Structure of Fluorides. Part XII.† Single-crystal Neutron Diffraction Study of Uranium Hexafluoride at 293 K

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A single-crystal neutron diffraction study of UF_6 has been carried out at 293 K. UF_6 is orthorhombic, space group *Pnma* with $a = 9.900(2)$, $b = 8.962(2)$, $c = 5.207(2)$ Å, $Z = 4$. 475 independent $F_o^2(hkl)$ values were obtained, the three-dimensional intensity data being collected on an automatic neutron diffractometer. Least-squares refinement on F^2 led to R 0.090 (R' 0.094). Analysis of the thermal parameters indicated almost perfect rigid-body motion of the UF_6 octahedron, the translational and librational tensors being nearly isotropic with root-mean-square principal axis translations and librations of *ca.* 0.19 Å and 4.5°. The R factor for the agreement between the measured and calculated U_{ij} for the rigid-body hypothesis was 0.041. Corrections to measured bond lengths arising from the librational motions of the fluorine atoms were +0.015 Å for U–F and +0.020 Å for F ⋯ F distances. Corrected distances are U–F 1.992(3)—2.004(4) Å, F ⋯ F 2.804(6)—2.826(3) Å, and F–U–F angles 89.42(17)—90.20(11)°. In the crystal the molecules are slightly distorted from perfect octahedral symmetry.

As uranium hexafluoride is important in the nuclear power industry, we have studied its structure, and those of the related second- and third-row transition-metal hexafluorides. Before our structural studies, the only previous diffraction studies of UF_6 in the solid state were a two-dimensional *X*-ray study of UF_6 at 293 K by Hoard and Stroupe,[1] in which the orthorhombic structure was solved, and *X*-ray powder studies between 237 and 293 K of the whole series of hexafluorides by Siegel and Northrop.[2] The latter authors found that all the hexafluorides had a low-temperature orthorhombic form with a pattern similar to that of UF_6, and all (except UF_6) had a high-temperature body-centred cubic form. These hexafluorides are volatile moisture-sensitive substances and because of sublimation effects, these *X*-ray powder patterns were not suitable for structural analysis.

In our previous neutron diffraction studies of UF_6, MoF_6, and WF_6, we worked with powders because single crystals were difficult to grow, contain, and maintain. High reactivity with traces of moisture in a cyclic decomposition reaction involving silica tended to preclude containment and firm mounting for the period needed for a single-crystal diffraction experiment. The neutron powder profile[3] technique, however, proved valuable in this work. These powder studies[4-6] showed that, at 193 K, MoF_6 and WF_6 are isostructural with UF_6. The rotational disorder in the plastic cubic phases of MoF_6 and WF_6 was analysed by combining the profile method with Kubic Harmonics,[7,8] and the high degree of disorder found at 266 K was compatible with the fast reorientations of the octahedra observed by n.m.r.[9]

The problem of mounting a single crystal was solved by wedging crystals inside quartz tubes (8 mm o.d. and 6 mm i.d.) in a tapered end, and suppressing sublimation

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† Part XI, is ref. 7.

[1] J. L. Hoard and J. D. Stroupe, U.S. A.E.C. Report TID 5290, Paper 45, 1958.

[2] S. Siegel and D. A. Northrop, *Inorg. Chem.*, 1966, **5**, 2187.

[3] H. M. Rietveld, *J. Appl. Cryst.*, 1969, **2**, 65.

[4] J. C. Taylor and P. W. Wilson, *J. Solid State Chem.*, 1975, **14**, 378.

[5] J. H. Levy, J. C. Taylor, and P. W. Wilson, *Acta Cryst.*, 1975, **B31**, 398.

[6] J. H. Levy, J. C. Taylor, and P. W. Wilson, *J. Solid State Chem.*, in the press.

[7] J. H. Levy, P. L. Sanger, J. C. Taylor, and P. W. Wilson, *Acta Cryst.*, 1975, **B31**, 1065.

[8] J. H. Levy, J. C. Taylor, and P. W. Wilson, *J. Less Common Metals*, in the press.

