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The Structures of Fluorides. XV. Neutron Diffraction–Kubic Harmonic Profile Analysis of the Body-Centered Cubic Phase of Sulfur Hexafluoride at 193°K

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Sulfur hexafluoride has a body-centered cubic phase ($a = 5.915(3)$ Å) between its melting point (222.4°K) and 93°K, below which a lower symmetry phase exists. NMR studies show that in both phases there is rapid reorientation of the sulfur hexafluoride molecules. From a neutron diffraction pattern collected at 193°K with $\lambda = 1.086$ Å, the data were not satisfied by a model with a spherically symmetrical fluorine density nor by a refinement with conventional ellipsoidal-shaped atoms. The latter gave systematically low S–F distances and abnormally high β_{ij} thermal factors. Good agreement was obtained by a combination of Kubic Harmonics with full-matrix least-squares analysis of the neutron profile pattern. The refinement was made with one variable Kubic Harmonic coefficient $a_2 = 5.94(11)$, with $R_w = \{\sum w[y_0 - (1/s)y_c]^2/\sum wy_0{}^2\}^{1/2} = 0.079$ and $\chi^2 = \sum w[y_0 - (1/s)y_c]^2/(NO-NV) = 1.2$. Only four least-squares variables were required with 225 observations in the range of one or more hkl reflections to $2\theta = 58.3°$. A S–F distance of 1.542(4) Å, obtained from the neutron diffraction data, is in good agreement with the reported value of 1.564(10) Å found from electron diffraction measurements of the vapor. The disordered fluorine distribution has broad maxima on the cell edges similar to those found in the plastic cubic phases of MoF_6 and WF_6.

Introduction

Of all the hexafluorides which can be formed, SF_6 is both important and chemically interesting, yet very little is known about its bonds and its structure. SF_6 has a low melting point of 222.4°K, a very high bond strength, and a saturated valency state (cf. Mo, W, and U and the remaining group VIb hexafluorides). SF_6 shows considerable chemical inertness compared to other hexafluorides, although recently it has been used to fluorinate metals and metal oxides at elevated temperatures (*1*). NMR studies (*2*) show that SF_6 has a body-centered cubic phase down to about 93°K, below which it transforms to a phase of lower symmetry. In this respect, SF_6 is analogous to the transition metal hexafluorides which all have a body-centered cubic phase in a (narrow) temperature range below the melting point and an orthorhombic phase of the UF_6-type below the transition temperature (*3*). UF_6 does not show the cubic phase (*3*).

Neutron diffraction studies have been made in this laboratory on the orthorhombic and cubic phases of MoF_6 (*4, 5*) and WF_6 (*6, 7*) and the orthorhombic phase of UF_6 (*8, 9*) with the profile analysis technique; orthorhombic MoF_6, WF_6, and UF_6 were shown to be isostructural. The disordered plastic cubic phases of MoF_6 and WF_6 were studied with Kubic Harmonic functions combined with profile analysis. In the cubic phases, the octahedra were known to be in rapid rotational motion from previous NMR studies (*2, 10–13*). The continuous, curved fluorine distributions were readily described with these functions and were shown to have maxima along the cell

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edges, the positions of the maxima giving M–F bond lengths in good agreement with electron diffraction values.

The present study of cubic SF_6 at 193°K was commenced (a) to see whether the density distribution in this Group VIb hexafluoride would be similar to those already found for the Group VI transition metal hexafluorides, and (b) to continue our series of investigations into the correlation of fluoride structures with reactivity and other physical properties.

Experimental

Thirty to forty grams of SF_6 (J. T. Baker Chemical Co., Phillipsburg, New Jersey) was condensed from the cylinder into a machined Kel-F tube (19 mm o.d. × 89 mm) in a conventional metal vacuum system at 77°K. The Kel-F tube was dismantled and quickly transferred to the cryostat attachment (*4*), while maintaining cold conditions to keep the SF_6 as a solid.

