On the Lattice Parameters of the Orthorhombic Low Temperature Phase of Crystalline Acetylene-d_2

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Acetylene-d_2, C_2D_2, is known to exist in two crystal structures. The neutron powder diffraction data of the orthorhombic phase for temperatures between 4.2 K and 148.7 K have been analyzed and the refined lattice parameters and the calculated unit cell volume tabulated. By expressing the observations as functions of the vibrational energy, values for the Debye characteristic temperature and the static lattice and zero-point quantities are calculated with the method of least squares. Theoretical values for the coefficient of thermal expansion, quantities proportional to the isothermal compressibility, and the calculated density of solid C_2D_2 are given. The average frequencies associated with the characteristic temperatures for the lattice vibrations along the a- and b-axes are calculated. Finally, an estimate for the latent heat of the cubic-orthorhombic transition is obtained from the Clausius-Clapeyron equation.

Introduction

Acetylene, C_2H_2, is a linear symmetrical molecule with a carbon-carbon triple bond. In the gas phase the molecular dimension of C_2H_2 and its deuterated derivatives, C_2D_2 and C_2DH, is about[1] 3.3 Å. In the solid state, C_2D_2 and C_2H_2 are reported to undergo a phase transition at 138 . . . 149 K[2, 3] and 133 K[4] respectively. In single crystal X-ray studies[4] the high temperature phase of crystalline C_2H_2 was found to have the cubic Pa3 crystal structure with four molecules per unit cell. Neutron powder diffraction patterns recorded for the upper phase of solid C_2D_2 at about[5] 150 K are not in disagreement with the Pa3 (8c) special point group. Recently, the crystal structure of the low temperature modification of C_2D_2 was determined. Neutron powder diffraction patterns recorded at temperatures 4.2 K[6, 7], 77 K[8] and 109 K[9] could unambigiously be indexed and refined on the basis of the orthorhombic Acam (No. 64) space group. The high values for the refined temperature parameters would lead one to expect considerable thermal motion of the atoms. If succesfully interpreted as rigidbody molecular translational and librational motions[10] the results might give an estimate of the amplitudes of the lattice vibrations and the angular librations of the molecules.

The D_{2h}^{18}(Acam) structure with two molecules in the spectroscopic primitive unit cell enables three translational lattice modes, two of which being infrared active and one inactive[11, 12]. In the low frequency lattice region four Raman-active rotational modes are expected for both C_2H_2 and C_2D_2 with only[13, 14] three of them observed.

During the neutron powder diffraction experiments[3, 5–9] a considerable amount of information was collected on the dependence of the lattice parameters on temperature for crystalline C_2D_2. Compared with the conventional X-ray technique, the low intensity of the neutron beam and the relatively moderate resolution of the diffracted intensity maxima lead to peak positions of moderate accuracy. Further difficulties arise from the instrumental geometry and the accuracy of the wavelength[15] used. On the other hand, however, by a suitable choice of the cryostat material, the cryogenic coolant and the sample holder, the attenuation of the thermal neutron beam can be kept in reasonable limits. Some earlier X-ray diffraction studies have been reported[4, 16, 17] for C_2H_2 with incomplete lattice parameter determinations, whereas apparantly no data on C_2D_2 have been published. This led us to a reconsideration of the information available from the powder patterns.

In this paper the observed lattice parameters, the calculated unit cell volume, and the density of acetylene-d_2 as a function of temperature is reported. Expressing the lattice parameters and the unit cell volume as functions of the internal energy, Debye temperatures are obtained. Theoretical values for the coefficients of thermal expansion, values proportional to the isothermal compressibility, and

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the difference between the isothermal and the adiabatic compressibilities are given. Finally, the average frequencies for the lattice vibrations along the crystallographic a- and b-axes are calculated and an estimate for the latent heat of the solid-solid phase transition is obtained from the Clausius-Clapeyron equation.

