A Study of the Cubic Phase of Solid Acetylene-d_2

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The powder pattern of crystalline cubic deuterated acetylene recorded by thermal neutron diffraction technique and the Pa3 crystal structure assigned to the high phase of C_2H_2 are compared. The observations are not in disagreement with the theoretical pattern. Values for the lattice parameters in a narrow temperature range are given.

Introduction

Crystalline acetylene C_2H_2 and the deuterated isomorph, C_2D_2, both are known to exhibit a solid-solid phase transition [1-3]. Below the phase transition temperature several spectroscopic investigations [4-7] suggest that the space group of both compounds is the orthorhombic D_{2h}^{18} arrangement as based on the incomplete information obtained from an X-ray study [1] on C_2H_2. Thermal neutron powder diffraction experiments reported recently [8, 9] on observations of C_2D_2 at 4.2 K support the spectroscopically predicted D_{2h}^{18}(Acam) space group. In view of the isomorphism observed in the spectroscopic investigations published these results are expected to apply to C_2H_2 as well.

Above the transition point, 133 K for C_2H_2 [1] and 138 . . . 149 K for C_2D_2 [2, 3], both compounds belong to the cubic crystal system, the most probable space group of C_2H_2 being identified [1] as Pa3. In this work a comparison is made between the suggested crystal structure and the scanty information obtained for the cubic phase during the solid-solid transition experiments of C_2D_2 reported earlier [3].

2. Experimental

The experimental details are principally described earlier [3, 8]. The wavelengths used on the multicounter CURRAN [10] (A.E.R.E., Harwell, England) and the single-detector D2 (ILL, Grenoble, France) thermal neutron powder diffractometers were 1.363, 1.373 and 2.627 Å (CURRAN), and 1.909 Å (D2). The wavelength calibration and the testing of the individual efficiencies and angular separations of the five counters (CURRAN) were done using a standard powder specimen (Ni, Al_2O_3). Due to a relatively rapid recrystallization at temperatures near and above the transition point, a full scale recording of the powder diffraction pattern was not possible. The experiments on the CURRAN instrument [10] were carried out by recording the range $0.125 < \sin \Theta/\lambda < 0.5$ with each of the five detectors scanning 12 to 15° in $2\,\Theta$ with an overlap of about $3-5°$ over the pattern observed by the neighbouring counter. On the D2 diffractometer only the low angle reflections with $\sin \Theta/\lambda < 0.24$ were usually scanned.

3. Results

The lattice parameter for the cubic phase of acetylene-d_2 is given in Table 1 for seven independent runs. The mean lattice parameter a_{av} and temperature T_{av} were calculated using the formula

$$y_{\mathrm{av}} = \sum_i n_i\, X_i\, Y_i \Big/ \sum_i n_i\, X_i\,, \qquad (1)$$

$T\,(\pm 1)$	a	$\lambda\,(\pm 0.001)$	n
148.5	6.10_2	1.373	5
149	6.10_7	1.909	6
149.2	6.13_5	1.909	3
150	6.13_2	1.909	3
150.5	6.11_6	1.373	12
152.2	6.10_3	2.627	5
154	6.13_4	2.627	5

$T_{\mathrm{av}} = 150.6$, $a_{\mathrm{av}} = 6.11_5 \pm 0.01$ Å,
unit cell volume $= 229 \pm 1$ Å^3.

Table 1. Lattice parameter of the cubic phase of C_2D_2. The columns are: temperature (K), observed lattice parameter (Å), wavelength (Å) and number of reflections used in the calculations.

with the notations: n_i = the square of the number of reflections observed during an independent run i, X_i and Y_i are the lattice parameter and temperature, respectively, for the run i in question. A comparison of the observed and calculated intensities corrected for the geometrical Lorentz factor are shown in Figure 1. The parameters used in the theoretical pattern are listed in Table 3. The scaling

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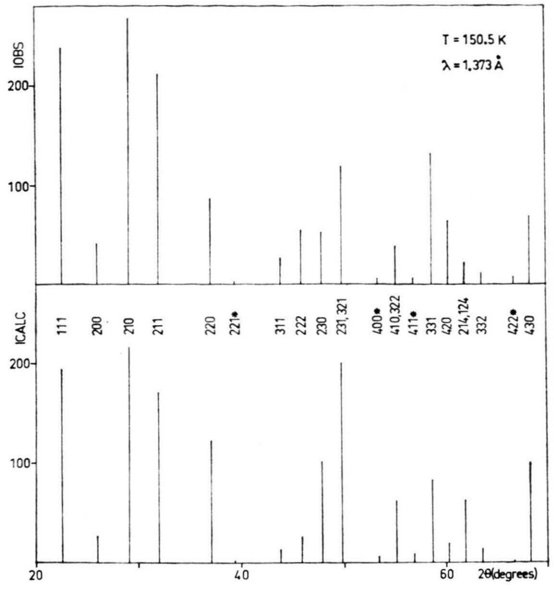

Fig. 1. A comparison of the observed pattern and intensities calculated for the Pa3 (8c) model using the initial parameters in Table 3, column 2.

of the patterns were adjusted according to

$$\sum I_{\text{calc}} = S \sum I_{\text{obs}} , \tag{2}$$

the coherent scattering lengths were taken from Bacon[11], the positional parameters were calculated by assuming the high-resolution equilibrium molecular distances of C_2D_2 in gas phase[12] to apply to the crystalline acetylene-d_2 as well, and the isotropic B-parameters were arbitrarily set equal to three times the refined appropriate value at 4.2 K[9].

