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Constrained Refinement of Orthorhombic Sulphur

By G. S. Pawley and R. P. Rinaldi

Department of Physics, Edinburgh University, Scotland

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Constrained refinement shows there is considerable distortion of the molecules of sulphur S_8 on forming a crystal. The diffraction data are fitted very well by a rigid-body motion model for the thermal motion. It is shown however that a deduction that the motion is in reality of rigid-body type would be erroneous as the rigid-body motion model includes most of the effects of the internal modes.

Introduction

The structure of orthorhombic sulphur has not received attention for many years. We are at present (see Pawley, Rinaldi & Windsor, 1971) making measurements of the phonon dispersion curves ,and in order to analyse the results a model for the dynamics is required. For this it is necessary to know the crystal structure as accurately as possible, and this has prompted us to do the constrained refinements reported here.

The data used in the present paper are those of Abrahams (1955). The structure is orthorhombic, *Fddd*,

$$a=10{\cdot}437\ (10),\ b=12{\cdot}845\ (10),\ c=24{\cdot}369\ (10)\ \text{Å}\ .$$

Refinement with an overall isotropic temperature factor reached an R value (see Table 2) of 0·162, but this cannot be compared directly with the present result as there are differences in the models used, one minor difference being that we used the neutral atom scattering factor of Doyle & Turner (1968). In all our refinements an empirical weighting scheme was used, following Cruickshank (1965). The weight for the ith observation was

$$[2F_{\rm min}+F_i^{\rm obs}+2(F_i^{\rm obs})^2/F_{\rm max}]^{-1}\ ,$$

with $F_{\rm min}=40$ and $F_{\rm max}=250$. Only those 669 observations not including the 'less-thans' were used, following Abrahams.

Although the structure is composed of molecules it is most likely that these are distorted and do not move as rigid bodies. This follows from the fact (see Cyvin, 1970) that the frequency of the lowest internal mode of the free molecule is 86 cm^{-1}, which is lower than the expected frequency of some lattice modes. The extent of molecular distortion and internal mode motion is here investigated through constrained refinements.

Refinements

(i) *Molecular symmetry*

In the free state the molecules of S_8 have the symmetry $\bar{8}m$. The shape can be completely determined by two parameters as in Fig. 1. Atoms 1, 2, 3′ and 4′ lie on a square in the plane $X=-x$, while the other four atoms lie on a similar square at $X=x$. The radial distance perpendicular to the X axis for all atoms is r.

Refinements of the crystal structure were performed using the techniques described by Pawley (1971), in such a way that all the molecules in the crystal maintained the free state symmetry. The parameters x and r were varied, reaching optimum values

$$x=0{\cdot}4920\pm0{\cdot}0024\ \text{Å}$$
$$r=2{\cdot}3368\pm0{\cdot}0020\ \text{Å}\ .$$

From these values the S–S bond length and S–S–S bond angle are 2·041 ± 0·005 Å and 108° 5′ ± 11′. These are to be compared with Abrahams's values, 2·037 ± 0·005 Å* and 107°48′ ± 25′, and the values used by Cyvin (from Berkowitz & Chupka, 1967) 2·060 Å and 108°0′ for the molecule in the free state.

The molecule is placed in the crystal as follows. The atomic coordinates of Fig. 1 are rotated about the Z axis by

$$\begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where the axes of Fig. 1 coincide with the crystal axes. The best value of the Euler angle φ is found to be

$$\varphi = 141°18' \pm 4' \, .$$

The molecule is then translated by $(\frac{3}{8}a, \frac{3}{8}b, z)$, where the best value of z is found to be

$$z = 0{\cdot}9834 \pm 0{\cdot}0021 \text{ Å} \, .$$

The results just given should be the best parameters for the symmetrical molecule that can be expected from the given diffraction data. The coordinates of the four atoms 1, 2, 3, 4 in the unit cell are given in Table 1, and the R values in Table 2. The treatment of the thermal motion in this model (model I) is discussed later.

Table 1. *Positions of the atoms in the crystal* (Å) *for models* I *and* II

The anisotropic temperature parameters (Å^2) derive from **T**, **L** & **S** of Table 4. The Debye–Waller factor is

$$\exp\left(-2\pi^2 \sum_{ij} h_i h_j U_{ij}/a_i a_j\right)$$

where a_i are the cell parameters.