[9] P. Rigny and J. Virlet, *J. Chem. Phys.*, 1969, **51**, 3807.

and moisture attack by filling the tube with fluorocarbon oil presaturated with UF_6. Only one of the six crystals mounted in this way remained firmly wedged. The present neutron single-crystal study of this particular crystal at 293 K is thus an extension of the previous neutron powder work at 193 K. In the powder work, it was not possible to study the atomic vibrations in detail as the structure was complex and reflexion superposition occurred at relatively low angles. In the present study, unsuperposed (hkl) data were collected to high values of $\sin\theta/\lambda$ and yielded precise positional and thermal parameters. The experimental work and analysis of these parameters is now described.

EXPERIMENTAL

Preparation and Mounting of UF_6 *Single Crystal.*—A sample of UF_6 was produced by the direct fluorination of UO_2. HF was removed from the sample by adsorption–desorption of the UF_6 on NaF. The UF_6 was then sublimed into the bottom of a Kel-F tube using an all-metal vacuum line. The tube was placed in a thermal gradient of *ca.* 0.5 K cm^{-1} which caused large crystals to grow on the tube wall.

The tube was transferred to a dry-box and a crystal suitable for structural analysis was wedged into a tapered silica tube as already described. To minimize sublimation and hydrolysis of the crystal, the remaining volume in the tube was filled with perfluoropolyether oil, which was resistant to UF_6 attack and had previously been saturated with UF_6 to restrict dissolution of the crystal. A Teflon plug was placed in the end of the open tube and sealed with epoxy-resin.

Data Collection.—A set of single-crystal neutron diffraction data at 293 K was collected on an automatic neutron diffractometer [10] on the AAEC research reactor HIFAR with ω, 2θ scans. The high-angle cut-off was at $\sin\theta/\lambda$ 0.67 Å^{-1}, with $\lambda = 0.859$ Å. A standard reflexion $(0\bar{3}3)$ was measured every 20 reflexions. The counting time per reflexion was *ca.* 0.5 h, and the scan range *ca.* 1.5° in 2θ. Lattice constants (Table 1), determined by least-squares analysis of the 2θ angles, agreed with, but were less precise than, those of Hoard and Stroupe,[1] so the latter dimensions were used in the following calculations. All reflexions were measured in at least two octants of reciprocal space.

TABLE 1

Crystal data for UF_6 at 293 K

UF_6, $M = 352.02$, orthorhombic, space group *Pnma*, $Z = 4$, $D_M = 4.93$ g cm^{-3} at 335.5 K, cell dimensions:

	a/Å	b/Å	c/Å	U/Å^3	D_m (g cm^{-3})
Ref. 1	9.900(2)	8.962(2)	5.207(2)	462.0	5.060(5)
Ref. 4	9.924(10)	8.954(9)	5.198(5)	461.9	5.06(1)
This work	9.92(5)	8.97(5)	5.22(3)		

The crystal was mounted with [010] nearly along the ϕ-axis with the crystal at the lower end of the tube. Reflexions with $\chi > 70°$ were not measured to prevent the tube containing the crystal from tilting too far from the vertical, and possibly loosening the crystal from its wedged position. Periodic checks of the reflexion angles showed that the tube was moving slowly in its mounting. Reflexions were kept centred in the scan range by redetermining the orientation matrix twice during the experiment.

From the experiment, which took several weeks, it was concluded that the crystal was slowly being attacked by traces of moisture as the background-corrected intensity, Q, of the standard reflexion $(0\bar{3}3)$ had declined from 23 100 counts to 19 700 counts. Data were therefore corrected for this effect by normalizing each Q_{hkl} to the nearest previous standard intensity. Six months after the data collection was completed, the crystal was found to be decomposed to a yellow powder, probably UOF_4. Crystallographic data for UF_6 are summarized in Table 1.

Absorption Corrections and Data Reduction.—The linear absorption coefficient, μ, of the UF_6 crystal was estimated by measuring the transmission of a 0.5 mm diameter thermal neutron beam (diffracted from a KCl crystal) through (*a*) the tube and oil above the UF_6 crystal, and (*b*) the silica walls and wedged UF_6 crystal. For the 8 mm pathlengths in (*a*) the transmission was $83 \pm 2\%$ and in (*b*), where the pathlength through the crystal was *ca.* 6 mm, the transmission was $79 \pm 2\%$. Thus, the absorption coefficients of the tube, UF_6 crystal, and non-hydrogenous oil were about the same.

