On the Molecular Motion in the Orthorhombic Solid Acetylene-d$_2$

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(Z. Naturforsch. 30b, 554-560 [1975]; received April 14, 1975)

Molecular Motion, Acetylene-d$_2$, Organic Crystals

The mean square thermal displacements of the carbon and deuterium atoms in crystalline orthorhombic acetylene-d$_2$, C$_2$D$_2$, derived from earlier thermal neutron powder diffraction studies were interpreted as rigid-body translational and librational motions of the C$_2$D$_2$ molecule. An attempt to assign the derived amplitudes of the angular vibrations to the Raman-active rotational lattice modes was not unambiguous. Finally, a calculation was made to correct the apparent shortening in the bond lengths and the molecular dimension.

Introduction

Crystalline acetylene-d$_2$ is known to undergo a solid-solid phase transition at $T_{tr} = 138...149$ °K. From thermal neutron powder diffraction studies at 4.2 °K, 77 °K and 109 °K the low temperature structure can unambiguously be attached to the D$_{4h}$ (Acam) space group since no further phase transitions are observed at temperatures above 109 °K and below $T_{tr}$. With the view of the isomorphism observed for solid C$_2$H$_2$ and C$_2$D$_2$ in spectroscopic investigations in the infrared and far-infrared regions and in Raman studies some conclusions may be drawn with certainty:

1) Both substances belong to the D$_{4h}$ (Acam) space group, Acam (8f) special point group. In the crystallographic unit cell there are 4 molecules, in the spectroscopic primitive unit cell 2 molecules at sites of C$_2$ symmetry.

2) The C$_2$-axis at the site is perpendicular to the molecular axis.

3) The molecules are lying in planes parallel to the crystallographic (001) plane in layers $c/2$ apart.

In this structure a prediction for the lattice vibrations gives four Raman-active rotational and three translational modes with two of them infrared active. Recently, studies on the lattice parameter variation with temperature resulted in characteristic Debye temperatures $\theta_i$ associated with the average thermal vibrations along the crystal axes. The calculated average frequencies $\nu(\theta_i)$ are not in disagreement with the infrared-active observed frequencies for B$_{1g}$ and B$_{2g}$ lattice modes vibrating along the crystal $a$- and $b$-axes. The theoretical result for the vibration mode along $c$-axis could not be tested since the translational lattice mode A$_u$ is inactive both in infrared and Raman spectra.

The relatively high values of the refined anisotropic thermal parameters indicate considerable thermal motion of the atoms even at liquid helium temperature. A reasonable estimate for the magnitude of the vibrational amplitudes in the lattice regions may be obtained if the atomic thermal motions are successfully interpreted as rigid-body translational and librational motions. In this work the refined anisotropic thermal parameters are analyzed on the basis of the rigid-body linear C$_2$D$_2$ molecular model and the derived mean square amplitudes for the translational and average torsional vibrations reported.

Calculations

The mean square displacement $u^2$ of the thermal motion of an atom in the direction given by the unit vector $\mathbf{l} = (l_1, l_2, l_3)$ and by the components $U_{ij}$ of a symmetrical tensor of second rank is

$$u^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j. \quad (1)$$

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It is usually assumed that the axes defined either by the molecule or the crystal axes are orthogonal. The transformations between the molecular-tensor arrangement and the one defined by the crystal-setting are given by Cruickshank. In this paper the directions of the thermal motions are referred to directions along the three crystal axes. In Fig. 1 the asymmetric unit of the orthorhombic structure of acetylene-d₂ is drawn. The angle derived from the positional parameters at three temperatures is given in Table I along with the calculated components of the symmetrical tensor. The absence of the two off-diagonal components, U₁₂ and U₁₃, is due to the coincidence of the crystal c-edge with the third principal axis of the thermal vibration tensor. The two principal angular vibration axes, perpendicular to the acetylene molecule, are assumed to intersect at the molecule centre. The out-of-plane ψ- and in-plane Φ-liberations are about axes of which one is parallel to the crystal c-edge and the other parallel to the (001) plane. The following simplifying assumptions are made:

i) The components of the symmetrical tensor (Table I) are superpositions of mutually independent internal and external vibrations.

ii) All the contributions from internal vibrations U(kk) arise from two stretching modes only, namely the C≡C and the molecular D...D vibrations.

iii) The apparent shortening of the bond lengths is corrected with respect to the equilibrium direction. The contribution of the shortening to the vibration tensor is presumed to be negligible.