Experimental

Details of the experimental procedure are given elsewhere [3, 5–9]. The simultaneously observed powder patterns on the multicounter powder diffractometers CURRAN and PANDA (UKAERE, Didcot, England) were amalgamated [7, 15] to a single powder pattern. The monochromated thermal neutron beam wavelengths and the instrumental zero angles on these instruments and the two single-counter diffractometers PANDA (older version) and D2 (ILL, Grenoble, France) were calibrated using a standard powder specimen (Ni, Al_2O_3). All the measurements were carried out on the instrumental focussing side only. Some difficulties were experienced to position the C_2D_2 sample in the cryostat at the same location as the standard sample on the diffractometer. In order to correct this misalignment it was presumed that the observed angle $2\,\Theta$ contains a small zero-angle shift $\Delta\, 2\,\Theta$

$$2\,\Theta_i(\text{obs}) = 2\,\Theta_i(\text{“true”}) + 2\,\Delta\Theta\,, \quad \Delta\Theta \ll \Theta_i\,. \qquad (1)$$

Derived from Bragg's equation the function to be minimized with respect to the parameters a, b, c and $\Delta\Theta$ is for an orthorhombic lattice

$$F = [\,(2/\lambda)^2\,(\sin^2\Theta_i - \Delta\Theta \sin 2\,\Theta_i) - h_i^2/a^2 - k_i^2/b^2 - l_i^2/c^2]\,. \qquad (2)$$

The lattice parameters a, b and c and the calculated unit cell volume V at various temperatures are given in Table 1. The figures in parenthesis are proportional to the estimated standard deviations corrected for the “mean path” scattering (weighing scheme) of the values quoted. In the last columns, the wavelengths and the instruments used are given along with the number of independent single reflexions used in the least-squares calculations according to Equation (2). Lattice parameters marked with an asterisk are derived with the aid of the more powerful modified profile fitting technique [18, 19].

The Analysis *

In the diatomic potential model [20] a linear polyatomic molecule is approximated by two interaction centres of fixed distance. The intermolecular pair

T (K)	a (Å)	b (Å)	c (Å)	V (Å^3)	λ (Å), Ins./n
4.2	6.188 (1)	6.002 (1)	5.547 (1)	206.0 (1)	1.848, *P/Ref. [7]
4.2	6.193 (1)	6.005 (1)	5.551 (1)	206.4 (1)	1.848, P/Ref. [6]
4.2	6.191 (1)	6.007 (2)	5.549 (1)	206.4 (1)	1.373, *C
4.2	6.191 (2)	6.010 (3)	5.549 (2)	206.5 (2)	1.373, C/13
4.2	6.191 (2)	6.009 (3)	5.549 (2)	206.4 (2)	1.837, PS/8
4.2	6.196 (3)	6.000 (2)	5.540 (3)	205.9 (2)	1.903, D2/5
4.2	6.187 (3)	6.004 (2)	5.547 (2)	206.0 (2)	1.965, PS/6
77.	6.214 (1)	6.018 (3)	5.615 (1)	210.0 (1)	1.363, *C/Ref. [8]
77.	6.214 (1)	6.027 (1)	5.613 (1)	210.2 (1)	1.848, P/23
77.	6.212 (1)	6.026 (2)	5.611 (1)	210.0 (1)	2.624, C/9
83.6	6.218 (2)	6.028 (2)	5.628 (2)	210.9 (2)	2.624, C/10
109.	6.235 (1)	6.047 (1)	5.676 (1)	214.0 (1)	1.373, *C/Ref. [9]
114.5	6.240 (2)	6.046 (2)	5.690 (2)	214.7 (2)	2.624, C/9
127.	6.254 (3)	6.053 (2)	5.704 (3)	215.9 (2)	1.373, C/8
135.5	6.255 (2)	6.060 (2)	5.736 (2)	217.4 (2)	2.624, C/7
143.9	6.267 (4)	6.070 (3)	5.768 (3)	219.4 (3)	1.373, C/8
145.3	6.252 (4)	6.065 (2)	5.745 (4)	217.9 (3)	2.624, C/6
147.	6.255 (3)	6.069 (2)	5.776 (3)	219.3 (2)	1.373, C/11
147.3	6.263 (2)	6.064 (2)	5.768 (2)	219.0 (2)	2.624, C/4
148.2	6.267 (2)	6.067 (2)	5.780 (3)	219.8 (3)	1.373, C/13
148.2	6.265 (2)	6.078 (3)	5.772 (2)	219.8 (3)	2.624, C/6
148.3	6.259 (2)	6.081 (4)	5.773 (2)	219.7 (3)	1.903, D2/4
148.3	6.266 (2)	6.055 (5)	5.758 (3)	218.4 (3)	2.624, C/5
148.7	6.253 (4)	6.071 (2)	5.772 (2)	219.1 (2)	2.624, C/6

Table 1. Observed lattice parameters a, b and c and unit cell volume V of the orthorhombic phase of acetylene-d_2. The wavelength (λ) and instrument used and the number of reflections in the l.s.q. refinement of the parameters are also given.