From measurement (*b*) the value of μ for the crystal was taken as 0.30 ± 0.05 cm^{-1}. Diffracted beams proceeded in and out of the cylindrical environment of tube and oil around the crystal. Thus, for the purpose of the absorption corrections, the crystal shape was assumed to be approximately cylindrical; in fact it was an octagonal prism bounded by $\pm[(010), (100), (001), (101), \text{and } (10\bar{1})]$ faces and nearly filling the tube. The set of data absorption-corrected on this crystal shape gave better agreement between theory and experiment in structure refinements than other sets based on a more realistic crystal shape but ignoring the effects of the surrounding tube and oil. The set of UF_6 diffraction data absorption-corrected on the nearly cylindrical crystal shape is the basis of all the following calculations. Absorption was not severe as the transmission factors calculated with the program DRACULA [11] were in the range 0.849—0.877. The F_{hkl}^2 values were obtained with the same program; estimated standard deviations in F_{hkl}^2 being based on the formula: $\sigma^2(Q) = \sigma_1^2 + \sigma_2^2$, where $\sigma_1 = \sigma(I)A$ is the estimated standard deviation of the counts measured, and σ_2 allows for other uncertainties in the data, and is given by: $\sigma_2^2 = (\alpha + \beta I)A^2 + I^2\sigma^2(A)$, where A is the absorption factor, $\alpha = 70$ counts, and $\beta = 0.05$.

Some weak Q_{hkl} values were negative (background greater than peak intensity). These were set to zero by the program, but were manually reconverted to the negative values to give a truer picture of the statistical distribution of the data. On averaging equivalent intensities, the 1 098 original F_{hkl}^2 reduced to 475 independent values for the refinement of the structure.

Structure Refinement and Extinction Corrections.—The structure parameters found [4] for UF_6 at 193 K were used as a starting point for a least-squares refinement with the program LINUS.[12] The neutron scattering lengths [13] used were 8.5 fm for uranium and 5.6 fm for fluorine. Assuming

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[10] A. W. Pryor, P. J. Ellis, and R. J. Dullow, *J. Appl. Cryst.*, 1968, **1**, 272.

[11] M. M. Elcombe, G. W. Cox, A. W. Pryor, and F. H. Moore, Australian Atomic Energy Commission Report AAEC TM 578, 1971.

[12] P. Coppens and W. C. Hamilton, *Acta Cryst.*, 1970, **A26**, 71.

[13] Neutron Diffraction Commission, *Acta Cryst.*, 1972, **A28**, 357.

isotropic B factors, the refinement on F^2 converged to $R = \Sigma\,|F_o^2 - S^2F_c^2|/\Sigma F_o^2 = 0.22$, and $R' = [\Sigma w(F_o^2 - S^2F_c^2)^2]^{\frac{1}{2}}/[\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.23$. The statistical $\chi = [\Sigma w(F_o^2 - S^2F_c^2)^2/(NO - NV)]^{\frac{1}{2}}$, the standard deviation of an observation of unit weight, was 1.86; S is the scale factor. The refined value of B_U was 1.99(6) Å^2, and the B_F lay between 3.56(13) Å^2 and 4.22(10) Å^2.

An isotropic extinction parameter,[12] y, was applied to the $F_c^2(hkl)$, and was of the form (primary extinction being neglected): $y = \{1 + [(2g^1\overline{T}F_c^2\lambda^3 \times 10^4)/U \sin 2\theta]\}^{-\frac{1}{2}}$, where $\overline{T}$ is an absorption-weighted mean pathlength of the beam in the crystal, $\langle Te^{-\mu T}\rangle$, U is the unit-cell volume, and g^1 is an isotropic extinction coefficient. The factor g is interpreted either as a root-mean-square mosaic spread η for extinction dominated by mosaic spread (Type I crystal), or as a mean particle radius $\bar{r}$, for extinction dominated by particle size (Type II crystal). The two types are difficult to distinguish unless measurements are made at different wavelengths, or there is extreme anisotropy in the extinction (see later).

