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A DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TETRAFLUORIDE

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A DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TETRAFLUORIDE*

David H. Templeton, Allan Zalkin, J. D. Forrester
and Stanley M. Williamson

April 1963

A Determination of the Crystal Structure of Xenon Tetrafluoride*

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The crystal and molecular structure of XeF_4 has been determined by single-crystal x-ray diffraction techniques. The intensities of Mo Kα x-rays diffracted by the crystal were measured with a scintillation counter. The monoclinic unit cell dimensions are a = 5.050 Å, b = 5.922 Å, c = 5.771 Å (each ± 0.003 Å), and $\beta = 99.6^\circ \pm 0.1^\circ$. The space group is $P2_1/n$ with two molecules per unit cell. The xenon atoms occupy the corners and body centers so that the molecular packing is pseudo body-centered cubic. The molecule has a square planar configuration. The Xe-F bond distance is 1.93 ± 0.02 Å, after a correction of +0.02 Å for thermal vibration effects; the F-Xe-F bond angle is a right angle ($90.4 \pm 0.9^\circ$) within the accuracy of the determination.

INTRODUCTION

This paper is an extended and slightly modified version of our earlier report[1] which described our determination of the crystal and

*This work was done in part under the auspices of the U. S. Atomic Energy Commission.

(1) D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, J. Am. Chem. Soc. 85, 242 (1963).

molecular structure of XeF_4.

The earliest x-ray study of this compound was by Siegel and Gebert[2] who determined the cell dimensions and space group. The atomic coordinates were determined simultaneously by Ibers and Hamilton[3] and ourselves[1] by x-ray diffraction. Ibers and Hamilton used photographic data from precession films, while we used stationary scintillation counter data. This work was soon followed by a neutron-diffaction study by Burns, Agron and Levy[4] which gives somewhat higher precision for the fluorine coordinates than is feasible with the x-ray data.

EXPERIMENTAL

Xenon tetrafluoride was prepared by heating the elements to 300° in a flow system.[1] Subsequently a slightly modified procedure was adopted. A 4 to 1 molar ratio mixture of F_2 and Xe was mixed well in a half liter copper chamber which contained baffles with twice as much helium, which acted as a carrier gas. The gas mixture then flowed through a copper U-trap at -120° into a 12 in. length of 3/4 in. nickel tubing. The nickel and copper were joined by a silver-soldered connection. The last six inches of the reactor tube was heated to 350° by an electric furnace. The reactor ended with 4 in. of 1/2 in. copper tubing so that there was a thermal gradient before the copper-to-glass seal. A glass U-trap was then either sealed to the glass of the copper-to-glass seal or connected through an ungreased ground joint. The joint was used if the XeF_4 sample was to be transferred to other containers in a dry-box and the seal was used if the trap were equipped with

(2) S. Siegel and E. Gebert, J. Am. Chem. Soc. 85, 240 (1963).

(3) J. A. Ibers and W. C. Hamilton, Science 139, 106 (1963).

(4) J. H. Burns, P. A. Agron, and H. A. Levy, Science

a break-seal so that the sample could be transferred into a vacuum system. The trap was cooled with solid CO_2 and the other end went by tubing directly to a hood. The glass from the copper-to-glass seal to the CO_2(s) level was maintained at about 75° by means of a heating tape to prevent condensation upstream from the trap. Good conversion of the Xe to XeF_4 was attained with a flow rate such that the residence time in the reactor was one minute. The apparatus is very similar in design to that of Holloway and Peacock[5] except that our apparatus had only one trap. This procedure yielded the material described by Gunn and Williamson[6] for which the chemical analysis was close to theoretical for XeF_4. Our x-ray studies of material prepared in this way detected crystals only of the structure described here, except when samples had been exposed to water.