The mean square amplitudes of the simplified internal stretching modes in the gas phase are given at the bottom of Table I. The C≡C internal vibration is nearly negligible compared with the estimated errors in the tensor components, whereas the contribution of the molecular DCCD stretching appears to be significant. The rigid-body tensor components are obtained by subtracting the projection of the mean square amplitude U(kk) from the appropriate uncorrected tensor component U₁₁(k). In the first-order approximation the mean square displacement components for the corrected values along the three crystal axes are written

\[ U_{11}(k) = t^2_1 + r^2_2 \cos^2 \Phi, \]  
\[ U_{22}(k) = t^2_2 + r^2_3 \sin^2 \Phi, \]  
\[ U_{33}(k) = t^2_3 + r^2_3 \cos^2 \Psi = t^2_x + r^2_y \rho^2, \]

where \( t_i \) (i = 1, 3) are the translational amplitudes along the crystal edges, \( \Psi \) (in-plane)- and \( \Psi \) (out-

### Table I. Components of the symmetrical tensor, \( U_{ij} = B_{ij}/8\pi^2 \), in (Å²) and multiplied by \( 10^4 \); the angle \( \Phi \) between molecular and the crystal b-axes; contributions from internal stretchings in (Å²) and multiplied by \( 10^4 \).

<table>
<thead>
<tr>
<th>( U_{ij} )</th>
<th>( T [^\circ K] \rightarrow )</th>
<th>4.2 no constr.</th>
<th>4.2 constr.</th>
<th>77 ref.</th>
<th>109 ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₁₁(C)</td>
<td></td>
<td>101(9)</td>
<td>109(9)</td>
<td>279(25)</td>
<td>241(25)</td>
</tr>
<tr>
<td>U₂₂(C)</td>
<td></td>
<td>95(11)</td>
<td>77(11)</td>
<td>152(25)</td>
<td>51(25)</td>
</tr>
<tr>
<td>U₃₃(C)</td>
<td></td>
<td>74(9)</td>
<td>82(9)</td>
<td>304(13)</td>
<td>431(13)</td>
</tr>
<tr>
<td>U₁₂(C)</td>
<td></td>
<td>-71(9)</td>
<td>-65(9)</td>
<td>-139(13)</td>
<td>-38(13)</td>
</tr>
<tr>
<td>U₁₃(C)</td>
<td></td>
<td>365(17)</td>
<td>402(15)</td>
<td>849(51)</td>
<td>646(38)</td>
</tr>
<tr>
<td>U₁₁(D)</td>
<td></td>
<td>284(15)</td>
<td>253(13)</td>
<td>481(38)</td>
<td>519(38)</td>
</tr>
<tr>
<td>U₂₂(D)</td>
<td></td>
<td>281(10)</td>
<td>275(10)</td>
<td>532(25)</td>
<td>874(25)</td>
</tr>
<tr>
<td>U₃₃(D)</td>
<td></td>
<td>-80(6)</td>
<td>-74(6)</td>
<td>-114(25)</td>
<td>-203(13)</td>
</tr>
<tr>
<td>( \Phi ) (isotropic)</td>
<td></td>
<td>40.3(1)</td>
<td>40.0(1)</td>
<td>41.0(2)</td>
<td>40.6(2)</td>
</tr>
<tr>
<td>( \Phi ) (anisotr.)</td>
<td></td>
<td>39.0(1)</td>
<td>39.7(1)</td>
<td>40.0(2)</td>
<td>40.1(2)</td>
</tr>
</tbody>
</table>

Internal stretchings:\( C≡C 3, \ DC≡CD 23. \) Angle \( \Phi \) of ref.³ at 4.2 °K.
plane)-angular librational amplitudes, \( \Phi \) and \( \Psi \) the angles between the molecule main axis and the crystal \( b \)- and \( c \)-edges, \( r_k \) is the average distance from the centre of the molecule to atom \( k \) (\( k = C, D \)).

The solutions for the translational and angular vibrations are derived as

\[
\hat{t}_i^2 = U_{ii}(D) - AD_{ii}/4r^2, 
\]

(3a)

\[
\hat{\varphi}_{obs} = AU_{33}/4r^2, 
\]

(3b)

\[
\hat{\varphi}_{obs} = \sum_{i=1}^{2} AU_{ii}/4r^2, 
\]

(3c)

where \( AU_{ii} = U_{ii}(D) - U_{ii}(C) \), \( i = (1,3) \), \( \Delta r^2 = r_D^2 - r_C^2 \). The results are represented in Table II.