TABLE 2

Anisotropic extinction parameters resulting from least-squares refinement with UF_6 single-crystal neutron diffraction data. The tensors Z'_{ij} and W'_{ij} are defined in ref. 12. Equivalent reflexions were not averaged

(a) Type I refinement

R' (isotropic extinction)	R' (anisotropic extinction)	χ	Z'_{11}	Z'_{22}	Z'_{33}	Z'_{12}	Z'_{13}	Z'_{23}
0.118	0.114	0.79	0.44(10)	0.16(3)	0.02(26)	−0.04(3)	0.16(10)	0.01(4)

Principal axis i	Root-mean-square mosaic spread (s) = $5.819/\sqrt{Z_{ii}}$
1	8.8(20)
2	14.5(27)
3	4.13(537)

(b) Type II refinement

R' (isotropic extinction)	R' (anisotropic extinction)	χ	W'_{11}	W'_{22}	W'_{33}	W'_{12}	W'_{13}	W'_{23}
0.118	0.114	0.78	5.7(10)	5.0(17)	9.5(21)	−1.8(7)	2.0(10)	0.8(14)

Principal axis i	Mean particle radius $\bar{r}$/Å = $10^{-4}\lambda/\sqrt{W_{ii}}$
1	3 600 (630)
2	3 840 (1 300)
3	2 800 (620)

TABLE 3

Positional and thermal parameters (× 10^4) in crystalline UF_6 at 293 K

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	1 295(2)	2 500	0 799(4)	72(2)	87(4)	248(7)	0	−4(4)	0
F(1)	0 126(4)	2 500	−2 289(7)	111(5)	153(9)	330(15)	0	−51(7)	0
F(2)	2 471(4)	2 500	3 895(7)	101(5)	153(8)	308(14)	0	−48(6)	0
F(3)	0 143(3)	0 947(4)	2 378(5)	110(3)	121(6)	389(11)	−28(3)	22(5)	25(6)
F(4)	2 443(3)	0 937(4)	−0 760(5)	117(4)	125(6)	433(11)	30(3)	33(5)	−33(6)

When anisotropic temperature factors were introduced, there were 38 variables in the refinement (12 positional, 24 thermal, scale, and extinction parameters). The residuals were now much lower; R 0.094, R' 0.090, and $\chi = 0.77$. The observed and calculated $F^2(hkl)$ values with the estimated errors of measurement are deposited as Supplementary Publication No. SUP 21545 (3 pp., 1 microfiche).*

Contrary to expectations, the UF_6 single crystal seemed reasonably perfect and the extinction corrections were considerable. The value of g^1 was 0.41(3) corresponding to a root-mean-square mosaic spread of 14 s or a mean spherical domain radius, $\bar{r}$, of 3 500 Å. The worst-affected reflexions were the strongest in intensity: (400), (800), (231), (202), and (033) for which y values were 0.57, 0.69, 0.57, 0.56, and 0.54.

It was thought worthwhile to check whether the extinction was anisotropic[12] (effective ellipsoidal mosaic spread distribution, Type I, or ellipsoidal particle shape, Type 2). The data (not averaged over equivalent reflexions) were refined with six anisotropic extinction parameters assuming (a) a Type I and (b) a Type II crystal. Results of these refinements are shown in Table 2.

The Type I refinement gave an apparent anisotropy in the mosaic spread distribution, but the tensor Z'_{33} seemed abnormally low compared with those in the other two principal directions. The Type II refinement gave a near-spherical particle shape and sensible errors. The $\bar{r}$ values along the principal axes agreed with that from the isotropic extinction refinement. The crystal thus appeared to be Type II, but since the size ellipsoid was essentially a sphere, there seemed to be no point in adopting anisotropic in preference to isotropic extinction corrections. The introduction of anisotropy did reduce R by 0.4%, but the standard deviations in all the parameters increased, in the case of some thermal parameters by a factor of two. Thus the former isotropic extinction refinement parameters were taken as final.

Final positional and thermal parameters for UF_6 at 293 K are given in Table 3, and interatomic distances and angles (uncorrected for thermal motion) in Table 4.

DISCUSSION

Crystal Structure of UF_6 *at* 293 K.—Positional and thermal parameters for crystalline UF_6 at 293 K

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

(Table 3) are precise to <0.004 Å and 5%, respectively. The positional parameters compared with the previous neutron powder diffraction parameters at 193 K (Table 5), agree within the errors. These errors are several times larger in the powder experiment, because the relative complexity of the structure introduces reflection overlap into the powder pattern at relatively low angles.