Atom		Model I Full symmetry	Model II Distorted	Anisotropic temperature parameters (× 10^3) U_{11} / U_{23}	U_{22} / U_{31}	U_{33} / U_{12}
	x	8·957	8·935	63	44	35
S_1	y	12·245	12·239	9	6	3
	z	−1·176	−1·182			
	x	8·167	8·191	59	43	47
S_2	y	13·232	13·237	−11	3	3
	z	1·878	1·859			
	x	7·399	7·382	46	56	43
S_3	y	12·617	12·588	2	−5	11
	z	0·089	0·100			
	x	8·189	8·201	37	70	33
S_4	y	11·630	11·663	0	7	−3
	z	3·142	3·159			

Table 2. $R = \sum_i |F_i^{\text{obs}} - F_i^{\text{calc}}| / \sum_i F_i^{\text{obs}}$, *and* $R_w = \sum_i w_i (F_i^{\text{obs}} - F_i^{\text{calc}})^2$ *for the four models*

	Constraint	Number of parameters	R	R_w
I	Shape + TLS	17	0·1470	1561
II	TLS	25	0·1264	1170
III	TLS + ε	26	0·1263	1170
IV	Unconstrained	37	0·1263	1158

In order to investigate the possible straining of the molecules in the crystal, a calculation without the symmetry shape constraint was necessary. In this case each of the four atoms requires three positional parameters, giving twelve in all, in contrast to the four parameters (x, r, φ, z) previously necessary. The effect of an increase of eight parameters caused R to fall from 0·147 to 0·126 (model II); but is this improvement significant?

To test for significance we use the test proposed by Hamilton (1965). The ratio

$$\mathscr{R}^{\text{obs}} = \frac{R(\text{I})}{R(\text{II})}, \ \left(\text{better} \left\{ \frac{R_w(\text{I})}{R_w(\text{II})} \right\}^{1/2}, \text{ see Table 2}\right)$$

is calculated and compared with the statistical distribution of $\mathscr{R}$. The percentage points of the $\mathscr{R}$-distribution are given in Table 3, calculated for the degrees of freedom appropriate to our problem by the method of Pawley (1970). It is clear from these tables that the improvement is highly significant at all the levels tabulated. We therefore conclude that the differences between the coordinate sets given in Table 1 have physical significance.

It is interesting to compare the level of significance of the distortion found here with that found in other molecular structures. Pawley (1971, p. 62) has suggested that

$$\mathscr{S} = \frac{\mathscr{R}^{\text{obs}} - 1}{\mathscr{R}(0{\cdot}01) - 1}$$

be calculated and used as a comparison between the results of similar constrained refinements on different

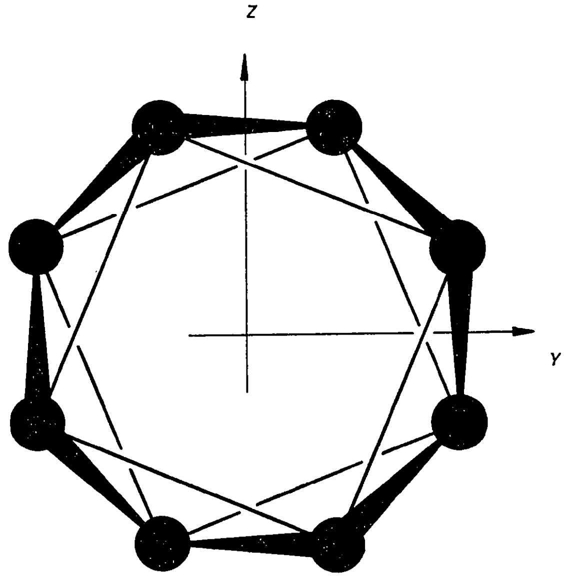

Fig. 1. The molecule of S_8, where the perfect squares emphasise the symmetry. The upper square is at $X = x$, the lower at $X = -x$.

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* This error seems rather small.

structures. In the present case

$$\mathscr{S}=0{\cdot}154/0{\cdot}015=10{\cdot}3$$

which is considerably larger than that for any other molecular crystal structure so far studied by these techniques. For comparison we have $\mathscr{S}$ values:

anthracene	4·0
naphthalene	1·3
pyrene	3·9
ovalene	6·7
P_4S_3*	0·4
1,2,3-trichlorobenzene†	1·8

