# Low-Frequency Raman Spectra and Phase Transition of the 1,2-Dichloroethane Crystal

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In order to study the phase transition of 1,2-dichloroethane crystal at 177°K, the low-frequency Raman spectra were measured at various temperatures, and normal coordinate analysis was carried out. It was found that the phase transition is of rotational type in which the librational motion of the molecule about the axis passing through two chlorine atoms of the molecule changes into a nearly free rotation about the same axis.

## Introduction

It is well-known that 1,2-dichloroethane in gas and liquid phases consists of two rotational isomers of *gauche*- and *trans*-forms, but only the *trans*-form is stable in the solid.

The 1,2-dichloroethane crystal has a phase transition at 177°K, on which a number of investigations have been made. According to the X-ray diffraction studies by Lipscomb *et al.*[1,2] both high[1] and low temperature phases[2] (hereafter referred to as crystals I and II, respectively) are monoclinic, the space group $C_{2h}^5$-$P2_1/c$ with two molecules in a unit cell, and have very similar cell dimensions. The positions of the carbon atoms could readily be identified for crystal II, but not for crystal I. The chlorine atoms were located at nearly the same positions in both phases (Table 1). They concluded that a nearly free rotational motion of the molecule about the axis passing through the two chlorine atoms takes place in crystal I.

TABLE 1. CRYSTAL STRUCTURES OF 1,2-DICHLOROETHANE

| Crystal I | Crystal II |
|---|---|
| monoclinic | monoclinic |
| $Z=2$ | $Z=2$ |
| $C_{2h}^5-P2_1/c$ | $C_{2h}^5-P2_1/c$ |
| $a=5.04$ Å | $a=4.66$ Å |
| $b=5.56$ Å | $b=5.42$ Å |
| $c=8.00$ Å | $c=7.88$ Å |
| $\beta=109°30'$ | $\beta=103°30'$ |
| $x$(C)=− | $x$(C)=0.099 |
| $y$(C)=− | $y$(C)=0.003 |
| $z$(C)=− | $z$(C)=0.094 |
| $x$(Cl)=0.303 | $x$(Cl)=0.318 |
| $y$(Cl)=0.279 | $y$(Cl)=0.278 |
| $z$(Cl)=0.074 | $z$(Cl)=0.084 |
| at 223°K | at 133°K |

In this paper, we report a new evidence available from the low-frequency Raman spectra supporting Lipscomb's conclusion about the nature of the transition.

## Experimental

1,2-Dichloroethane was obtained from Junsei Pure Chemical Co., and distilled twice in a vacuum. The Raman spectra were obtained with a Narumi model 750Z-1200 double monochromator. The 6328Å line from He-Ne gas laser was used as an exciting light. An S-20 photomultiplier followed by a photon counting system was employed for detection of the spectra. The optical arrangement for laser Raman measurements is the same as described previously.[3] Temperature control of the sample was made by regulating flow speed of dry nitrogen gas cooled with liquid nitrogen. Accuracy of temperature was estimated to be ±3°C.

## Results

From the crystal structure of 1,2-dichloroethane,nine optical active lattice vibrations are expected, of which three are of translational lattice modes ($2A_u+B_u$) active only in the infrared spectrum. The remaining six are of rotational lattice modes ($3A_g+3B_g$) active only in the Raman spectrum.

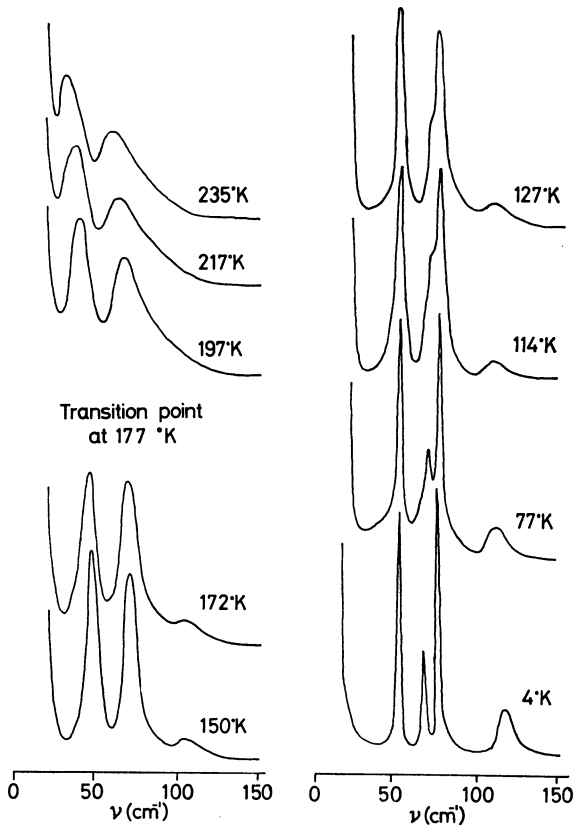


Fig. 1. Lattice vibrational Raman spectra of the 1,2-dichloroethane crystal at various temperatures.