TABLE 4

Interatomic distances (Å) and angles (°) in crystalline UF_6 at 293 K, uncorrected for the effects of thermal motion

(*a*) In UF_6 octahedron

U–F(1)	1.981(4)	F(1) · · · F(4)	2.803(4) (2×)
U–F(2)	1.989(4)	F(3)–U–F(4)	90.20(11) (2×)
U–F(3)	1.979(3) (2×)	F(3)–U–F(1)	90.04(12) (2×)
U–F(4)	1.978(3) (2×)	F(3)–U–F(2)	90.03(11) (2×)
F(3) · · · F(3)	2.784(6)	F(3)–U–F(3)	89.42(17)
F(2) · · · F(3)	2.806(3) (2×)	F(4)–U–F(4)	90.18(18)
F(1) · · · F(3)	2.801(3) (2×)	F(4)–U–F(1)	90.15(13) (2×)
F(3) · · · F(4)	2.802(3) (2×)	F(4)–U–F(2)	89.78(13) (2×)
F(4) · · · F(4)	2.801(6)	F(2)–U–F(1)	179.9(17)
F(2) · · · F(4)	2.799(4) (2×)	F(4)–U–F(3)	179.6(2) (2×)

(*b*) Intralayer F · · · F contacts

F(1) · · · F(3)	3.106(3)	F(2) · · · F(4)	3.087(3)
F(1) · · · F(3)	3.101(3)	F(2) · · · F(4)	3.116(4)
F(3) · · · F(3)	3.015(5)	F(4) · · · F(4)	3.100(3)
F(3) · · · F(3)	3.227(5)		

(*c*) Interlayer F · · · F contacts

F(4) · · · F(3)	3.180(3)	F(3) · · · F(2)	3.062(4)
F(4) · · · F(1)	3.171(4)	F(2) · · · F(1)	3.168(5)
F(4) · · · F(3)	3.201(3)	F(2) · · · F(1)	3.056(5)
F(4) · · · F(3)	3.083(3)		

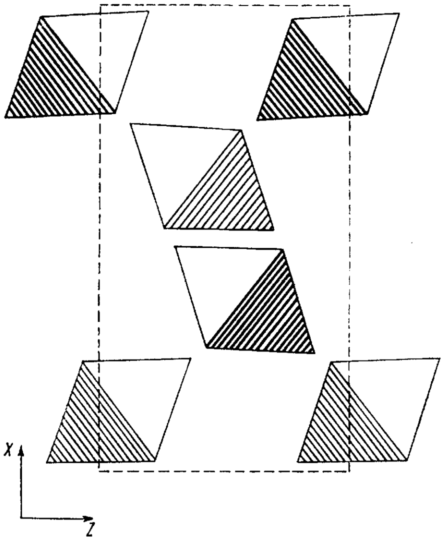
TABLE 5

Comparison of single-crystal neutron positional parameters in UF_6 at 293 K (listed first for each atom), with neutron powder profile analysis parameters at 193 K

Atom	10^4x	10^4y	10^4z
U	1 295(2)	$\frac{1}{4}$	0 799(4)
	1 279(6)	$\frac{1}{4}$	0 797(15)
F(1)	0 126(4)	$\frac{1}{4}$	−2 289(7)
	0 118(9)	$\frac{1}{4}$	−2 265(16)
F(2)	2 471(4)	$\frac{1}{4}$	3 895(7)
	2 488(11)	$\frac{1}{4}$	3 968(41)
F(3)	0 143(3)	0 947(4)	2 378(5)
	0 162(7)	0 910(8)	2 356(11)
F(4)	2 443(3)	0 937(4)	−0 760(5)
	2 452(7)	0 971(23)	−0 864(48)

The crystal structures of UF_6 at room temperature and 193 K have been described in previous powder studies.[1,4] The bond lengths, uncorrected for thermal motion, from the present study (Table 4) are now discussed here, since the corrections (see later) do not alter the general conclusions. The features observed at 193 K still occur in the present room temperature structure. The mean uncorrected U–F distance in the UF_6 octahedron (1.981 Å) is smaller than the U–F ionic radius sum (2.08 Å), so covalent bonding must be present. The bond U–F(2) is marginally longer than the other U–F bonds, as was also observed in the 193 K study[4] where it was explained in terms of non-isotropic U · · · U coulombic repulsions. The uncorrected F · · · F distances in the octahedron [2.784(6)—2.806(3) Å] are slightly longer than the ionic radius sum (2.66 Å) and the F–U–F angles in the octahedron [89.42(17)—90.20(11)°] are very nearly 90°. The F–U–F 'diameters' are essentially 180°.