(ii) *Molecular rigid body motion*

If the molecules in a crystal structure are rigid, then it is expected that the thermal motion will be predominantly of rigid-body type. In this case all the atomic anisotropic temperature factors are determined by the three tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968), where **T** describes the molecular translational motion, **L** the librational motion and **S** the correlated translation–libration motion. For the structure of sulphur these tensors are

$$\begin{pmatrix} T_{11} & T_{12} & 0 \\ T_{12} & T_{22} & 0 \\ 0 & 0 & T_{33} \end{pmatrix},$$

$$\begin{pmatrix} L_{11} & L_{12} & 0 \\ L_{12} & L_{22} & 0 \\ 0 & 0 & L_{33} \end{pmatrix},$$

$$\begin{pmatrix} S_{11} & S_{12} & 0 \\ S_{21} & S_{22} & 0 \\ 0 & 0 & S_{33} \end{pmatrix}.$$

The components of these tensors can be found by constrained refinements. However, the diagonal components of **S** cannot be found uniquely and have to be presented in the form $(S_{33}-S_{22})$ and $(S_{11}-S_{33})$. Models I and II have temperature factors restricted to agree with these tensors, thus requiring 12 parameters instead of 24. The values obtained for model II are presented in Table 4, and the corresponding atomic temperature factors are given in Table 1.

Table 4. *The non-zero components of* **T**, **L** *and* **S** *obtained from model* I

T_{ij} in Å$^2\times10^{-2}$, L_{ij} in deg^2 and S_{ij} in deg.Å$\times10^{-1}$. The average errors for T_{ij}, L_{ij} and S_{ij} in these units are 0·15, 0·9 and 0·2 respectively.

T_{11}	2·12	L_{11}	18·4	S_{12}	−1·2
T_{22}	2·65	L_{22}	16·3	S_{21}	−1·3
T_{33}	2·99	L_{33}	30·8	$S_{33}-S_{22}$	−0·6
T_{12}	−1·45	L_{12}	− 8·3	$S_{11}-S_{33}$	1·6

Again we test the validity of this model by removing the constraint (model IV), but obtain the surprising result that there is no significant improvement. It would indeed be precipitate to deduce that the molecules actually behave as rigid bodies, as we shall see. Such a conclusion would be contradictory to our statement that the molecule is highly distorted.

(iii) *Molecular internal motion*

The rigid body motion model states that in the absence of internal mode motion the atomic anisotropic temperature factors $\mathbf{U}_i$ are derived entirely from the tensors **T**, **L** and **S**, given the position of the *i*th atom. This statement remains unaltered if the coordinate system in which **T**, **L** and **S** are expressed is transformed, though of course the values of the coefficients alter. For the purposes of the present argument the coordinate system of Fig. 2 is most convenient. The components of $\mathbf{U}_i$ are given by the expressions

$$\begin{aligned} U^i_{11}&=T_{11}+L_{22}x_3^2+L_{33}x_2^2-2L_{23}x_2x_3+2S_{21}x_3-2S_{31}x_2\\ U^i_{23}&=T_{23}+L_{31}x_1x_2+L_{12}x_3x_1-L_{23}x_1^2-L_{11}x_2x_3\\ &\quad+(S_{33}-S_{22})x_1+S_{12}x_2-S_{13}x_3 \end{aligned}$$

first derived by Schomaker & Trueblood (1968). The remaining terms are found by cyclic permutation of the indices.

It is now shown that the equations of the rigid-body motion model include almost all the contribution expected from the internal modes. Fig. 2 shows half of the atoms in one molecule, where the coordinates of the atoms along X' are $+x$ or $-x$, as in Fig. 1, and are indicated by the signs. The full coordinates are given in Table 5, and it is seen that the full molecular symmetry is assumed. The mean atomic motion caused by the internal modes in the free molecule must obey the symmetry of the atomic site in the molecule. We assume that this fact still applies in the crystalline environment, although it is accepted that the mole-

Table 3. *Percentage points of the* $\mathscr{R}$*-distribution calculated for* 669 *observations for comparing the models indicated*

N_c and N_{unc} are the number of parameters used in the constrained and unconstrained models respectively.

Models compared	$\mathscr{R}_{\text{obs}}$	N_c	N_{unc}	Probability levels of $\mathscr{R}$-distribution 0·25	0·01	0·001
I/II	1·154	17	25	1·008	1·015	1·020
II/III	1·000	25	26	1·002	1·005	1·008
II/IV	1·005	25	37	1·012	1·021	1·026

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* Nelmes & Pawley (1972).

† Hazell, Lehmann & Pawley (1971)

cule itself is significantly distorted. To comply with the symmetry, the ellipsoid for atom 4 (Fig. 2) must have two principal axes in the symmetry plane $Y'=0$, and one axis parallel to the Y' axis. There is no restriction on the directions of the axes in the symmetry plane, and Fig. 2 is arbitrarily drawn so as to suggest that the ellipsoid points upwards and outwards. This ellipsoid requires four independent parameters for its description, and these are α, β, γ, ε in the matrix of Table 5. This table also gives the components describing the three other atomic ellipsoids, obtained by transforming those of atom 4.