The neutron diffraction pattern of polycrystalline SF_6 at 193°K was collected, with the sample in a cryostat cooled with a dry-ice acetone slush bath, on the reactor HIFAR, using the elastic diffraction technique (*14*) and a neutron wavelength of 1.086 Å. The pattern showed body-centered cubic peaks corresponding to a cell edge of 5.915(3) Å. The pattern was collected to $2\theta = 58.3°$. There were 225 observations in the range of one or more (*hkl*) reflexions, and 15 independent Bragg reflexions in the range of the pattern.

Analysis of the Cubic SF_6 Pattern

1. Conventional refinement assuming a normal ordered structure. The data were analyzed according to the profile-fitting technique of Rietveld (*15*) assuming sulfur atoms at (0, 0, 0) + B.C. and S–F bonds aligned along the cell edges. Vibration ellipsoids were assumed for the fluorine atoms of the form $\exp(-\beta_{11}h^2 + 2\beta_{12}hk + \cdots)$, while

TABLE I

CONVENTIONAL REFINEMENT OF CUBIC SF_6 NEUTRON DATA AT 193°K[a]

Quantity	Refinement in: *Im*3*m*, *I*432	*Im*3	*I*43*m*
x (F)	0.2506(8)	0.2518(11)	0.2507(8)
M–F (Å)	1.482(5)	1.489(7)	1.483(5)
$B_{(S)}$ (Å^2)	17.6(6)	16.7(7)	17.6(6)
B_{11} (F)	4.1(3)	4.0(3)	4.0(3)
B_{22} (F)	20.1(4)	21.8(13)	19.7(4)
B_{33} (F)	$=B_{22}$	18.6(10)	$=B_{22}$
B_{23} (F)	0	0	1.0(4)
U (degree^2)	9.0(15)	8.8(15)	8.4(15)
V	−4.0(7)	−4.0(6)	−3.8(6)
W	0.67(6)	0.66(6)	0.65(6)
Z (degree)	−0.062(7)	−0.062(7)	−0.062(7)
R_1	0.126	0.126	0.124
R_2	0.062	0.060	0.059
R_{expected}	0.066	0.066	0.066
χ^2	2.8	2.8	2.8

[a] x (F) is the x coordinate of fluorine, and U, V, W are halfwidth parameters according to $H^2 = U\tan^2\theta + V\tan\theta + W$, H being the F.W.H.M. $R_1 = \sum |y_0 - (1/s)y_c|/\sum |y_0|$. $R_2 = \{\sum w(y_0 - (1/s)y_c)^2/\sum wy_0^2\}^{1/2}$. $R_{\text{expected}} = ((NO-NV)/\sum wy_0^2)^{1/2}$. $\chi^2 = \sum w(y_0 - (1/s)y_c)^2/(NO-NV)$. The y's are background-corrected measured intensities and s is a scale factor.

the sulfur vibrations were isotropic by symmetry. The form of the vibration tensor varied over the possible space groups *Im*3*m*, *I*432, *Im*3, and *I*43*m*, so refinements were carried out separately for each space group. The neutron scattering lengths used were $b_S = 2.8$ fm and $b_F = 5.6$ fm (*16*). The computer program was written by Rietveld and modified by Hewat (*17*). The results are given in Table I. The temperature factors are written in the form B_{ij} where $B_{ij} = \beta_{ij}/4a^{*2}$, a form comparable with the usual isotropic Debye–Waller *B* factors.

Refinements in the different space groups gave essentially the same overall result. The B_{ij} factors were abnormally large, even for sulfur. The smaller value for $B_{11}(\mathrm{F})$ suggested that the fluorine distribution was saucer-shaped, elongated normal to [100], and narrow in a plane normal to it. The bond lengths determined from these refinements (1.48–1.49 Å) were probably low as the fluorine vibrations were assumed to be linear, whereas the rigid-body molecular librations probably caused a curved distribution to be seen by the neutron beam. It was considered that corrections of the Cruickshank type (*18*, *19*) would not be meaningful as such calculations depended on the joint distribution of the sulfur and fluorine densities, and the sulfur temperature factor was abnormal, as was that of fluorine. Although it gave low *R* factors, the above conventional model was unsatisfactory, leading to abnormal thermal vibration factors and probably a systematically low estimated S–F distance.