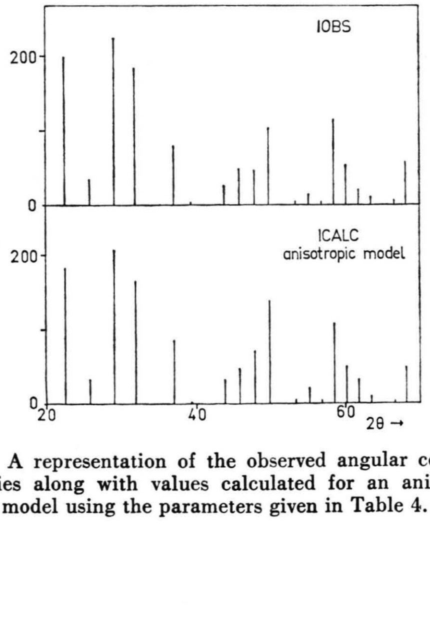

Fig. 2. A representation of the observed angular corrected intensities along with values calculated for an anisotropic model using the parameters given in Table 4.

In Fig. 1 the reflections not observed are marked with an asterisk. The intensities assigned to them are based on an estimate of the maximum peak height not detectable within the limits of the background fluctuation. The observed pattern of C_2D_2 is not in disagreement with the predicted Pa3 structure. On examining Table 2 it can be concluded that from the powder data the systematic absences cannot be determined. The only model tested, however, was the cubic-C_2H_2[1] arrangement based on the observed isomorphism. The structural parameters were refined using the crystallographic least-squares ORXFLS3 program[13]. The refinements were carried out on (F^2) and the final residual factors were $R(I) = 0.14$ and $R(F^2) = 0.09$, with the R-factors defined as

$$R(x) = \sum (X_{\text{obs}} - X_{\text{calc}}) / \sum X_{\text{obs}} . \tag{3}$$

Table 2. The systematic absences in the Pa3 (8c) space group, expected absences and the overlapping reflections present.

Absent: $(hk0)$ for h odd, $(h0l)$ for l odd, $(0kl)$ for k odd.

Absent (Pa3)	Overlapping reflection	Absent (Pa3)	Overlapping reflection
100, 010, 001	none	320, 203, 032	230, 302, 023
110, 101, 011	none	140, 401, 014	410, 104, 041 322, 232, 223
120, 201, 012	210, 102, 021		
300, 030, 003	221, 212, 122	330, 303, 033	411, 141, 114
310, 301, 031 130, 103, 013	none	500, 050, 005 340, 403, 034	430, 304, 043

Table 3. Equivalent positions of space group Pa3 (8c), coherent scattering lengths (10^{-12} cm), positional atomic parameters ($*10^4$), isotropic temperature parameters and anisotropic thermal parameters for the initial model and two refined sets obtained.

$$\text{Pa3 (8c)} \begin{cases} \pm (x, x, x), & \pm (1/2 + x,\ 1/2 - x,\ \bar{x}) \\ \pm (\bar{x},\ 1/2 + x,\ 1/2 - x), & \pm (1/2 - x,\ \bar{x},\ 1/2 + x) \end{cases}$$

	Initial model (Fig. 1)	Isotropic refinement	Anisotropic refinement
b_C	0.665	0.665	0.665
b_D	0.667	0.667	0.667
x_C	568	506 (7)	541 (4)
x_D	1570	1545 (5)	1542 (10)
$B_C (*10)$, Å^2	24.6	39 (4)	—
B_D „	79.7	72 (2)	—
$^*B_{ii,C}$ „	—	—	30 (5)
$^*B_{ij,C}$ „	—	—	1 (2)
$^*B_{ii,D}$ „	—	—	89 (4)
$^*B_{ij,D}$ „	—	—	−34 (3)
Final R-factors:			
$R(F^2)$ (16 non-composite peaks)		0.20	0.09
$R(I)$ (all observations)		0.26	0.14

* $i, j = 1, 3$ with notation $ij = (i \neq j)$.

In the anisotropic refinements the β-restrictions[14] were taken into account. The refined values for the positional parameters x_C and x_D and the isotropic B-parameters along with the anisotropic B_{ij} values from two least-squares analyses are given in Table 3. In Table 4 the observed intensities are given along with the theoretical values calculated using the anisotropic thermal parameters. The calculated molecular dimensions and some distances of the carbon and deuterium atoms located at (x_i, x_i, x_i), ($i =$ C, D) from atoms in neighbouring molecules are listed in Table 5.