In some of our earlier work we attempted quick transfers of the material in damp air into capillaries, but the resulting samples survived only long enough for a few preliminary x-ray patterns. It was only when the capillaries were loaded by sublimation under vacuum that we obtained stable specimens. The capillaries were thin-walled vitreous silica of 0.5 mm diameter. During the investigation of the final crystal, it is estimated to have undergone about 10 hours of irradiation with no evidence of decomposition, and in fact the crystal continued to grow at the expense of other crystals in the capillary. A few weeks after the experiment, the crystal disappeared by sublimation to regrow in another location in the capillary. Four months later it was still there. Photographs of the crystal taken the day following

(5) J. H. Holloway and R. D. Peacock, Proc. Chem. Soc. 1962, 389.

(6) S. R. Gunn and S. M. Williamson, Science 140, 177 (1963).

the intensity measurements are shown in Fig. 1. The crystal diameter ranged from 0.13 to 0.24 mm in various directions. Eleven faces of the pseudo-cubic dodecahedron were developed; the twelfth surface was attached to the curved surface of the capillary.

Molybdenum Kα x-rays were produced with a General Electric XRD-5 unit operated at 25 ma. and 40 kvp. A 0.001 in. Zr foil was used to filter the diffracted radiation just before it entered the scintillation counter. The range of intensities measured was from 1 to 14,000 counts per second. The counter was checked and found to be linear over this range.

The cell dimensions were measured with a take-off angle of 2° using the resolved $K\alpha_1$ peaks of Mo (λ = 0.70926 Å). The crystal was set on the goniostat with the a^* axis perpendicular to the phi circle; this axis coincides very roughly with the axis of the capillary.

The intensities were measured using the stationary technique and counting each reflection for 20 seconds, with a take-off angle of 4°. A fixed-time count is appropriate for approximately equal weighting of the data in the least-squares analysis. The background, plotted as a function of the diffraction angle 2θ, was ordinarily applied to the data; in a case where the reflection was a multiple of a strong reflection, the background was checked near the reflection. All of the 293 independent independent reflections up to a 2θ angle of 50° ($\sin\theta/\lambda \sim 0.59$) were measured; 35 of these were below the detection limit and were recorded as zero. The crystal grew about 30 percent during the measurements (two days), and the data were normalized by repeated measurement of a few standard reflections. The data were corrected for the Lorentz-polarization factor using the formula: $I_{cor} = I \sin 2\theta/(1+\cos^2 2\theta)$.

The least-squares program of Gantzel, Sparks and Trueblood[7] was used on an IBM7090; this program minimizes the function $\sum||F_o|-|F_c||^2/\sum|F_o|^2$ where F_o and F_c are the observed and calculated structure factors. The weighting factors were all unity. The program utilizes a full-matrix calculation for the parameter shifts. Our results are stated in terms of temperature factors of the form $\exp(-\beta_{11}h^2 - 2\beta_{12}hk - \ldots)$, although the program actually uses $\exp(-B_{11}h^2 - B_{12}hk - \ldots)$.

Scattering factors for the neutral Xe and F atoms were obtained from Tables 3.3.1B and 3.3.1A respectively as given in the International Tables.[8] Due to an oversight the Xe scattering factors were not corrected for the dispersion correction $\Delta f'$ which is approximately -0.5 electrons.

STRUCTURE DETERMINATION

Reflections are strong when $h+k+\ell$ is even and weak when it is odd, showing that the Xe atoms are at 0,0,0 and 1/2,1/2,1/2. Trial coordinates for fluorine atoms were estimated by some simple calculations which in principle were equivalent to making projections of the fluorine electron density down the a and c axes with use of only a few terms in which the effect of the fluorine atoms was large. The electron densities were not actually calculated, but were roughly approximated graphically. For example, reflections 060 and 110 were judged to be stronger than average, while 031 and 200 were weaker than average. In these cases the phases are fixed by xenon. Reflections 012, 014, and 520 were judged to be strong among reflections depending only on fluorine. In these cases phases

(7) P. Gantzel, R. Sparks and K. Trueblood, private communication (1961).

(8) International Tables for X-ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England (1962).

were chosen in all permutations. These calculations resulted in six coordinates for the two fluorine atoms which in five cases were within 0.05 of the final values. For F(2) the trial value of y was 0.18, in error by 0.15. Refinement by least squares quickly corrected this error.