The crystal seems better described as an interlocking assemblage of UF_6 molecules, rather than a fully ionic arrangement of hexagonal close-packed anions with uranium ions in the octahedral holes. This view is also supported by n.m.r. observations,[9] which suggest UF_6 molecules are reorientating at room temperature, and even at 193 K. The reorientations are facilitated by the larger F · · · F separations outside a UF_6 octahedron, 3.015(5)—3.227(5) Å. The U–F bonds are not short enough to contract the F · · · F distances below 2.66 Å; the threshold U–F distance for introduction of tensions in the U–F bonds in this way[14] is $2.66/\sqrt{2} = 1.88$ Å, and is not reached in this case.



The structure of UF_6, as seen along *b*, showing isolated octahedra. Those centred on the mirror plane $y = \frac{1}{4}$ are slightly shaded, those on the mirror plane $y = \frac{3}{4}$ are heavily shaded. The diagram shows the molecular lattice more effectively than previous packing diagrams (ref. 1)

The Figure shows individual octahedra in the structure, and shows that it is molecular, since the UF_6 octahedra are discrete, there being no corner-, edge-, or face-sharing. A diagram of the structure of UF_6 in terms of the hexagonal close packing of the fluorine layers, is given in ref. 1.

Analysis of the Thermal Motion in UF_6 *at* 293 K.—The β_{ij} (Table 3) or $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ define vibration ellipsoids for each atom. The orientations of the three principal axes *R*1 (minor), *R*2, and R_3 (major) of the ellipsoids and the root-mean-square thermal displacements $(\overline{\mu^2})^{\frac{1}{2}}$ along each were calculated[15] and are given in Table 6, as well as corresponding Debye–Waller B_i values ($B_i = 8\pi^2\bar{\mu}^2$).

While the uranium vibration is nearly isotropic, the

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[14] H. D. Megaw, *Acta Cryst.*, 1968, **B24**, 149.

[15] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report ORNL TM305, 1962.

fluorine ellipsoids are all anisotropic, and of similar size and shape. The value of $(\overline{\mu^2})^{\frac{1}{2}}$ for each fluorine atom along $R1$ is *ca.* 0.19 Å, and *ca.* 0.25 Å along both $R2$ and $R3$. The value along the fluorine $R1$ axes is about the same as the isotropic uranium displacement and suggests the shortest principal axis of each fluorine atom is directed along the F–U bond, the fluorine vibrations being larger and nearly isotropic in a plane perpendicular to the U–F bonds. The angles between the shortest principal axes $R1$ and the U–F bonds are given in Table 7. It is striking that the $R1$ axes of all the fluorines are precisely aligned on the U–F bonds, within experimental error.

TABLE 6

Angles subtended by the principal axes R_i of the atomic vibration ellipsoids and the unit-cell edges, and the thermal displacement amplitudes along R_i

Atom	Principal axis	Angle (°) of axis with: *a*	*b*	*c*	Root-mean-square thermal displacement $\bar{\mu}^2$/Å	B_i/Å^2 *
U	$R1$	63(13)	90	153(13)	0.183(4)	2.65(6)
	$R2$	90	0	90	0.188(8)	2.79(12)
	$R3$	26(30)	90	64(30)	0.190(5)	2.85(8)
F(1)	$R1$	55(3)	90	145(3)	0.190(4)	2.85(6)
	$R2$	90	0	90	0.250(6)	4.94(12)
	$R3$	35(3)	90	55(3)	0.254(4)	5.10(8)
F(2)	$R1$	54(3)	90	144(3)	0.182(4)	2.62(6)
	$R2$	144(3)	90	126(3)	0.244(5)	4.70(10)
	$R3$	90	0	90	0.250(6)	4.94(12)
F(3)	$R1$	55(3)	135(3)	66(3)	0.188(4)	2.79(6)
	$R2$	101(8)	68(6)	25(3)	0.239(3)	4.51(6)
	$R3$	38(5)	53(6)	95(8)	0.254(4)	5.10(8)
F(4)	$R1$	125(2)	135(3)	115(3)	0.188(4)	2.79(6)
	$R2$	94(10)	56(7)	146(8)	0.253(3)	5.06(6)
	$R3$	35(3)	116(9)	111(13)	0.264(3)	5.51(6)

* $B_i = 8\pi^2(\bar{\mu}_i^2)$.