Table 4. Structural data on the Pa3 (8c) model. The columns are: Miller indices, peak position in 2θ, observed and calculated intensities. $T = 150.5$ K, $\lambda = 1.373$ Å. Parameters used: $x_C = 540.6$, $x_D = 1542.2$, both multiplied by 10^4; anisotropic thermal parameters ($*10$) are $B_{ii} = 30.21$ and $B_{ij} = 0.73$, $B_{ii} = 89.39$ and $B_{ij} = -33.47$ for carbon and deuterium, respectively.

hkl	2θ	I_{obs}	I_{calc}
111	22.41	197.9	182.0
200, 020, 002	25.91	34.0	32.0
210, 102, 021	29.07	223.4	206.0
211, 121, 112	31.90	183.0	164.1
220, 202, 022	37.01	78.7	85.0
221, 212, 122	(39.29)	(2.3)	0.8
311, 131, 113	43.72	24.5	31.4
222	45.78	47.6	45.6
230, 302, 023	47.77	45.6	70.1
231, 312, 123	49.69	102.5	50.3
321, 213, 132			85.8
400, 040, 004	(53.31)	(4.0)	3.0
322, 232, 223	55.09	14.7	19.1
410, 104, 041			1.0
411, 141, 114	(56.83)	(4.3)	4.1
331, 313, 133	58.55	113.7	104.8
420, 402, 042	60.22	53.2	48.8
240, 204, 024			
421, 214, 142	61.87	20.3	17.4
412, 241, 124			12.8
332, 323, 233	63.49	10.3	9.1
422, 242, 224	(66.68)	(5.0)	2.4
430, 304, 043	68.25	57.4	46.9

Figures in parenthesis are values assigned to reflections not observed. A graphical representation of the values is shown in Figure 2.

4. Discussion

Although the structural refinement led to a reasonable result, it is obvious that as a basic source for the space group determination the powder method has its disadvantages. The average positional parameters refined, $x_C = 0.052(2)$ and $x_D = 0.154(1)$, are in fair agreement with the values reported for C_2H_2 [1], 0.056 for x_C and 0.155 for x_H, respectively. However, as pointed out earlier [3], serious difficulties may be faced when cycling the C_2D_2 powder specimen for longer periods of time in the vicinity of the transition point. As experienced during the phase transition experiments the random orientation of the powder sample may gradually be lost. A single crystal neutron diffraction study would probably have improved the results, but the method was outside the scope of the work done. The high vapour pressure of acetylene[15] due to the plasticity of the substance[16] is attributed to the behaviour observed.

This study was started during the author's visit to Queen Mary College, London. The calculations were completed on the Burroughs B6700 and Univac U-1108 computers at the University Computing Centre and the State Computing Centre, Helsinki, Finland.

Table 5. Molecular bond lengths and some interatomic non-bonded distances r_{kl} (Å). The reference atom is located at (x_k, x_k, x_k), ($k =$ C, D). The positional parameters used are taken from the refinement using the anisotropic thermal parameters.

	C≡C = 1.15(1),	C−D = 1.06(1),		DC≡CD = 3.27(2).	
k−l	r_{kl}	*k−l*	r_{kl}	*k−l*	r_{kl}
C−C(ii)	3.89(1)	D−D(ii)	3.27(2)	C−D(vii)	3.09(1)
C−C(iv)	3.89(1)	D−D(iv)	3.27(2)	C−D(ix)	3.09(1)
C−C(vi)	3.89(1)	D−D(vi)	3.27(2)	C−D(xii)	3.09(1)
C−C(xii)	3.89(1)	D−D(xii)	3.27(2)	D−C(ii)	3.09(1)
C−C(i)	3.94(1)	D−D(i)	3.78(2)	C−D(viii)	3.28(1)
C−C(iii)	3.94(1)	D−D(iii)	3.78(2)	C−D(xi)	3.28(1)
C−C(x)	3.94(1)	D−D(x)	3.78(2)	D−C(i)	3.28(1)
C−C(v)	3.94(1)	D−D(v)	3.78(2)	D−C(v)	3.28(1)

Symmetry codes:

i	$1/2+x,\ 1/2-x,\ \bar{x}$	vii	$1/2-x,\ -1/2+x,\ x$
ii	$1/2-x,\ 1/2+x,\ x$	viii	$-1/2+x,\ 1/2-x,\ \bar{x}$
iii	$1/2-x,\ \bar{x},\ 1/2+x$	ix	$-1/2+x,\ x,\ 1/2-x$
iv	$1/2+x,\ x,\ 1/2-x$	x	$1/2-x,\ \bar{x},\ -1/2+x$
v	$\bar{x},\ 1/2+x,\ 1/2-x$	xi	$\bar{x},\ -1/2+x,\ 1/2-x$
vi	$x,\ 1/2-x,\ 1/2+x$	xii	$x,\ 1/2-x,\ -1/2+x$

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