2. *Kubic Harmonic refinement.* The Kubic Harmonic method, as applied here, assumes a continuous but nonuniform fluorine density on the surface of a sphere of radius equal to the S–F distance, obeying cubic symmetry, and an overall Debye–Waller temperature factor for the SF_6 group. This method has been applied before in the determination of the disordered hydrogen distribution in NH_4I (*20*) and the disordered fluorine distributions in MoF_6 (*5*) and WF_6 (*7*).

Assuming no diffusion of the molecules, the fluorine density distribution is defined as

$$t_F(\mathbf{r}) = \frac{6}{4\pi c^2} \sum a_m K_m \delta(r - c),$$

where K_m are the Kubic Harmonic functions and a_m are the amplitude coefficients to be determined by least-squares analysis. The delta function constrains the fluorine density to lie on the surface of a sphere of radius equal to the S–F distance.

The term K_0 implies a spherically symmetrical density ($a_0 = 1$), while $a_1 = 0$. K_2 introduces maxima along $\langle 100 \rangle$, K_3 along $\langle 111 \rangle$, and so on, the effects of lower-order

TABLE II

KUBIC HARMONIC REFINEMENT OF THE NEUTRON POWDER DATA OF CUBIC SF_6 AT 193°K[a]

Quantity	Refinement with:			
	K_0	K_0, K_2	K_0, K_2, K_3	K_0, K_2, K_3, K_4
Scale factor, *s*	123(10)	85.5(16)	85.8(16)	85.9(16)
a_2	—	5.94(11)	5.93(11)	6.00(11)
a_3	—	—	−15.7(68)	−8.9(67)
a_4	—	—	—	−49.3(160)
c (Å)	1.66(2)	1.542(4)	1.543(4)	1.542(4)
B (Å²)	5.3(8)	5.5(2)	5.6(2)	5.7(2)
R_w	0.22	0.079	0.078	0.077
χ^2	9.17	1.18	1.16	1.11
Number of cycles	7	6	6	9
Number of variables	3	4	5	6

[a] *c* is the S–F distance: $R_w = \{\sum w(y_o - (1/s)y_c)^2/\sum w y_o^2\}^{1/2}$, $\chi^2 = \sum w(y_o - (1/s)y_c)^2/(NO-NV)$.

terms being included in the higher-order terms.

The calculated intensity at a point in the pattern, analogous to the MoF_6 and WF_6 cases above, was (assuming the *hkl*'s to be Gaussian)

$$I_c = \sum_{hkl} s\cdot w_{hkl}\cdot\exp(-2B\sin^2\theta/\lambda^2) \times \{b_S + b_F T_F(hkl)\}^2,$$

s being a scale factor, w_{hkl} a Gaussian weight depending on the distance of the point from the theoretical 2θ value, B an overall Debye–Waller factor for the SF_6 group, and b_S and b_F the neutron scattering lengths for S and F. The $\sum$ sign denotes that different (hkl) contributions can be added at this point, and T_F is the Fourier transform of $t_F(\mathbf{r})$, equal to $6\sum a_m A_m J_{2m}$. The functions A_m were given by Sanger (*21*), and J_{2m} is the Bessel function of order $2m$. The problem was linearized for least-squares refinement by the Taylor theorem, and observations were weighted according to the counting statistics, account being taken of background subtraction errors. For further discussion of the method, reference can be made to the earlier papers (*5*, *7*, *20*). Essentially, the Kubic Harmonic approach was combined with the effective profile analysis technique.

Full-matrix least-squares refinement was carried out for cases with an increasing number of harmonic terms. The S–F distance, scale factor, and B factor were refined as well as the "a" coefficients. The results are given in Table II.