Notations: P = PANDA (multicounter), PS = PANDA (single-detector), C = CURRAN (5-counter), D2 = D2 (ILL, Grenoble), an asterisk is for Rietveld profile analysis.

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* A short list of the notations is given in Table 2.

potential is then

$$\varphi_m = \sum_{h=1}^{2} \sum_{k=1}^{2} \varphi_{hk}, \tag{3}$$

where φ_{hk} may be assumed to be a Lennard-Jones type pair potential between such centres:

$$\varphi_{hk} = 4\,\varepsilon\,[(\sigma/r_{hk})^{12} - (\sigma/r_{hk})^{6}]. \tag{4}$$

We use this model. The total potential U of the crystal is

$$U = \tfrac{1}{2} N \sum_m C_\mathrm{m}\, \varphi_m, \tag{5}$$

C_m = number of equipotential by interacting molecules around the reference molecule, N = number of molecules. By identifying the centres of the model with the positions of the carbon atoms and expressing the distances r_{hk} and the volume V of the orthorhombic unit cell in terms of one of the axes X_i we have

$$r_{hk} = P_{hk}\, X_i; \quad V = \delta_i\, X_i^3; \quad \delta_i = \prod_{j=1}^{3} (X_j/X_i), \tag{6 a, 6 b, 6 c}$$

where P_{hk} is a dimensionless parameter. We express the potential energy U as a function of the volume

$$U = A_\mathrm{V}\, V^{-4} - B_V\, V^{-2}; \tag{7 a}$$

$$A_V = 2\,N\,\varepsilon \sum_m C_m \sum_h \sum_k \delta_i^4 (\sigma/P_{hk})^{12}; \tag{7 b}$$

$$B_V = 2\,N\,\varepsilon \sum_m C_m \sum_h \sum_k \delta_i^2 (\sigma/P_{hk})^{6}. \tag{7 c}$$

At static equilibrium the derivative $\mathrm{d}/\mathrm{d}V\,(U)_V$ vanishes and we have

$$B_V = 2\,A_V\, V_\mathrm{s}^{-2}. \tag{8}$$

The thermal expansion of the unit cell volume and the axes referred to the static equilibrium state are written as

$$\Delta V = V - V_\mathrm{s}; \quad \Delta X_i = X_i - X_{is}. \tag{9 a, 9 b}$$

The relative coefficient of expansion is approximately defined as

$$\frac{\Delta X_i}{X_{is}} \simeq \frac{1}{e_i} \frac{\Delta V}{V_s}; \tag{10 a}$$

$$\frac{1}{e_i} = (\Delta X_i/X_{is}) \Big/ \sum_{i=1}^{3} (\Delta X_i/X_{is}). \tag{10 b}$$

Pautamo [21] derived from the Mie-Grüneisen equation of state expressions for the temperature variation of the volume and for the lattice parameters as functions of the vibrational energy E for cubic alkali halides. By accounting for the anisotropy in the thermal expansion of the crystal axes with the aid of Eq. (10 a) the Eqs. (56, 57) [21] are slightly modified and are written

$$(\Delta V_i/V_{is}) = g_i E_i + (2\,K - 1)\, g_i^2 E_i^2; \tag{11 a}$$

$$(\Delta X_i/X_{is}) = [g_i E_i + (2\,K - 1)\, g_i^2 E_i^2]/e_i, \tag{11 b}$$

with $\Delta V_i = X_{js} X_{ks}\, e_i\, X_i$, $\Delta X_i = X_i - X_{is}$, $j \neq k \neq i$ (for axes); $\Delta V_i = V - V_\mathrm{s}$ (for volume); E_i = the vibrational energy; $g_i = \gamma_\mathrm{E}\, \beta_\mathrm{is}/V_\mathrm{s}$. By splitting E_i in to the zeropoint energy and a function of the characteristic Debye temperature Θ_i the energy will be approximately

$$E_i \cong \tfrac{9}{8}\, R\,\Theta_i + f(\Theta_i/T)\, T = E_{i0} + E_{i\mathrm{T}}. \tag{12}$$