1) M. E. Milberg and W. N. Lipscomb, *Acta Cryst.*, **4**, 369 (1951).

2) T. B. Reed and W. N. Lipscomb, *ibid.*, **6**, 45 (1953); W. N. Lipscomb and F. E. Wang, *ibid.*, **14**, 1100 (1961).

3) M. Suzuki, T. Yokoyama, and M. Ito, *Spectrochim. Acta*, **24**, 1091 (1968).

Table 2. Observed raman frequencies of the lattice vibrations of the 1,2-dichloroethane crystal ($cm^{-1}$)

| Crystal I | | | Crystal II | | | | | |
|---|---|---|---|---|---|---|---|---|
| 235°K | 217°K | 197°K | 172°K | 150°K | 127°K | 114°K | 77°K | 4.2°K |
| 33 | 37 | 40 | 47 | 49 | 51 | 52 | 54 | 56 |
| | | | — | — | — | 72 | 74 | 74 |
| 62 | 65 | 69 | 72 | 74 | 76 | 77 | 79 | 80 |
| | | | 101 | 107 | 109 | 112 | 117 | 121 |

The Raman spectra of the lattice vibrational region at various temperatures between 4.2°K and 235°K are shown in Fig. 1, and the observed frequencies are summarized in Table 2. Four Raman lines were observed in crystal II, although some bands were not resolved at high temperatures.

The highest frequency line at 110 $cm^{-1}$ is probably due to $A_g$ rotational lattice mode around the axis of the least moment of inertia of the molecule nearly coinciding with the direction connecting the two chlorine atoms of the molecule. Weak intensity of this line may be explained by this assignment as a result of small anisotropy of the molecular polarizability around the Cl–Cl axis. Fairly strong intensities and low frequencies of the other lines suggest that they are assigned to rotational modes around the molecular axes perpendicular to the Cl–Cl axis. We assigned tentatively the strong lines at 52 and 77 $cm^{-1}$ at 114°K to the $A_g$ mode and the weaker line at 72 $cm^{-1}$ to the $B_g$ mode.

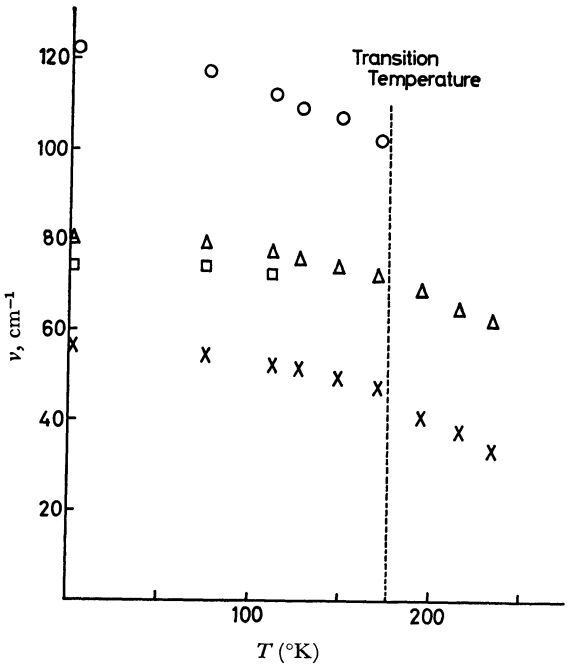


Fig. 2. Effects of temperature on frequencies of lattice vibrational Raman lines.