### Lattice Modes

The crystallographic unit cell of \( C_2D_2 \) contains four molecules. To calculate the mean square amplitudes of the translational vibrations in the dimolecular model\(^{18,19} \) the actual unit cell is presumed to consist of three subcells each containing two acetylene-\( d_2 \) molecules. A particular subcell \( [i = 1(a), 2(b), 3(e)] \) is thought to have rigid-body vibrations in the acoustical and optical branch with respect to one crystal axis alone. Hence in the lattice model\(^{18} \) the variations of translational and librational\(^{19} \) squared amplitudes are written

\[
\hat{t}_{i,a} = 3h^2(4\pi^2 M k \theta_i)^{-1}(T/\theta_i) \{ \Phi(x) + x/4 \}, 
\]

(4)

\[
\hat{\varphi}_k = h(8\pi^2 n J)^{-1} \sum (g_{jk}/r^2) \coth(h v_{jk}/2kT) = B_J \sum (g_{jk}/r^2) \coth(h v_{jk}/2kT). 
\]

(5)

The standard notations\(^{18-20} \) have their usual meaning, \( \hat{t}_{i,a} = r.m.s. \) translational amplitude due to the acoustic branches along axis \( i \), \( \hat{\varphi}_k = r.m.s. \) librational amplitude (\( k = x, y \)), \( J \) = moment of inertia, \( M = \) molecular mass, \( B_J = h(8\pi^2 n J)^{-1} \).

The contribution from vibrations in the optic branches\(^{18} \) (Eq. (4)) to the translational amplitudes is arbitrarily taken into account here by assuming \( \theta_i(0^\circ K, \text{optic}) = 2\theta_i(0^\circ K, \text{acoustic}) \). The relatively scanty amount of data collected by means of the neutron powder diffraction studies\(^{4-6,12} \) and spectroscopic methods\(^{7-10} \) is hardly improved by a more definite correction. In the first-order approximation the observed translational amplitudes at 4.2 \( ^\circ K \) (Table II) arise from zero point acoustical vibrations. The calculations (Eq. (4), Ref.\(^{18} \); Eq. (4), this work) give for the acoustic characteristic temperatures: \( \theta_1 \approx 130^\circ K \), \( \theta_2 \approx 139^\circ K \), \( \theta_3 \approx 178^\circ K \). These values are of the magnitude found for appropriate quantities from the thermal expansion of the lattice\(^{13} \) parameters. In further calculations the quantities \( \theta_i \) in Eq. (4) are replaced by the Debye temperatures\(^{13} \) found earlier. The corrected translational\(^{18} \) mean square amplitudes are thus simplified to

\[
\hat{t}_{i,a} \approx 0.5 \left( \hat{t}_{i,a}^2 + \frac{1}{3} \hat{t}_{i,a}^2 (0^\circ K)(\theta_0/\theta_i) \coth(\theta_i/T) \right). 
\]

(6)

The theoretical dependence of \( \theta_i \) on temperature is taken into consideration\(^{13} \) in Eq. (4). In Fig. 2 the four Raman-active rotational lattice modes associated with the observed librations\(^{9,9} \) and \( \phi \) modes are

Table II. The observed rigid-body translational and librational squared amplitudes from neutron diffraction data.

<table>
<thead>
<tr>
<th>( T ) ( ^\circ K )</th>
<th>( 2r_C [\text{Å}] )</th>
<th>( 2r_D [\text{Å}] )</th>
<th>( \hat{t}_{i,C}^2 [\text{Å}^2] \times 10^{-3} )</th>
<th>( \hat{t}_{i,D}^2 [\text{Å}^2] \times 10^{-3} )</th>
<th>( \hat{\varphi}_{obs} [\text{deg}^2] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>1.180(6)</td>
<td>3.301(7)</td>
<td>7(3)</td>
<td>7(3)</td>
<td>4(2)</td>
</tr>
<tr>
<td>4.2</td>
<td>1.180(6)</td>
<td>3.301(7)</td>
<td>7(3)</td>
<td>5(2)</td>
<td>5(2)</td>
</tr>
<tr>
<td>77</td>
<td>1.14(1)</td>
<td>3.25(1)</td>
<td>20(8)</td>
<td>11(6)</td>
<td>27(4)</td>
</tr>
<tr>
<td>109</td>
<td>1.16(1)</td>
<td>3.27(1)</td>
<td>18(7)</td>
<td>2(7)</td>
<td>37(4)</td>
</tr>
</tbody>
</table>
shown. In the rigid-body molecular model the intensity ratios \(^1\) of the four lattice vibrations are given as