The temperature variation of the volume and the crystal axes are now written

$$y_i = y_\mathrm{is} + (y_\mathrm{is}/e_i)\, g_i (E_i/T)\, T + (y_\mathrm{is}/e_i)\,(2\,K - 1)\; g_i^2 (E_i/T)^2\, T^2, \tag{13}$$

which for computational reasons is rewritten

$$y_i = y_{i0} + B_i\, f(\Theta_i/T)\, T + C_i [f(\Theta_i/T)]^2\, T^2, \tag{14}$$

$$y_{i0} = y_\mathrm{is} \{1 + E_{i0}\, g_i [1 + E_{i0}\, g_i (2\,K - 1)]/e_i\}, \tag{15 a}$$

$$B_i = y_\mathrm{is}\, g_i [1 + 2\, g_i\,(2\,K - 1) E_{i0}]/e_i; \tag{15 b}$$

$$C_i = y_\mathrm{is}\, g_i^2 (2\,K - 1)/e_i. \tag{15 c}$$

In this work the characteristic Debye temperatures Θ_i associated with the thermal expansion of the dimensions are assumed to be dependent on the volume [Eq. (49) [21]]

$$\Theta_i \cong \Theta_{is} (1 - K\,\Delta V/V_\mathrm{s}). \tag{16}$$

For the Debye temperature Θi_0 at the absolute zeropoint one has then

$$\Theta_{i0} \cong \Theta_{is} [1 - K(V_0 - V_\mathrm{s})/V_\mathrm{s}]; \tag{17 a}$$

$$\Theta_i \approx \Theta_{i0} [1 - K(V - V_0)/V_0]. \tag{17 b}$$

An estimate of the temperature dependence of the refined experimental values is easily obtained from Figure 1. For the initial computations it is sufficient to assume a constant value Θ_{i0} for the Debye temperature below some temperature T_i^* (30 K $\leqq T_i^* \leqq$ 50 K). Above T_i^* the temperature dependence is thought to be nearly linear, $\tau = -(\mathrm{d}\Theta_\mathrm{i}/\mathrm{d}T)$. For the energy function $f(\Theta_i/T)$ the internal energies tabulated in Landolt-Börnstein [22] were used linearly interpolated. Every observation was weighted by $1/w_j^2$, where

$$w_j^{-2} = \{w_j^2(\mathrm{obs}) + [1 + \delta_T (T/\Theta_j - 0.5)]^2\}^{-1}, \tag{18}$$

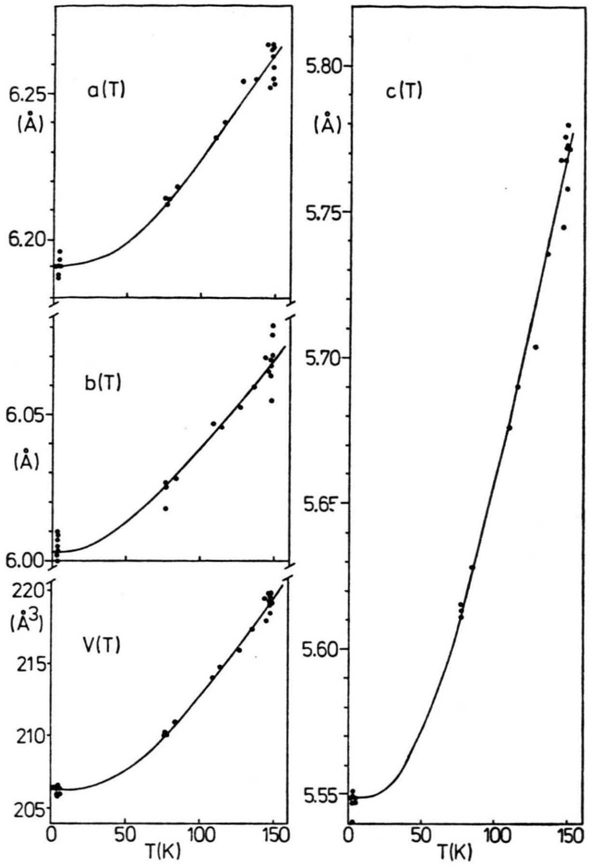

Fig. 1. Temperature dependence of the lattice parameters *a*, *b* and *c* and the unit cell volume *V* of the orthorhombic phase of C_2D_2. Solid line = theoretical values, full circles (○) = experimental data.