Discussion

The refinement (a) with K_0 only (Table II), assuming a spherically symmetrical fluorine distribution, gave a poor fit with the data. The SF_6 molecule was certainly not rotating freely as seen by the neutron beam. Instead, preferred orientations of the molecule occurred as shown for the refinements with (b) $(K_0 + K_2)$, (c) $(K_0 + K_2 + K_3)$, and (d) $(K_0 + K_2 + K_3 + K_4)$ in Table II. The R factor $\{\sum w[y_0 - (1/s)y_c]^2/\sum w{y_0}^2\}^{1/2}$ dropped from 0.22 to 0.08 on going from the spherically symmetric case to the Kubic Harmonic model, whereas

$$\chi^2 = \sum w[y_0 - (1/s)y_c]^2/(NO\text{–}NV),$$

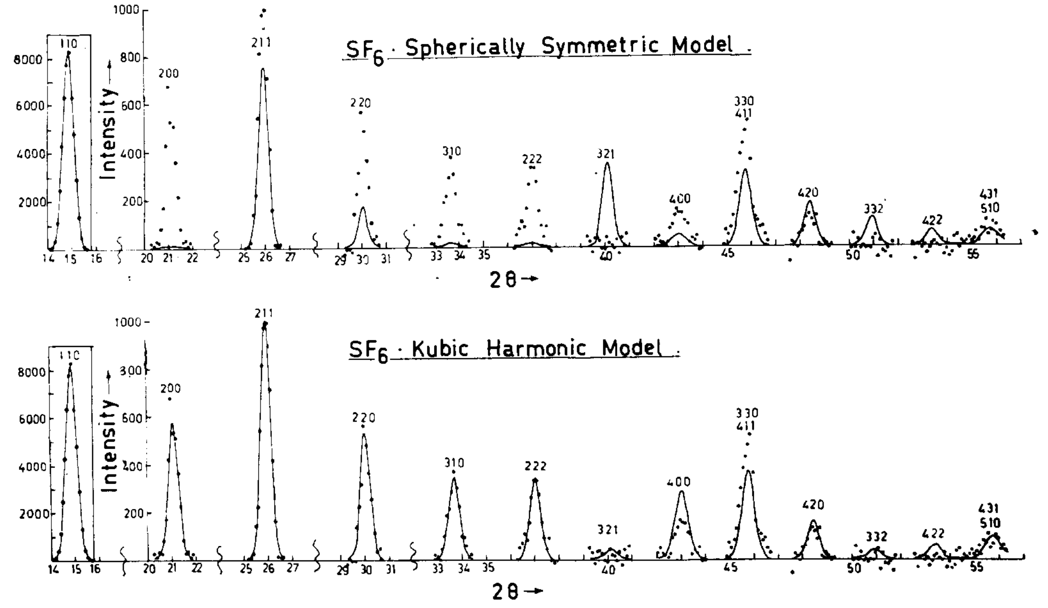

FIG. 1. Observed and calculated profiles for the neutron diffraction pattern of the body-centered cubic phase of SF_6 at 193°K, for the spherically symmetrical model (K_0) and the Kubic Harmonic model with K_0 and K_2.

which should approach unity for best fit between theory and experiment, dropped from 9.2 to 1.2. There was little improvement on adding terms beyond K_2; the value of $a_2 = 5.94(11)$ was significantly different from zero, but the values of a_3 and a_4 were not. Model (b), with K_0 and K_2, corresponded to maxima on the cell edges as mentioned above.

The fits with models (a) and (b) are illustrated in Fig. 1. There is a poor fit for the weaker peaks with the spherically symmetric model, but a good fit with the Kubic Harmonic model (b). It is a pleasing feature of this method that only a simple assumption is made and there are few least-squares variables, four in this case.

The S–F distance cited in the literature for electron diffraction by the vapor is 1.564(10) Å (*22*). The value estimated from the Kubic Harmonic analysis of the solid at 193°K, with an inbuilt correction for molecular libration, is 1.542(4) Å, only two e.s.d. lower than the vapor distance. Clearly, the value of 1.483(5) estimated from the conventional ordered-atom refinement is systematically low because of the curvilinear motion discussed above.

The term K_2 includes powers of 4 in the coordinates, and is termed fourth order. Including K_0 and K_2 (K_1 is eliminated as $a_1 = 0$), the fluorine distribution in real space becomes proportional to

$$\{1 + a_2[(x^4 + y^4 + z^4)/c^4 - 3/5]\},$$

x, y, and z being Cartesian coordinates on the spherical surface.