\[
I(A_g) : I(B_{1g}) : I(B_{2g}) : I(B_{3g}) = 4a : (b/sin^2\Phi) : (b/cos^2\Phi) : a \frac{\cos^2\Phi - \sin^2\Phi)^2}{\cos^2\Phi \sin^2\Phi},
\]

with abbreviations \(a = (av - aw)^2\), \(b = (av - au)^2\); \(av\), \(au\), \(aw\) = molecular polarizabilities with respect to the Cartesian coordinates \(U\), \(V\), and \(W\). In the gas phase \(aw = au\), but in solid \(C_2D_2\) they are expected to differ due to the relation between the thermal expansion\(^2\) of the axes and the anisotropy of the crystal field.

The quantities \(q^2_{\text{obs}}\) and \(q_{\text{obs}}\) derived from neutron diffraction experiments at \(4.2\) °K arise in the first-order approximation from zero-point rotational oscillations. For the lattice modes in question \(g_{\text{obs}} = 1\) and \(B_3 = \text{constant}\), and hence at liquid helium temperature Eq. (6) is reduced to

\[
\sqrt{2} B_j v_k^1 = B_j \sum \sqrt{2} \eta_{kj},
\]

for \(k = \psi\), \(j = (B_{1g}, B_{2g})\),

\(8\)

for \(k = \varphi\), \(j = (A_g, B_{3g})\).

The apparent single-mode value \(v_k\) is associated with the derived amplitude of \(k\) from neutron diffraction data. For \(v_k\) it is then valid

\[
2 v_k^1 = \frac{\sqrt{2}}{B_j} B_j^2 \sum_{j=1}^{2} \eta_{kj},
\]

\(9a\)

\[
2 v_k^1 > v_{kj},
\]

\(9b\)

\[
v_k < 2 v_{kj}.
\]

\(9c\)

The apparent frequencies are calculated using the \(\eta_{kj}\)'s in Table II, with results \(v_\psi \approx 102 \pm 8\) cm\(^{-1}\), \(v_\varphi \approx 51 \pm 5\) cm\(^{-1}\). It is presumed here that the probabilities of the occurrence of the four lattice modes are equal and that all the vibrations are included in the three\(^3\) observed bands. The best fit of \(v_\psi\) and \(v_\varphi\) in Eq. (9a-c) would imply the following assignment of the modes:

\[
\wedge \psi^2 \ldots 71.1, 74.1\text{ cm}^{-1} \ldots A_g, B_{2g} \text{ pair};
\]

\[
\wedge \varphi^2 \ldots 152.1\text{ cm}^{-1} \ldots B_{1g}, B_{2g} \text{ pair}.
\]

The halfwidth of the \(\varphi\)-peak, 6 cm\(^{-1}\), is relatively broad compared to the widths of the \(\psi\)-components, 1.5 to 2 cm\(^{-1}\). This may be caused by two very near singlets forming the composite peak. The crystal \(a\)- and \(b\)-axes are roughly equal\(^3\) and the molecule is lying nearly along the diagonal of the (001) plane. Hence, the differences between the changes of the interatomic distances in the \(B_{1g}\) and \(B_{2g}\) modes are relatively small and the frequencies should be of the same magnitude. It has to be taken into account that the \(\psi\)-components cause changes in the fairly short\(^3\) non-bonded \(D...D\) distance, 2.95(2) Å at 4.2 °K, between nearest deuterium atoms in adjacent planes \(c/2\) apart. As a result the intermolecular forces between two planes might be higher than the forces inside the layer-plane, and one would expect for higher frequencies and smaller amplitudes in the \(\psi\)-modes. In Table III the assignment of the Raman-active rotational lattice modes (this work), the observed frequencies and intensities, the calculated intensity ratios (Eq. (7)) and \(q_{\text{obs}}^2\)'s (Eq. (5)) along with the squared angular amplitudes \(q_{\text{obs}}^2\) and \(q_{\text{obs}}^2\) (Table II) are given. The intensity ratios based on the assumption of additive polarizabilities\(^1\) and the interpretation of the observed bands are hardly compatible. The total intensity of the \(B_{1g} + B_{2g}\) modes may be adjusted to the theoretical scale by assuming \(2(av - au) \approx (av - aw)\). The ratio 25:1 between the observed and calculated intensities of