with $\delta_T(T/\Theta_j<0.4)=0$, $\delta_T(T/\Theta_j>0.4)\approx 0.1$; $w_j(\text{obs})$ = relative deviation of the observation corrected for the scattering from the estimated "mean path" of the quantity *j* versus temperature. The temperature dependent part was chosen to give less weight within the high-temperature range. For a number of initial values $30\,\text{K} \leqq \Theta_{i0} \leqq 240\,\text{K}$ the least-squares computations on the observed values were carried out for the Equations (13, 14). Two residual factors are defined as

$$R_u = 10^4 \sum_j [y_j(\text{obs}) - y_j(\text{calc})] / \sum_j y_j(\text{obs}) \,, \quad (19\,\text{a})$$

$$R_w = 10^4 \sum_j w_j^{-2} [y_j(\text{obs}) - y_j(\text{calc})] / \sum_j w_j^{-2} y_j(\text{obs}) \,. \quad (19\,\text{b})$$

For the final Debye temperature the value Θ_{i0} ($R_{w,\min}$, $R_{u,\min}$) was chosen when possible. The scattering of the observations around the "mean path" resulted in reasonably sharp minima only for *V* and the lattice parameter *c* within ±3 K from Θ_{i0}. For *a* and *b* the minima are shallow, and the estimated error in Θ_{i0} is about ±8 K. The final parameters are given in Table 3.

Table 3. Calculated and derived parameters from least-squares procedures on Equations (14), (15), (20).

	a-axis	*b*-axis	*c*-axis	volume
y_{is} (Å^n)	6.1365	5.9702	5.3404	194.95
y_{io} (Å^n)	6.1907	6.0037	5.5489	206.28
B_i (Å^n mole/J) 10^{-5}	3.2918	2.5955	10.915	622.78
C_i (Å^n mole/J) 10^{-11}	1.1569	0.9972	3.553	215.50
θ_{io} (K)	176±8	138±8	204±3	194.5±3
θ_{is} (K)	202.5	158.8	234.7	223.7
T^* (K)	40	30	50	40
$\tau\,10^{-3}$	1.8	1.8	1.8	1.8
e_i	5.668	7.124	1.464	1
R_w	2.5	3.7	4.0	8.3
R_u	4.9	6.4	7.8	13.7

$n=1$ for lattice parameters, $n=3$ for volume. $M(C_2D_2) \cong 28.05$.

Temperature Variation of Some Quantities

The lattice parameters, unit cell volume, density and the coefficients of thermal expansion of the volume and along the axes are calculated from Eqs.

Table 2. List of some notations in Equations (3÷26).

E = vibrational energy of the crystal;
R = gas constant;
V = volume of the unit cell;
y_i = general notation for a quantity of type *i* (*i*=a, b, c or V);
i = subscript for a quantity of type *i* at temperature *T*;
α_i = coefficient of linear or volume thermal expansion;
β_i = linear or volume isothermal compressibility;
$K = -V_s (d^3U/dV^3)_{V_s} / [4 (d^2U/dV^2)_{V_s}]$,
N = number of molecules in the crystal;
U = potential energy of the lattice;
X_i = lattice parameter (*i*=a, b or c);
i_0 = subscript for a quantity of type *i* at absolute zero;
is = subscript for a quantity of type *i* at static lattice state;
θ_i = characteristic Debye temperature associated with linear or volume thermal expansion;
γ_E = Grüneisen parameter in the Mie-Grüneisen equation of state of solids.
$e_i^{-1} = \Delta X_i (dV/dX_i) / \sum [\Delta X_i (dV/dX_i)]$.

Table 4. Calculated temperature dependence of some quantities*. Temperature (T), Debye temperature (Θ), crystal axis or volume, thermal linear or volume expansion coefficient (α), compressions along an axis or the compressibility multiplied by γ_E ($\gamma_E \beta$), $\gamma_E(\beta - \beta_a)$ and temperature coefficient of $\gamma_E \beta$; crystal density (ϱ).

T (K)	Θ (K)	a (Å)	α (K^{-1}) 10^{-4}	$\gamma_E \beta$ (m^2 N^{-1}) 10^{-10}	$\gamma_E \Delta\beta$ (m^2 N^{-1}) 10^{-12}	ε (K^{-1}) 10^{-3}
Static	202.5	6.1365	—	1.72	—	—
0	176	6.1907	0	1.80	0	0
25	175.6	6.1918	0.3	1.80	0.1	0.1
50	172.9	6.1993	0.8	1.83	0.7	0.3
75	167.7	6.2122	1.1	1.86	1.4	0.8
100	160.8	6.2285	1.2	1.91	2.1	0.5
125	153.2	6.2464	1.2	1.95	2.7	1.0
150	145.0	6.2653	1.3	2.00	3.5	1.0