Table 5. *The atoms of half a molecule of* S_8, *their positions and internal motion thermal vibration tensors*

The coordinate axes (see Fig. 2) are chosen to make the first matrix simple.

Atom i	X'	Y'	Z'	$\mathbf{U}_i$ (top triangle)
4	x	0	r	$\begin{pmatrix} \alpha & 0 & \varepsilon \\ & \beta & 0 \\ \text{sym.} & & \gamma \end{pmatrix}$
3	x	$-r$	0	$\begin{pmatrix} \alpha & -\varepsilon & 0 \\ & \gamma & 0 \\ & & \beta \end{pmatrix}$
2	$-x$	$-\frac{r}{\sqrt{2}}$	$\frac{r}{\sqrt{2}}$	$\begin{pmatrix} \alpha & \varepsilon/\sqrt{2} & -\varepsilon/\sqrt{2} \\ & \frac{1}{2}(\beta+\gamma) & \frac{1}{2}(\beta-\gamma) \\ & & \frac{1}{2}(\beta+\gamma) \end{pmatrix}$
1	$-x$	$-\frac{r}{\sqrt{2}}$	$-\frac{r}{\sqrt{2}}$	$\begin{pmatrix} \alpha & \varepsilon/\sqrt{2} & \varepsilon/\sqrt{2} \\ & \frac{1}{2}(\beta+\gamma) & -\frac{1}{2}(\beta-\gamma) \\ & & \frac{1}{2}(\beta+\gamma) \end{pmatrix}$

The internal modes which give the $\mathbf{U}^i$ of Table 5 should not be ignored, but if they are ignored there will be certain errors in some components of **T**, **L**, **S**. We shall show that these errors are contributions

$$\begin{gathered} \alpha \text{ to } T_{11}\,, \\ \gamma \text{ to } T_{22} \text{ and } T_{33} \\ \text{and } (\beta-\gamma)/r^2 \text{ to } L_{11}, \end{gathered}$$

where α, β and γ cannot be determined from the diffraction data. To demonstrate this we substitute these values in the equations for U^i_{jk}, setting all other components of **T**, **L**, **S** to zero. The contributions to U^i_{jk} are for the atom at (X',Y',Z')

$$\begin{aligned} \Delta U^i_{11} &= \alpha \\ \Delta U^i_{22} &= \gamma+(\beta-\gamma)Z'^2/r^2 \\ \Delta U^i_{33} &= \gamma+(\beta-\gamma)Y'^2/r^2 \\ \Delta U^i_{23} &= -(\beta-\gamma)Y'Z'/r^2 \\ \Delta U^i_{31} &= 0 \\ \Delta U^i_{12} &= 0\,. \end{aligned}$$

Substitution of the values of (X',Y',Z') from Table 5 readily yields the matrices $\mathbf{U}_i$, excepting those components involving ε. Therefore, account is already inadvertently taken of the important parameters α,β,γ in the TLS model, and only the parameter ε can be found from the diffraction data. The main effect of the internal modes is thus to prevent **T**, **L**, **S** from being interpreted as rigid body parameters and it is therefore not surprising in this case that the TLS model fits the diffraction data so well.

Finally we must find whether ε is a parameter whose inclusion produces a significant improvement. To this end we must transform

$$\begin{pmatrix} 0 & 0 & \varepsilon \\ & 0 & 0 \\ \text{sym.} & & 0 \end{pmatrix}$$

of atom 4 to the system of Fig. 1. Rotation of the molecule through θ anticlockwise gives

$$\begin{pmatrix} 0 & -\varepsilon\sin\theta & \varepsilon\cos\theta \\ & 0 & 0 \\ \text{sym.} & & 0 \end{pmatrix},$$

and the appropriate value of θ is $\pi/8$. Using $\theta=5\pi/8$ gives the matrix for atom 3. For atoms 2 and 1 we use $\theta=3\pi/8$ and $7\pi/8$ respectively, but reverse the sign on ε. These tensors are then transformed using the Euler angle φ as before to give

$$\begin{pmatrix} -\varepsilon\sin\theta\sin2\varphi & -\varepsilon\sin\theta\cos2\varphi & \varepsilon\cos\theta\cos\varphi \\ & \varepsilon\sin\theta\sin2\varphi & -\varepsilon\cos\theta\sin\varphi \\ \text{sym.} & & 0 \end{pmatrix}$$

in the crystal system. This single parameter ε was then included in the TLS model, giving the TLS+ε model. The best value of ε was 0·0018 Å^2 but it had a standard deviation of 0·0018 Å^2. The R_w values in Table 2 show no significant improvement on introducing ε, and this model must therefore be abandoned until more accurate data are available.