It should be emphasized that existence of the weak band at 110 $cm^{-1}$ was clearly recongnized even at a temperature just below transition point. However, the weak band is hardly seen as soon as it is transformed into crystal I, while good correspondence is observed for the other lines between the two phases. Figure 2 shows the effect of temperature on the Raman frequencies. The effect is rather large for the highest frequency Raman line of 110 $cm^{-1}$ and it amounts to 20 $cm^{-1}$ between 4.2°K and 172°K as compared with about 10 $cm^{-1}$ for the other lines. We see that smooth curves can be drawn for the Raman lines commonly observed in both phases with no discontinuity at transition point. On the other hand, width of these lines shows discontinuity at transition point as seen in Fig. 3, where the line widths are plotted against temperatures.

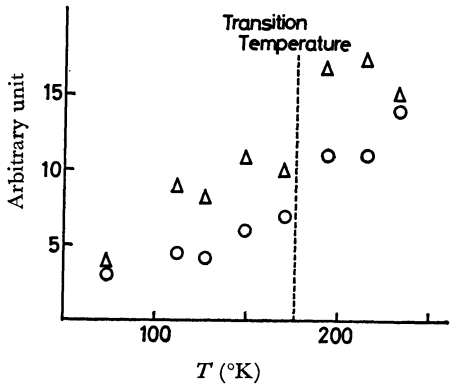


Fig. 3. Effects of temperature on widths of lattice vibrational Raman lines (Plots are given for the Raman lines commonly observed in crystals I and II at about 70 $cm^{-1}$ (△) and 50 $cm^{-1}$ (○)).

## Normal Coordinate Calculation

The normal coordinate calculation of the lattice vibrations was carried out for crystal II according to the GF matrix method developed by Shimanouchi *et al.*[4,5] in a rigid body approximation. The approximation may be valid for the Raman active lattice vibrations of the *g* species, since the lowest frequency intramolecular vibration of the *g* species of the molecule which may interact with the *g* lattice vibrations comes out at about 300 $cm^{-1}$ and is well separated from the highest frequency lattice vibrations. The fact that the lowest frequency intramolecular vibration varies within 3 $cm^{-1}$ in the transformation from liquid to the crystal[6] also supports the approximation.

The crystal structure of 1,2-dichloroethane at 133°K is shown in Fig. 4. The positions of hydrogen atoms were located by assuming the C–H distance of 1.08 Å and the ∠CCH and ∠HCH of 109°28′. The principal axes of the moment of inertia of the molecule are also shown in Fig. 4. U and V axes lie in the ClCCCl plane

4) T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).
5) T. Shimanouchi and I. Harada, *ibid.*, **40**, 2651 (1964).
6) S. Mizushima and Y. Morino, *Proc. Ind. Acad. Sci.*, **8**, 315 (1938).

Table 3. Parameters of atom-atom potentials

| | | C–C | H–H | Cl–Cl | C–H | C–Cl | H–Cl |
|---|---|---|---|---|---|---|---|
| Williams (Set I) | *A* | 51.76 | 2.81 | 180.50 | 6.54 | 96.66 | 22.52 |
| | *B* | 3.60 | 3.74 | 3.65 | 3.67 | 3.63 | 3.70 |
| | *C* | 37.19 | 2.50 | 129.99 | 9.66 | 69.53 | 18.03 |
| Kitaigorodsky (Set II) | *A* | 28.19 | 28.19 | 180.50 | 28.19 | 71.33 | 71.33 |
| | *B* | 3.60 | 4.86 | 3.65 | 4.12 | 3.63 | 4.26 |
| | *C* | 24.03 | 3.64 | 129.99 | 9.83 | 55.89 | 21.75 |
| Bartell-Crowell (Set III) | *A* | 27.20 | 4.58 | 180.50 | 11.17 | 70.07 | 28.75 |
| | *B* | 3.55 | 4.08 | 3.65 | 3.81 | 3.60 | 3.87 |
| | *C* | 23.90 | 3.42 | 129.99 | 9.04 | 55.74 | 21.08 |
| Dashevsky (Set IV) | *A* | 26.19 | 6.31 | 159.07 | 12.86 | 64.54 | 31.69 |
| | *B* | 3.52 | 4.64 | 3.52 | 4.08 | 3.52 | 4.08 |
| | *C* | 32.93 | 1.49 | 201.44 | 7.00 | 81.44 | 17.31 |

*A*, in unit of $10^{-10}$ erg, *B*, in unit of $Å^{-1}$, *C*, in unit of $10^{-12}$ erg $Å^6$