T (K)	Θ (K)	b (Å)	α (K^{-1}) 10^{-4}	$\gamma_E \beta$ (m^2 N^{-1}) 10^{-10}	$\gamma_E \Delta\beta$ (m^2 N^{-1}) 10^{-12}	ε (K^{-1}) 10^{-3}
Static	158.8	5.9702	—	1.41	—	—
0	138	6.0037	0	1.45	0	0
25	137.7	6.0052	0.3	1.46	0.1	0.1
50	135.6	6.0132	0.8	1.48	0.6	0.4
75	131.5	6.0255	1.0	1.50	1.0	0.7
100	126.1	6.0396	1.1	1.53	1.5	0.8
125	120.1	6.0546	1.1	1.56	2.0	0.8
150	113.7	6.0699	1.1	1.59	2.5	0.8

T (K)	Θ (K)	c (Å)	α (K^{-1}) 10^{-4}	$\gamma_E \beta$ (m^2 N^{-1}) 10^{-10}	$\gamma_E \Delta\beta$ (m^2 N^{-1}) 10^{-12}	ε (K^{-1}) 10^{-3}
Static	234.7	5.3404	—	5.79	—	—
0	204	5.5489	0	6.96	0	0
25	203.6	5.5512	0.7	7.01	0.9	0.1
50	200.4	5.5728	2.5	7.34	7.5	1.1
75	194.4	5.6088	3.6	7.93	17.0	3.2
100	186.5	5.6581	4.2	8.71	26.8	4.0
125	177.6	5.7143	4.5	9.69	37.0	4.7
150	168.1	5.7745	4.7	10.90	46.0	5.4

T (K)	Θ (K)	V (Å^3)	α (K^{-1}) 10^{-4}	$\gamma_E \beta$ (m^2 N^{-1}) 10^{-10}	$\gamma_E \Delta\beta$ (m^2 N^{-1}) 10^{-12}	ε (K^{-1}) 10^{-3}
Static	223.8	194.95	—	9.13	—	—
0	194.5	206.28	0	12.63	0	0
25	194.1	206.44	1.2	12.80	2.5	0.2
50	191.1	207.61	4.1	14.04	19.5	2.3
75	185.3	209.83	5.8	16.46	42.6	6.9
100	177.8	212.76	6.6	20.30	64.2	9.5
125	169.3	216.04	6.9	26.58	85.4	13.1
150	160.3	219.53	7.0	38.34	102.4	19.2

T (K)	**ϱ (kgm^{-3}) 10^3**	T (K)	ϱ (kgm^{-3}) i10^3	T (K)	ϱ (kgm^{-3}) i10^3
Static	**0.956**	50	0.897	125	0.862
0	**0.903**	75	0.888	150	0.849
25	**0.903**	100	0.876	cubic [5]	0.815

* Note: The transition temperature $T_{tr} = 138 \ldots 149$ K.

(14, 16), from their first derivatives with respect to temperature and the parameters listed in Table 3. The results are given in Table 4. As a second order approximation [Eq. (54) [21]] we derive

$$\gamma_E \beta_{is} E_i = \Delta V_i [1 - (2K - 1) \Delta V_i / V_s] . \quad (20)$$

The quantity $\gamma_E \beta_{is}$ is calculated from Eq. (20) at the absolute zero. In this paper K is assumed to be a constant value 9/4 [Table 2, Eqs. (7, 8)], and

$$\gamma_E \beta_{is} \cong 8 \Delta V_i / (9 R \Theta_{i0}) [1 - 7 \Delta V_i / (2 V_s)] . \quad (21)$$

The thermal variation of $\gamma_E \beta_i$ and the isochoric temperature coefficient [Eqs. (74, 79)[21]] are now

$$(1/\gamma_E \beta_i) \cong (1/\gamma_E \beta_{is}) - [7 E_i - 9 (E_i - T C_{iv})/4] V^{-1}, \quad (22)$$

$$\varepsilon_i = (\partial \beta_i / \partial T)_V / \beta_i \approx \gamma_E \beta_i [7 C_{iv} + 9 T (\partial C_{iv} / \partial T)_V / 4] V^{-1}, \quad (23)$$