TABLE 7

Angle (°) subtended by the shortest principal axis of a vibration ellipsoid, $R1$, and the corresponding U–F bond direction

Atom	Angle	Root-mean-square vibn. amplitude along U–F/Å
F(1)	1(3)	0.190(5)
F(2)	0(3)	0.182(4)
F(3)	0(3)	0.188(4)
F(4)	1(2)	0.188(4)

Rigid-body Vibration of the UF_6 *Molecule*.—In view of the molecular reorientations,[9] it is reasonable to expect some rigid-body movement of the octahedra in UF_6. This view is reinforced on noting the similar orientations of the fluorine vibration ellipsoids around the uranium atom. Cruickshank [16] has given a method for analysing the U_{ij} for rigid-body motion, describing the motion as the superposition of translational and librational modes (T and W tensors). The principal mean-square amplitudes U_{ij} are expressed in terms of the inertial axes of the molecule. The six U_{ij} for each atom give rise to $6N$ observational equations, N being the number of atoms in the molecule, from which the $6T_{ij}$ and $6W_{ij}$ are determined by least squares.

The β_{ij} in Table 3 were analysed for rigid-body motion by use of a computer program [17] which follows the Cruickshank procedure. The observations are given statistical weights $(\sigma^2)^{-1}$ and the atoms symmetry-weighted where required. The axes of inertia pass through the uranium atom; Z_I passes through U and the centre of the triangle F(2)–F(3)–F(3)′, Y_I passes through U in a direction parallel to the crystal *y* axis, and X_I forms a right-handed Cartesian set. The matrix (0.9246,0,−0.381/0,1,0/0.381,0,0.9246) relates the crystal and inertial axes. The T and W matrices are given in Table 8. The T and W tensors were nearly isotropic, and the values of T_{ij} and W_{ij} corresponded to root-mean-square translations of the UF_6 group along the principal axes of 0.19 Å and root-mean-square librational amplitudes of 4.5°. The fit between the U^{o}_{ij} and U^{c}_{ij} was good, giving a residual: $R = (\Sigma w(|U^{o}_{ij} - U^{c}_{ij}|)^2/\Sigma w U^{o}_{ij}{}^2)^{\frac{1}{2}} = 0.041$, and $\chi = \{(NO - NV)^{-1}\cdot\Sigma[|U^{o}_{ij} - U^{c}_{ij}|/\sigma(U^{o}_{ij})]^2\}^{\frac{1}{2}} = 1.054$. The values of R and χ showed good agreement between theory and experiment for the Cruickshank rigid-body hypothesis. U^{o}_{ij} and U^{c}_{ij} values are given in Table 9.

TABLE 8

T and W Tensors for the UF_6 molecule shown in the Figure. Tensors T_{12}, T_{23}, W_{12}, and W_{23} vanish by space-group symmetry

Translation tensors/Å^2 × 10^4 T_{11}	T_{22}	T_{33}	T_{13}	Rotation tensors/rad^2 × 10^4 W_{11}	W_{22}	W_{33}	W_{13}
349(8)	352(11)	349(8)	−4(7)	65(4)	69(4)	82(5)	5(3)

Burns *et al.*[18] have suggested the following criteria for assessing rigid-body motion of an atom. The sizes of the observed and calculated ellipsoids of an atom are said to correlate when the trace of $(U^{o} - U^{c})$ is less than twice tr. $[\sigma(U^{o})]$. Shape correlation factors S (<150)

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[16] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

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and orientation correlation factors θ (<25°) are also suggested. A further criterion[17] is that: A = root-mean-square $[(U^o_{ij} - U^c_{ij})/(\sigma(U^o_{ij})] < 2$. Values of these criteria are given in Table 10. All criteria are satisfied for all atoms, excepting θ for uranium, which is indeterminate as the U ellipsoid is nearly spherical. The criteria confirm almost perfect rigid body motion of the octahedra in UF_6.