Table III. The assignment of the rotational lattice modes (this work), the observed frequencies (in cm\(^{-1}\)), the experimental and calculated intensity ratios (I(Ag) = 100) and the observed (neutron data) and the theoretical (Eq. (5)) values calculated for the spectroscopic frequencies.

| \(T\) [°K] | \(v_{\text{obs}}\) | \(B_{3g}\) | \(I_{\text{obs}}\) | \(v_{\text{obs}}\) | \(A_g\) | \(I_{\text{obs}}\) | \(I_{\text{calcd}}\) | \(\wedge\phi^2\) [deg\(^2\)] | \(\wedge\psi^2\) [deg\(^2\)] | ref. | \(T\) [°K] | \(v_{\text{obs}}\) | \(B_{1g} + B_{2g}\) | \(I_{\text{obs}}\) | \(I_{\text{calcd}}\) | \(\wedge\phi^2\) [deg\(^2\)] | \(\wedge\psi^2\) [deg\(^2\)] | ref. |
| 4.2 | — | — | 3 | — | 100 | 56(4) | — | 4 | 4.2 | — | 103b/a | 28(3) | — | 4 |
| 30 | 71.1 | 78 | — | 74.1 | 100 | — | — | 70 | 12 | 30 | 152.1 | 28 | — | 31 | 12 |
| 50 | 71.9 | — | — | 75.2 | — | — | 82 | 12 | 50 | 155.1 | — | — | 31 | 12 |
| 63 | 67 | — | — | 74 | — | — | 102 | 7 | 77 | — | 103b/a | 32(4) | — | 5 |
| 77 | — | 3 | — | 70 | — | — | 100 | 119(10) | — | 5 | 109 | — | 103b/a | 62(4) | — | 6 |
| 100 | 65.6 | — | — | 70 | — | — | 100 | 115(9) | — | 155 | 8 | — | 31 | 12 |
| 109 | — | 3 | — | 100 | 115(9) | — | 6 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
the $B_{3g}$ arbitrarily assigned to the vibration at about 71 cm$^{-1}$ is in serious disagreement. At the time being, however, the author prefers the lattice vibration model with high-frequency $\varphi$-components along the crystal $c$-axis since a conclusive interpretation$^{11,12}$ of the observed bands seems not to be available. The discrepancy of the $B_{3g}$ band is thought to result due to the considerable interaction of the molecules in adjacent layer-planes. In Table IV and Fig. 3 the calculated translational

![Fig. 3. The calculated (solid lines) and observed mean square amplitudes of the translational and librational lattice vibrations. Observed mean square angular values: $\hat{\varphi}^2$ (O) and $\hat{\psi}^2$ (●); translational quantities: $t_1^2$ (+), $t_2^2$ (X) and $t_3^2$ (●). Error bars only partly drawn.](image)

and librational squared amplitudes from Eqs (5-6) are tabulated. The temperature variation of the Raman-active frequencies is estimated on the basis of the reported$^{8,11,12}$ values scaled by the average experimental ratio $v_H/v_D \approx 1.157$ on isotopic substi-
tution of hydrogen by deuterium. The calculated angular squared amplitudes were derived by assuming no upper limits for the $\varphi$ and $\psi$ librations. In the actual vibrations, however, it might be possible that the amplitude $\hat{\varphi}$ of the in-plane rotational vibrations is restricted below some value $\hat{\varphi}_{\text{max}}$ connected to the force field of the crystal. When reaching the state where $\hat{\varphi} \approx \hat{\varphi}_{\text{max}}$ one might assume that any increase in the angular amplitude will be fed into the off-plane $\psi$ librations. This might explain the perhaps significant difference between the observed and calculated amplitudes at 109 °K.

The difference between the translational squared amplitudes in Tables II and IV might be significant for the quantity $t_3^2$ along the crystal $c$-axis. Other possible explanations apart from the $\varphi/\psi$-interaction for the discrepancy are i) contributions from the vibrations in the optic$^{18}$ branch are stronger than the values set by the crude estimate and ii) the characteristic temperature $\theta_3$ is decreasing considerably faster than presumed$^{13}$ earlier. Both the translational and librational lattice vibrations along the $c$-edge are influenced by a probably very rapidly decreasing force field with increasing temperature. As a result the lattice parameter $c$ and the r.m.s. amplitudes would increase as functions of temperature. The $t_3^2$ value at 109 °K, $-2(7) \cdot 10^{-3}$ Å$^2$, is probably due to all inaccuracies of the model, experimental errors and the fact that in the translational amplitudes (Eq. (3a)) errors are cumulating.