There is little point in searching for a better model for the inclusion of the internal mode effect, unless such a model is based on one parameter. Any model

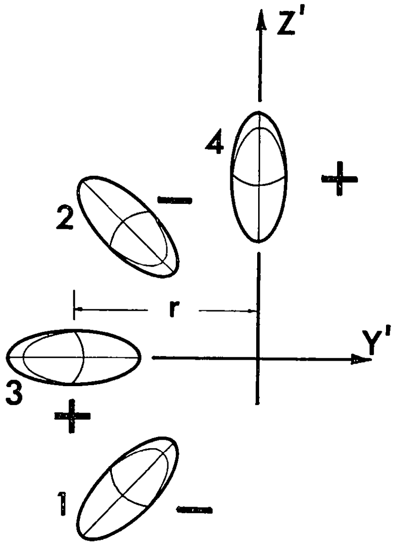

Fig. 2. Half the molecule of S_8, showing ellipsoids for the internal motion. These ellipsoids are assumed to obey the free state symmetry when the molecules are in the crystal.

which uses two parameters cannot produce a significant improvement over the result using model II. This assertion is made assuming that model IV will be the appropriate unconstrained model. From Table 3 we have

$$\mathscr{R}^{\rm obs}({\rm II/IV})=1\cdot005$$

which corresponds to a significant improvement only if $N_{\rm unc}-N_c=1$, (see Table 3, *cf.* entry for II/III).

Conclusion

The molecules of S_8 are significantly distorted in the crystal, but no attempt is made yet to interpret the distortion. We plan to use the free molecule force field of Cyvin and our own crystal potential model to calculate both the distortion and the change in the internal mode frequencies and eigenvectors. By this time more accurate X-ray and neutron data may be available for analysis, as measurements are currently in progress under the direction of Professor P. Coppens (X-rays) and Dr Krebs Larsen (neutrons).

The rigid-body motion model is shown to fit the data very well, but it is made clear that on no account can one make the deduction that the molecules behave as rigid bodies. This result is so forceful because of the high symmetry of the S_8 molecule, so the reader is left to wonder just how important is the effect of the internal modes on the values of **T**, **L**, and **S** in other cases.

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The Structure of α-UO_3 by Neutron and Electron Diffraction

By C. Greaves and B. E. F. Fender

Inorganic Chemistry Laboratory, University of Oxford, England

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The structure of α-UO_3 has been re-examined by neutron and electron diffraction. Analysis of the intensity of the neutron Bragg reflexions indicates that 12 ± 1% of the uranium sites are vacant in a disordered manner and that neighbouring U–O distances along the uranium–oxygen chains are shortened to $1\cdot64\pm0\cdot04$ Å. The earlier descriptions of the structure are inadequate and it is shown that the average sub-cell contents are similar to those expected for uranium deficient α-U_3O_8. The results explain earlier density and infrared observations. The superlattice reflexions observed in both neutron and electron diffraction patterns can be indexed on an orthorhombic unit cell with dimensions $a_o=6\cdot84$, $b_o=43\cdot45$, $c_o=4\cdot157$ Å. There is a strong resemblance between the structures of α-UO_3 and *L*-Ta_2O_5.

Introduction

α-UO_3 is regarded as a basic structure type simply related to other well known structures (Hyde, 1971). In particular α-U_3O_8 is usually described as oxygen deficient α-UO_3 with ordered oxygen vacancies. However there is evidence to suggest that the presently accepted structure is too simple and needs reconsideration. The present paper, therefore, examines the structure of α-UO_3 in the light of new electron and neutron diffraction data.

An early X-ray diffraction study by Zachariasen (1948) suggested a trigonal structure for α-UO_3 ($P\bar{3}m1$, $a=3\cdot971$; $c=4\cdot17$ Å) with one UO_3 molecule per unit cell as shown in Fig. 1. This model however fails to account for the powder neutron diffraction data of Loopstra & Cordfunke (1966) (the minimum *R* value obtained was 0·35 even after readjustment of the oxygen positions) so that they proposed the orthorhombic unit cell ($C2mm$, $a=3\cdot961$; $b=6\cdot860$; $c=4\cdot166$ Å) shown in Fig. 2. It can be seen that the two structures are similar; in both there are linear