The fluorine distribution in real space over the spherical surface of radius 1.542 Å, calculated with $a_0 = 1$, $a_1 = 0$, and $a_2 = 5.94$, is shown in Fig. 2. Maxima occur where the {100} axes cut the sphere, while the true minima are at the intersections of the {111} axes and the sphere. It is noted that in the region near {111} the distribution becomes negative, whereas ideally it should always be positive. This is considered to reflect an inadequacy in the model, probably arising from a residual thermal vibration effect caused by anharmonic vibrations of the fluorine atoms. This would not be surprising, as the short S–F distance requires the F–F separation to be 2.18 Å, while the ionic contact distance is 2.66 Å (see below), and this effect distorts the fluorine electron density. A residual thermal vibration effect is also apparent in Fig. 1, where some deviations occur between the observed and calculated neutron powder intensities for some higher-order lines. By analogy with conventional refinements, the S–F distance measured should be uncorrelated with this effect, and this is substantiated by the agreement of the measured distance with the electron diffraction value.

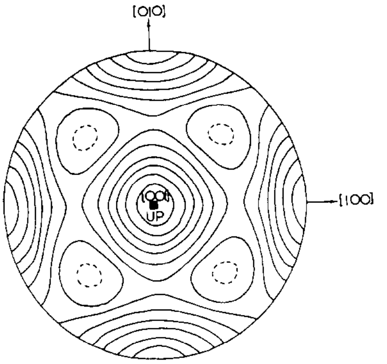

FIG. 2. The fluorine distribution in real space, on the spherical surface of radius 1.542 Å, calculated with $a_0 = 1$, $a_1 = 0$, and $a_2 = 5.94$. The negative contour line is dashed. One hemisphere is shown, in a Zenithal Equal-area Projection.

The Kubic Harmonic model here is very satisfactory because (a) it is essentially a one-parameter model (a_2), and (b) the measured S–F distance is better than that derived from conventional refinements with noncurved distributions. To remove the residual thermal effect in this instance, it would be necessary to add more variables and, since increasing the number of variables always improves the agreement, these further variables added to remove a minimal effect may be of doubtful physical significance. Also, modifying the computer program to make all computed densities positive would remove the effect but not the underlying cause. Thus, no attempt has been made to improve the agreement in Fig. 1 by anharmonic refinements, and the Kubic Harmonic results are considered the best that can be obtained based on reasonable assumptions.

Michel, Drifford, and Rigny (*2*) found that the intensities in X-ray powder patterns of SF_6, SeF_6, and TeF_6 could be explained by the presence of fluorine atoms on the axes, although they did not refine any interatomic distances. Their observations are in agreement with the present results and with our earlier studies of cubic phases of MoF_6 and WF_6, where maxima were also observed on the cell edges. The S–F bond in SF_6 is quite a strong bond, being much shorter than the M–F bonds in the transition metal hexahalides such as MoF_6 and WF_6 (~1.8 Å) and UF_6 (~2.0 Å).

The preferred orientation of the S–F bonds can be inferred from the cell dimensions. For b.c.c. packing of spherical molecules, the spheres would be in contact along [111]. This would mean that the distance from (000) to $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ should be $2(\text{S–F}) + 2rF^- = 5{\cdot}74$ Å. The observed distance is much smaller $[5.93(3/2)^{1/2} = 5.12$ Å$]$ indicating interlocking of the molecules. The molecules are nearly in contact along [100]. The SF_6 groups are very compact, so it is not surprising that the cubic phase extends down to lower temperatures than are found with the transition metal hexafluorides. The F–F contacts in the molecules, $1.542(2)^{1/2} = 2.18$ Å, are much less than the ionic diameter of fluorine (2.66 Å) and smaller than those found in MoF_6 and WF_6 (2.57 Å) and in UF_6 (around 2.80 Å). This increasing bumpiness of the molecular surface explains why UF_6 shows no cubic phase, MoF_6 and WF_6 have the phase in a narrow range, and SF_6 in a large temperature range. The fact that sulfur is a nonmetal while Mo, W, and U are metals does not make SF_6 greatly different in its properties from the other hexafluorides; these properties seem largely dependent on the properties of the molecular surface.

This analysis is a further example of the effectiveness of special functions, such as Kubic Harmonics, when combined with neutron profile analysis, in studying molecular distributions in high-symmetry disordered phases.

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