the Rayleigh scattering band lapped over the band. The result of Table 1 indicates that the highest frequency band at approximately 120 $cm^{-1}$ for 1,2-$C_2H_4Br_2$ or at approximately 100 $cm^{-1}$ for 1,2-$C_2D_4Br_2$ should be assigned to the rotational lattice vibration about the C axis, that is, the Br–Br axis.

*Temperature Dependence of the Raman Bands.* Figure 3 shows the Raman spectra of the crystals at several temperatures. Below $T_c$ three or four bands are observed for each crystal, while only one band was observed above $T_c$, although for the β-phase of 1,2-

Table 1. Observed frequencies near 95 K

| | | | |
|---|---|---|---|
| $C_2H_4Br_2$ (93.6K) | 43.6 $cm^{-1}$ | 55.4 | 121.4 |
| $C_2D_4Br_2$ (96.5K) | 43.1 | 54.9 | 99.0 |
| $\nu_D/\nu_H$ | 0.989 | 0.991 | 0.815 |

$\sqrt{I_H(A)/I_D(A)}=0.996$, $\sqrt{I_H(B)/I_D(B)}=0.998$, $\sqrt{I_H(C)/I_D(C)}=0.815$

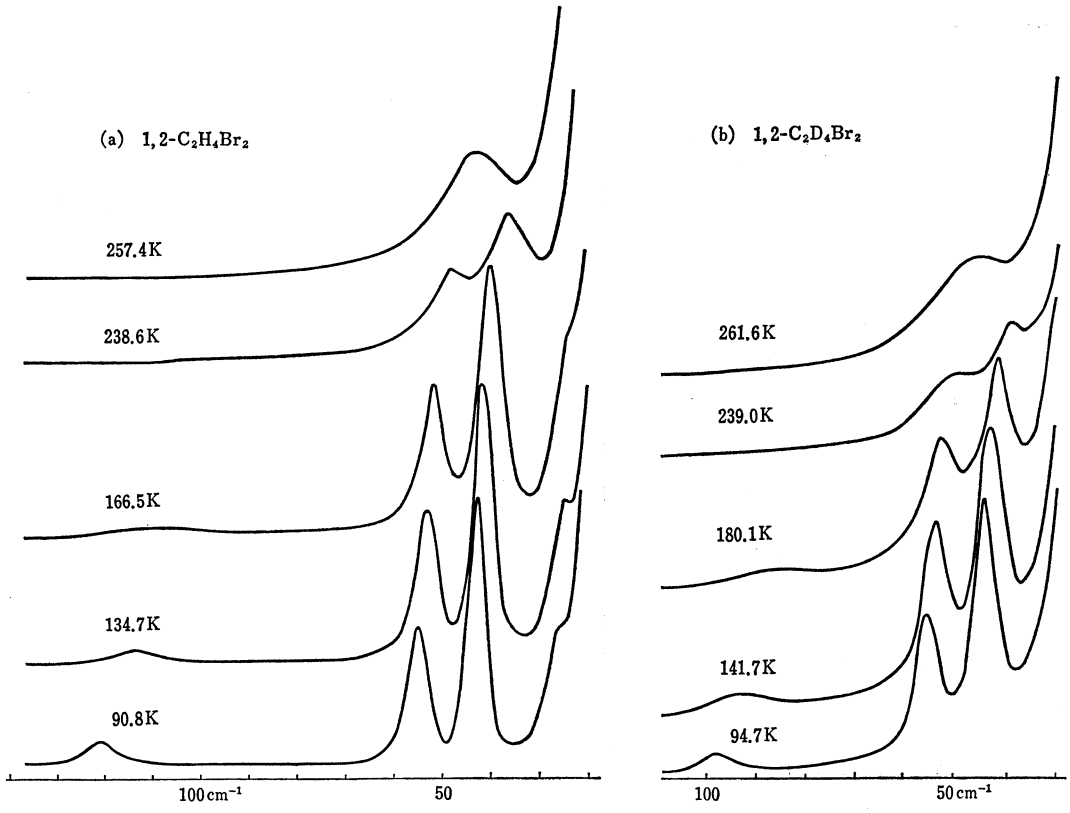


Fig. 3. The Raman spectra of (a) 1,2-$C_2H_4Br_2$ and (b) 1,2-$C_2D_4Br_2$ below 150 $cm^{-1}$ at several temperatures.

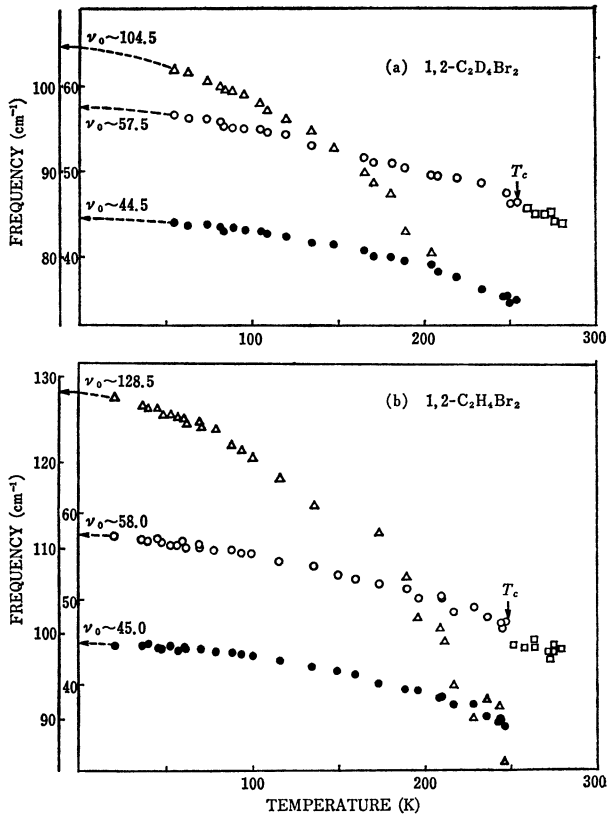


Fig. 4. The temperature dependence of the frequencies of the lattice vibrations.