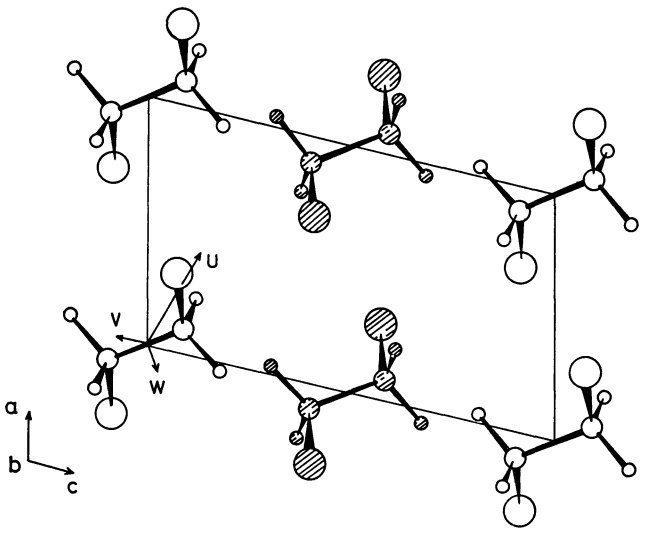


Fig. 4. The crystal structure of 1,2-dichloroethane at 133°K. The shaded molecules are located upward or downward by half a translation of *b*.

and the U axis makes an angle of 1°24′ with the line connecting the two chlorine atoms. The W axis is perpendicular to the U and V axes and coincides with the $C_2$ symmetry axis of the molecule.

For the intermolecular potential, we assumed the atom-atom interaction potential in the form

$$V(r) = A \exp(-Br) - Cr^{-6},$$

where $r$ is the interatomic distance and $A$, $B$, $C$ are constants characteristic of the type of atom pair. Usefulness of this type of potential in calculation of the lattice vibrations of molecular crystals was demonstrated on many occasions.[7]

Three sets of constants proposed by Williams, Kitaigorodsky and Bartell-Crowell[8] for the three types of atom pairs, C–C, C–H, and H–H (hereafter referred to sets I, II, and III, respectively) were used to calculate the lattice frequencies in combination with the Cl–Cl potential obtained by Hill.[9] The set of constants proposed by Dashevsky[10] was also used (hereafter it is referred to set IV). The four sets of constants are listed in Table 3. The constants for C–Cl and H–Cl were taken as geometric mean of the corresponding pairs of identical atoms for $A$ and $C$, and as arithmetic mean for $B$.

The atom-atom interactions were assumed for all the atom pairs whose interatomic distances are less than 5.0, 4.0, 5.5, 4.5, 5.0, and 5.0 Å for C–C, H–H, Cl–Cl, C–H, C–Cl, and H–Cl, respectively Further inclusion of the atom pairs beyond these limits have

Table 4. Observed and calculated frequencies of lattice vibrations for the 133°K structure ($cm^{-1}$)

| | | Set I | Set II | Set III | Set IV | Obsd[a] | Vibrational modes |
|---|---|---|---|---|---|---|---|
| $A_g$ | $\nu_1$ | 188 | 149 | 155 | 109 | 109 | 85%Ru, 5%Rv, 10%Rw |
| | $\nu_2$ | 114 | 101 | 102 | 87 | 76 | 14%Ru, 48%Rv, 38%Rw |
| | $\nu_3$ | 64 | 57 | 60 | 58 | 51 | 47%Rv, 53%Rw |
| $B_g$ | $\nu_6$ | 169 | 127 | 140 | 99 | — | 88%Ru, 12%Rv |
| | $\nu_7$ | 92 | 83 | 85 | 77 | 71 | 2%Rv, 98%Rw |
| | $\nu_8$ | 80 | 67 | 71 | 60 | — | 85%Rv, 15%Rw |
| $A_u$ | $\nu_4$ | 133 | 116 | 118 | 98 | — | 25%Tu, 75%Tv |
| | $\nu_5$ | 102 | 89 | 90 | 71 | — | 25%Tu, 5%Tv, 70%Tw |
| $B_u$ | $\nu_9$ | 78 | 69 | 69 | 53 | — | 50%Tu, 20%Tv, 30%Tw |

a) Extrapolated to 133°K from Table 2.

7) D. A. Oliver and S. H. Walmsley, *Mol. Phys.*, **17**, 617 (1969).
8) Cited in Ref. 7.
9) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).
10) P. G. Dashevsky, U. T. Steruchukof, and S. A. Akappayan, *J. Struct. Chem. USSR*, **7**, 594 (1966).

little effect on the calculated frequencies.