A possible model for the solid-solid phase transition may be obtained by assuming the transition to pass through an apparent orthorhombic structure similar to the space group D$_{2h}^5$ (Peab, No. 61): Acam (low phase)$^{3-6} \rightarrow$ Pcab* (apparent) $\rightarrow$ Pa3 (high phase)*. The apparent structure may be generated from the stable low temperature Acam arrangement

![Table IV. The calculated variation of the translational and librational squared amplitudes on the basis of the estimated temperature dependence of lattice modes; the $t^2$'s (in Å$^2$) are multiplied by $10^3$.](image)

<table>
<thead>
<tr>
<th>$T$ [°K]</th>
<th>$B_{3g}$</th>
<th>$A_g$</th>
<th>$B_{1g} + B_{2g}$</th>
<th>$\hat{\varphi}_E$ (deg$^2$)</th>
<th>$\hat{\psi}_E$ (deg$^2$)</th>
<th>$t_1^2$</th>
<th>$t_2^2$</th>
<th>$t_3^2$</th>
</tr>
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<tr>
<td>0</td>
<td>75</td>
<td>76.5</td>
<td>153</td>
<td>63</td>
<td>31</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>25</td>
<td>73</td>
<td>75.5</td>
<td>152.5</td>
<td>66</td>
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</tr>
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<td>50</td>
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<td>75</td>
<td>151.5</td>
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<tr>
<td>75</td>
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<td>153</td>
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<td>16</td>
<td>8</td>
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<tr>
<td>125</td>
<td>63</td>
<td>68</td>
<td>143.5</td>
<td>202</td>
<td>49</td>
<td>13</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>

* Investigations on cubic phase are referred in several references, e.g. $^{1-3,7-13}$. 
by rotating the C2D2 molecules off the (001)-type layer planes. A graphical representation of the tilting is similar to the one obtained by a static situation with "frozen" B2g lattice vibrations simultaneously in two adjacent layers with opposite amplitudes for the two molecules related by the b-glide operation. If there is a tendency to form the apparent Pcb system then one might expect the B2g mode to be predominant at the expense of the B1g vibration. At the time being, however, full-scale X-ray or neutron diffraction structure determinations and Raman studies of the lattice vibrations at temperatures between 120 °K — Ttr seem not to be available. Nevertheless, the drastic changes in the thermal neutron powder patterns1 and in the infrared spectra2 when passing over the transition point indicate that even if the hypothetical Pcb structure exists, it would be unstable. As a theoretical model, however, it is adequate since the high phase Pa3 may be generated from the Pcb arrangement simply by shrinking13 the orthorhombic a-axis and expanding the b- and c-edges.

Correction of the Apparent Shortening of the Bond Lengths

An apparent shortening13 of the bond lengths and the molecular dimension is expected as a result of the relatively large librational amplitudes of the molecules in the crystal. The value for the apparent shortening $\Delta L$ of inter-atomic distances is calculated using the expression

$$\Delta L = L \cdot \sum_{k=1}^{n} q_k^2 \sin^2 (\Phi_k/2),$$

(10)

where L is the appropriate noncorrected interatomic distance derived from crystal structure analysis, $\Phi_k$ is the angle between the equilibrium orientation of the molecule and the $k^{th}$ ($k = q, \psi$) principal axis of libration. For C2D2 the angles $\Phi_k = 90^\circ$ and Eq. (10) is reduced to

$$\Delta L = L(p^2 + q^2)/2.$$  

(11)

The results are given in Table V. No significant temperature variation was found. An interesting point is the smaller value of the C-D bond in the gas phase compared with the one in the condensed phase. This might be attributed to the relative weakening of the C-D bond due to the intermolecular forces in the crystal.

**Discussion**

It has been shown in this work that in the rigid-body molecular model the thermal parameters derived from neutron powder diffraction data are relatively easily described in terms of the translational and librational vibrations of the molecule. Ambiguities were experienced, however, when assigning the observed amplitudes with the allowed Raman-active modes and with the assumed frequency of the completely inactive translational $A_u$ vibration. Some likely reasons for the discrepancies were given, but a firm conclusion cannot be made due to the lack of necessary information.

<table>
<thead>
<tr>
<th>T [°K]</th>
<th>L</th>
<th>C=C</th>
<th>$\Delta L$</th>
<th>Lcorr</th>
<th>DC=C=CD</th>
<th>$\Delta L$</th>
<th>Lcorr</th>
<th>C-D</th>
<th>$\Delta L$</th>
<th>Lcorr</th>
</tr>
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<tbody>
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