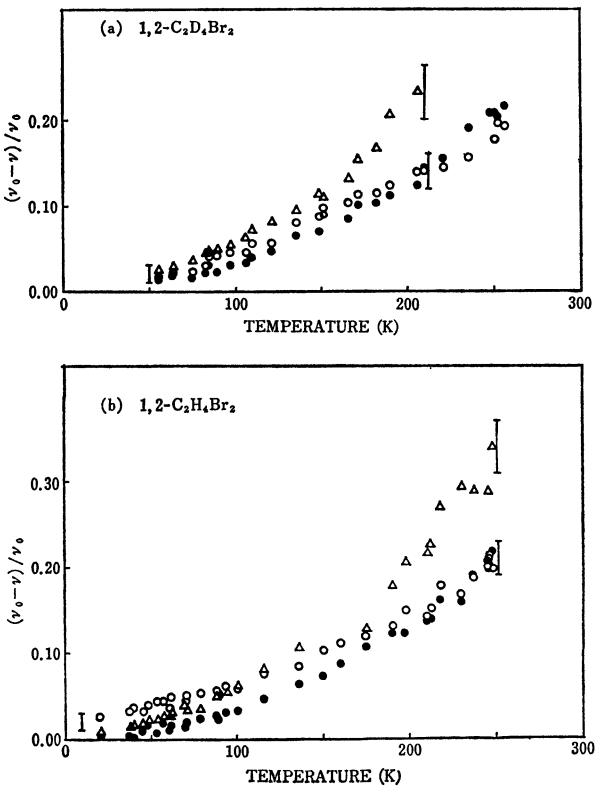


Fig. 5. The temperature dependence of $(\nu_0-\nu)/\nu_0$, where $\nu_0$ represents the frequency obtained by extrapolation to 0 K (see text).

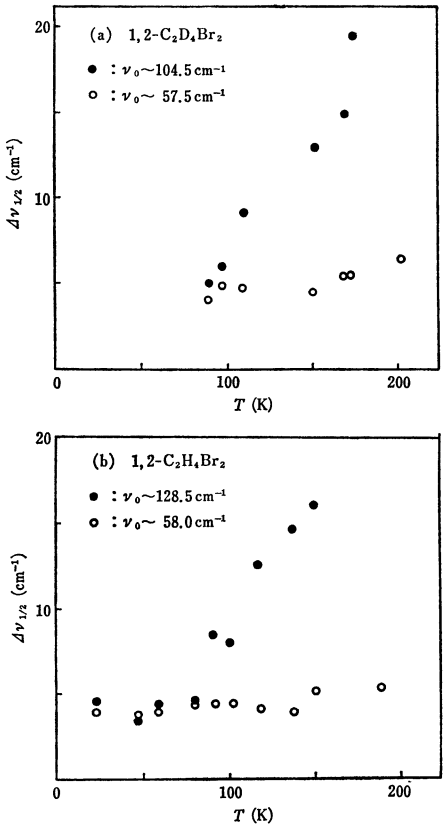


Fig. 6. The temperature dependence of the half width of the lattice vibrations.

dichloroethane two bands were reported.[5] The result may be explained in terms of a crystal structure of 1,2-dibromoethane different from that of 1,2-dichloroethane above $T_c$.

The widths and frequencies of lattice vibrations depend on temperature due to unharmonicity. Near $T_c$ the crystal is expected to be very unharmonic. If there is a lattice vibration which is associated with the phase transition, the frequency of the vibration will depend on temperature much more than the other vibrations.[10] As Fig. 4 shows, the frequencies of the lattice vibrations of the crystals decreases as the temperature approaches $T_c$. By extrapolating the frequencies to the limit at 0 K, the values of $\nu_0$ were estimated for each band; those are also given in Fig. 4. Figures 5 and 6 show the temperature dependence of $(\nu_0-\nu)/\nu_0$ and half width of each band. The lines in Figs. 5 and 6 represent the errors in the measurements. The frequencies of the rotational lattice vibrations about the Br–Br axis of the $\beta$-phase decrease and the half widths of the bands increases greatly with approaching Tc, as compared with the other rotational lattice vibrations. In other words, the rotational vibration about the Br–Br axis is more unharmonic than the others, which suggests that the phase transition of the crystal is associated with a rotational motion of the molecule around its Br–Br axis.

## References

1) K. S. Pitzer, *J. Amer. Chem. Soc.*, **62**, 331 (1940).
2) M. E. Milberg and W. N. Lipscomb, *Acta Crystallogr.*,

**4**, 369 (1951).
3) T. B. Reeds and W. N. Lipscomb, *ibid.*, **6**, 45 (1953).
4) W. N. Lipscomb and F. E. Wang, *ibid.*, **14**, 1100 (1961).
5) A. Ozora, T. Nakagawa, and M. Ito, This Bulletin, **45**, 95 (1972).
6) H. Enokido, T. Shinoda, and Y. Mashiko, *ibid.*, **44**, 108 (1971).
7) S. Mizushima and Y. Morino, *Proc. Ind. Acad. Sci.*, **8**, 315 (1938).
8) T. Shimanouchi, Tables of Molecular Vibrational Frequencies Consolidated Vol. 1. NSRDS-NBS 39, United States Department of Commerce (1972).
9) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).
10) See references cited by P. M. A. Sherwood in "Vibrational Spectroscopy of Solids," Cambridge University Press (1972).