Eight cycles of least squares refinement using isotropic temperature factors brought the unreliability factor $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ to 0.11. Four cycles using anisotropic temperature factors then diminished R to 0.089. Two obvious blunders in data taking were corrected by remeasurement of their intensities, and three more cycles of least squares brought R to 0.076.

Some of the low-angle data appeared to suffer from extinction and/or absorption, so the 7 reflections with $\sin\theta/\lambda$ less than 0.17 were deleted from the refinement. A final set of refinements of 5 cycles reduced R to our final value of 0.059 for 286 data. The results in Table 1 and Table 2 are from this last calculation. Table 1 lists the final parameters. Table 2 lists the observed and calculated structure factors; those marked with an asterisk were deleted from the final refinement.

Some additional calculations were performed with the 96 non-zero, odd $h+k+\ell$ data. These reflections are the result of fluorine atoms exclusively. A refinement with isotropic temperature factors resulted in coordinates for fluorine atoms which were the same as those in Table 1 within 0.005 or less. The corresponding R was 0.18.

The data were not corrected for absorption. The dimensions of the crystal correspond to μR of about 0.9. In the approximation of spherical shape, absorption would be almost perfectly compensated by systematic errors in the thermal parameters. We estimate that to compensate for the absorption error the temperature parameters of each atom in Table 1

should be increased by the following amounts:

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0.0007	0.0005	0.0005	0.0000	0.0001	0.0000

DISCUSSION

The space group symmetry requires the molecule to be planar, and within the accuracy of the determination it is square planar. Fig. 2 shows the molecular packing, and Fig. 3 the molecular dimensions before correction for thermal motion. If the fluorine atoms are assumed to ride on the xenon atoms, the Xe-F bond distances should be increased by 0.02 Å to the value 1.93 Å.

In Table 3 are listed interatomic distances, without correction for thermal motion. Each xenon has four fluorine neighbors in other molecules at an average distance of 3.25 Å. Each fluorine atom has 8 fluorine neighbors in other molecules at an average distance of 3.13 Å or 3.15 Å, as well as one xenon neighbor in another molecule. The average intermolecular F-F distance infers a van der Waals radius of 1.57 Å, which is considerably larger than the accepted value of 1.35 Å,[9] perhaps because of the considerable thermal motion of the molecules. Using the smaller value for fluorine, one gets an upper limit of 1.9 Å for the van der Waals radius of xenon in this tetravalent state.

We have three independent sets of results for the structure of this crystal: the neutron diffraction study of Burns, Agron and Levy,[4,10] the photographic x-ray study of Hamilton and Ibers,[3,11] and our own counter x-ray study. There is no significant disagreement with respect to

(9) L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, N. Y. (1960).

(10) J. H. Burns, P. A. Agron and H. A. Levy, private communication.

(11) J. A. Ibers and W. C. Hamilton, private communication.

the geometry of the structure; the three sets of coordinates agree in each case within two standard deviations or less. The thermal parameters of the fluorine atoms are in similar agreement. The agreement between the sets of thermal parameters for xenon is as good as for fluorine on an absolute scale, but is poorer than the ostensible precision of the measurements. Systematic errors which are a function of θ (for example, absorption) will have equal effect on thermal parameters of heavy and light atoms. We attribute the disagreement to systematic errors which have an effect on the thermal parameters at a level of the order of 0.3 in terms of the equivalent isotropic B value, but we have not identified the precise nature of these errors. We are not surprised that such errors are present; rather, we did not expect them to be so small.

Table 1. Crystal structure data for XeF_4

a = 5.050 ± 0.003 Å	Z = 2
b = 5.922 ± 0.003 Å	Space group $P2_1/n$ (C_{2h}^5)
c = 5.771 ± 0.003 Å	Molecular weight = 207.30
β = 99.6 ± 0.1°	X-ray density = 4.04 g/ml
V = 170.2 Å^3	

Atomic positions:

Xe: 0, 0, 0; 1/2, 1/2, 1/2.