The calculated frequencies obtained with the four sets of potentials are given in Table 4, together with the observed frequencies. It is seen that the Dashevsky's potential (set IV) shows fairly good agreement between the observed and calculated frequencies, while the other sets give higher calculated frequencies. The 1,2-dichloroethane crystal involves fairly short Cl–Cl and Cl–H distances, and slight changes in their interatomic potentials have a large effect on the calculated frequencies. When the force constants for these two atom pairs are compared, it was found that the force constant-interatomic distance curves for Cl–H differ a great deal between set IV and the other sets especially in the short distance range, while the Cl–Cl curves are very similar to each other. The difference in the Cl–H curves must be ascribed to difference in the H–H potentials, since we assumed the parameters for Cl–H to be geometric and arithmetic means of the Cl–Cl and H–H parameters. The force constant curves for H–H are compared in Fig. 5. It is seen that the curve obtained from Dashevsky's potential differs considerably from the others. This is probably the principal reason for the difference in the calculated frequencies between set IV and the others[11].

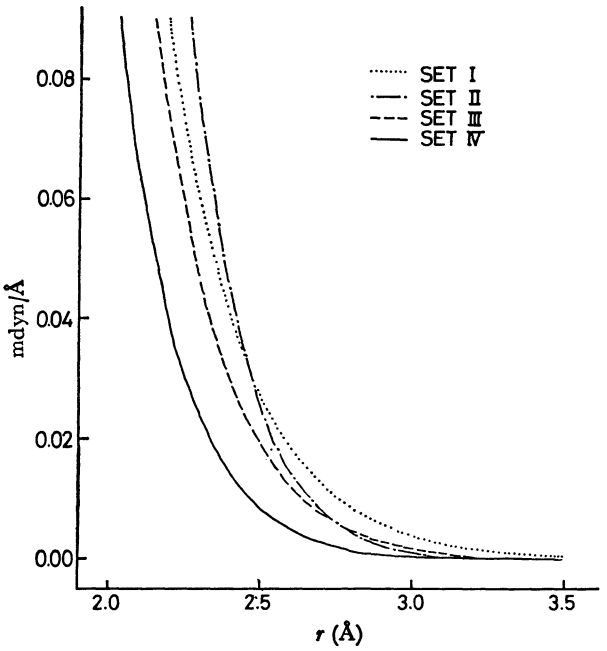


Fig. 5. Force constant curves for H–H.

In the last column of Table 4, approximate vibrational modes calculated with Dashevsky's potential are given. It is noted that the highest frequency vibrations $\nu_1(A_g)$ and $\nu_6(B_g)$ may be described approximately as due to rotational oscillations around the U axis. The situation is the same also in the vibrational modes obtained with other potentials.

## Nature of the Phase Transition

Main differences between the Raman spectra of crystals I and II may be summarized as follows: the $\nu_1(A_g)$ line of 110 $cm^{-1}$, which is weak but distinctly observed in crystal II, is hardly recognized in crystal I, and the widths of all the Raman lines change abruptly at transition temperature.

On the other hand, normal coordinate calculation showed that $\nu_1(A_g)$ (and also $\nu_6(B_g)$) of crystal II is mainly due to the rotational oscillation around the U axis, which almost coincides with the line connecting the two chlorine atoms of the molecule.

The results strongly suggest that the phase transition of the 1,2-dichloroethane crystal at 177°K is a transition in which the rotational oscillational motion about the Cl–Cl axis of the molecule changes into a nearly free rotational motion about the same axis and *vice versa*, supporting the conclusion obtained by Lipscomb *et al.* from their X-ray studies. The $\nu_1(A_g)$ line of crystal II is stilll broad even at 4.2°K, and its band width increases with increase of temperature more rapidly than that of other lines. This implies that the molecular rotational oscillation about the U axis is fairly easy even at very low temperatures, and the oscillational amplitude rapidly increases up to the transition point where a nearly free rotation of the molecule takes place.

11) In the calculation of lattice vibrations of naphthalene and anthracene crystals, the observed frequencies are fairly well reproduced with the potentials given by Kitaigorodsky and Bartell-Crowell, while considerably lower and higher frequencies are calculated with the potentials given by Dashevsky and Williams, respectively.