TABLE 9

Observed (upper) and calculated (lower) U_{ij} ($Å^2 \times 10^4$) tensors based on the rigid-body hypothesis. U_{ij} are based on the inertial axes of the molecule

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	348(10)	354(16)	350(10)		−13(10)	
	349	352	349		−4	
F(1)	443(23)	623(37)	560(20)		−130(20)	
	424	638	543		−124	
F(2)	402(23)	623(33)	523(19)		−117(17)	
	424	639	545		−125	
F(3) *	585(14)	492(25)	496(15)	−94(15)	37(14)	103(14)
	606	499	513	−93	47	113
F(4) *	644(18)	509(24)	532(15)	95(13)	66(14)	−124(14)
	607	497	514	94	46	−113

* Terms for F(3)′ and F(4)′ are the same as for F(3) and F(4) except for the reversed sign of U_{12} and U_{23}.

TABLE 10

Correlation parameters for observed and calculated thermal ellipsoids in UF_6, for assessment of the atomic rigid-body motion (see text)

Atom	$U^o - U^c$/ $Å^2 \times 10^4$	$\sigma(U^o)$/ $Å^2 \times 10^4$	S	θ/°	A
U	3	22	16	86	0.48
F(1)	21	48	9	1	0.64
F(2)	−61	44	1	1	0.84
F(3)	−44	32	4	3	0.88
F(4)	66	34	4	16	1.17

It was of interest to see if the matrix $(U^F_{ij} - U^U_{ij})$ defines rigid-body motion (the 'in-phase' assumption of Busing and Levy[19]). The rigid-body calculation was repeated using $(\beta^F_{ij} - \beta^U_{ij})$ values, the uranium atom being omitted from further calculations. The results indicated the translational component T disappeared, while the W matrix was unchanged in magnitude and orientation. The criteria for rigid-body motion still held, but R was increased to 0.104.

Bond-length Corrections for Thermal Motion.—Diffraction methods locate the centroids or maxima of the scattering density distribution. The measured distances only define true bond lengths when thermal vibrations are negligibly small. Busing and Levy[19] have given formulae for calculating corrections (always positive) to the measured atomic separation for various assumptions about the joint distribution of the two atoms A and B.

The correction for librational motion is $\frac{1}{2}\overline{\phi^2}\, S_0$ where ϕ is the mean-square angular amplitude of libration summed over the principal axis contributions normal to the bond. The bond lengths in UF_6, corrected for librational motion (Table 11), are close to the 'riding' model corrections of Busing and Levy,[19] where the fluorine atom 'rides' on the uranium atom. The corrections amount to an increase of *ca.* 0.015 Å on the uncorrected lengths (Table 4). The mean libration-corrected distance (1.996 Å) agrees very well with two independent electron-diffraction determinations in the vapour [1.999 (ref. 20) and 1.996 Å (ref. 21)]. The libration corrections to the F · · · F distances in the octahedron (Table 4) are *ca.* 0.020 Å.

TABLE 11

Bond lengths (Å) in the UF_6 molecule in crystalline UF_6 at 293 K, corrected for the effect of thermal motion

Bond	'Riding' motion	Libration
U–F(1)	1.995(4)	1.996(4)
U–F(2)	2.002(4)	2.004(4)
U–F(3)	1.992(3)	1.993(3)
U–F(4)	1.994(3)	1.992(3)

The present single crystal neutron diffraction study of UF_6 at 293 K has given precise values for the 12 positional and 24 thermal parameters, after correction for absorption and extinction. The thermal parameters are in strict agreement with rigid-body motion of the UF_6 group; thus UF_6 molecules exist as such in the solid state, as is also suggested by the bond lengths. After correction for librational motion, the U–F distances appear slightly irregular, being in the range 1.992(3) to 2.004(4) Å. The U–F bonds in the mirror plane [2.004(4) and 1.996(4) Å] appear to be marginally longer than those not in the plane [1.992(3) and 1.993(3) Å]. This agrees with the n.m.r. work of Rigny and Virlet,[9] who found one long and two short axes in solid UF_6.

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