$C_{iv} = C_{iv}(\Theta_i / T)$ is the heat capacity at constant volume. The approximation $\gamma_E \approx K$ is taken into account inside the brackets of the equations[21] in question. The well-known thermodynamical equation for the difference of the isothermal β and the adiabatic β_a is

$$\beta - \beta_a = T V \alpha^2 / C_p , \quad (24)$$

α = volume expansion coefficient, C_p = heat capacity at constant pressure. By applying the first-order approximation $C_p \approx C_V$ Eq. (24) is written in the form

$$\gamma_E \Delta \beta_i = \gamma_E (\beta_i - \beta_{ia}) \approx T V \alpha_i^2 K / C_{iv} . \quad (25)$$

The results are listed in Table 4. The compressibility quantity $\gamma_E \bar{\beta}_V$ was calculated on the basis of an average $\gamma_E \beta_{Vs}$

$$\gamma_E \beta_{Vs} = \sum_{i=1}^{4} e_i \gamma_E \beta_{is} , \quad (26)$$

where the three terms with $e_i \neq 1$ are the compressions along the crystal axes alone. For heat capacities the tabulated values in Landolt-Börnstein[22] were used. Taking into account the simplifying assumptions and the moderate accuracy of the measurements, the quantities proportional to the isothermal compressibility are given in the quasisolved form, i. e. $\gamma_E \beta_i$.

An Application

As mentioned in the introduction, acetylene-d_2 undergoes a structural phase transition at about 138 ... 149 K[2,3]. Although not confirmed, the drastic change from the plastic cubic phase to the orthorhombic system for both C_2H_2 and C_2D_2 appears to be of the first order. The narrow range for the thermal hysteresis[3], the considerable difference in volume (this work, Ref. [5]), the sudden change in X-ray spectra[4], the sharp change in the infrared spectra[23] and the rapidness of the reversible transition[2] do support the assumption of a first-order transition with a small latent heat of transition. The well-known Clausius-Clapeyron equation applied here is

$$(\mathrm{d}p / \mathrm{d}T)_V = \Delta H_{tr} / (T_{tr} \Delta V_{tr}) , \quad (27)$$

p = pressure, ΔH_{tr} = latent heat of transition. ΔV_{tr} = change in volume, T_{tr} = transition temperature. Taking into account $(\mathrm{d}p/\mathrm{d}T)_V = \alpha_V / \beta_V$ one has

$$\Delta H_{tr} = T_{tr} \Delta V_{tr} \alpha_V / \beta_V . \quad (28)$$

The calculation yields $\Delta H_{tr} \approx 80 \pm 30$ J/mole. The estimated error is based on the formula used

$$\partial \Delta H_{tr} \approx \Delta H_{tr} [\sum_i (\Delta z_i / z_i)^2]^{1/2} , \quad (29)$$

z_i's being the variables in Equation (28). The relative error for the compressibility and the expansion terms are arbitrarily set to 25%, the one for the volume change to 10% and the absolute uncertainty of the temperature to ±5 K.

Discussion

In this study several temperature dependent physical and thermodynamical quantities are calculated, which for reasons pointed out in the introduction, can at best be of only moderate accuracy. It appears, however, that information on the thermal expansion, solid state specific heat and isothermal compressibility of C_2H_2 and C_2D_2 is not available in the literature. A single-crystal phonon scattering project on the orthorhombic phase may face dif-

Table 5. Theoretical (this work) and experimental frequencies associated with the translational lattice vibrations.

T (K)	$\nu_a(T)$	$\nu_b(T)$	T (K)	High-freq. band	Low-freq. band	
25	122	96	25	124	104	[+]Ref. [12]
50	120	94	55	122	103	[+]Ref. [12]
			63	124	103	Ref. [24]
75	117	91	75	120	101	[+]Ref. [12]
			77	118	98.5	Ref. [11]
100	112	88	100	117	98	[+]Ref. [12]
125	107	84	125	114	95	[+]Ref. [12]

[+] Ref. [12], values taken from the graph.

ficulties due to the drastic transition of the cubic single crystal to a powder-like specimen when lowered below T_{tr}. On account of these considerations the author feels that at the time being the experimental and theoretical properties reported in this article are of some value. A comparison of the calculated frequencies on the basis of Θ_i's from Table 4 with experimental ν's associated with two infrared active bands in the lattice regions observed in the far-infrared[11, 12] and near-infrared combinations[24] are presented in Table 5. The simple theory applied in this work results in values which are compatible with the observations and have a fairly similar temperature dependence.

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