F: ±(x, y, z; 1/2 - x, 1/2 + y, 1/2 - z),

F(1):	F(2):
x = 0.260 ± 0.003	x = 0.229 ± 0.003
y = 0.146 ± 0.002	y = 0.033 ± 0.002
z = -0.153 ± 0.002	z = 0.297 ± 0.002

Anisotropic temperature parameters:

	Xe	F(1)	F(2)
β_{11}	0.0208 ± 0.0007	0.044 ± 0.006	0.044 ± 0.006
β_{22}	0.0097 ± 0.0005	0.025 ± 0.004	0.021 ± 0.004
β_{33}	0.0120 ± 0.0005	0.031 ± 0.004	0.029 ± 0.005
β_{12}	0.0012 ± 0.0004	-0.006 ± 0.004	0.00ϕ ± 0.004
β_{13}	0.007ϕ ± 0.0008	0.023 ± 0.005	0.002 ± 0.004
β_{23}	0.0000 ± 0.0006	0.004 ± 0.004	0.000 ± 0.004

(each multiplied by 10).

Table 2: Observed and calculated structure factors. An asterisk indicates a reflection given zero weight.

H,K= 0, 0

L	FOBS	FCAL
2	550	567
4	556	545
6	417	405

H,K= 0, 1

L	FOBS	FCAL
1	641	973*
2	245	202
3	692	724
4	85	-70
5	393	401
6	0	-7

H,K= 0, 2

L	FOBS	FCAL
0	730	1052*
1	124	95
2	571	616
3	74	66
4	577	585
5	50	-53
6	333	341

H,K= 0, 3

L	FOBS	FCAL
1	541	586
2	99	95
3	690	724
4	61	-61
5	328	354
6	0	14

H,K= 0, 4

L	FOBS	FCAL
0	610	598
1	140	-130
2	498	528
3	0	21
4	450	463
5	14	13

H,K= 0, 5

L	FOBS	FCAL
1	473	478
2	15	-24
3	431	440
4	0	-10

H,K= 0, 6

L	FOBS	FCAL
0	460	456
1	66	-73
2	339	356
3	0	19

H,K= 1, 0

L	FOBS	FCAL
-5	557	568
-3	611	605
-1	798	965*
1	758	837*
3	782	792
5	381	353

H,K= 1, 1

L	FOBS	FCAL
-6	344	362
-5	12	5
-4	771	740
-3	141	105
-2	615	551
-1	140	-98*
0	734	958*
1	145	-115*
2	807	942
3	88	65
4	415	404
5	0	10
6	356	339

H,K= 1, 2

L	FOBS	FCAL
-6	46	-41
-5	447	438
-4	64	56
-3	663	608
-2	175	130
-1	933	1047
0	366	-324
1	499	543
2	110	95
3	642	650
4	28	31
5	391	380
6	18	-20

H,K= 1, 3

L	FOBS	FCAL
-6	287	300
-5	0	13
-4	557	506
-3	17	-11
-2	746	703
-1	19	10
0	690	733
1	21	-25
2	541	548
3	0	-12
4	409	413
5	22	18

H,K= 1, 4

L	FOBS	FCAL
-5	336	333
-4	44	-40
-3	524	481
-2	33	38
-1	758	740
0	20	-38
1	430	427
2	38	46
3	467	468
4	33	-38
5	320	323

H,K= 1, 5

L	FOBS	FCAL
-4	398	377
-3	103	-53
-2	463	444
-1	57	58
0	504	497
1	46	43
2	439	435
3	72	-68
4	292	311

H,K= 1, 6

L	FOBS	FCAL
-3	335	330
-2	14	10
-1	398	383
0	23	-23
1	376	367
2	14	23
3	314	327

H,K= 2, 0

L	FOBS	FCAL
-6	305	335
-4	635	650
-2	912	977
0	417	364
2	810	813
4	472	428
6	245	253

H,K= 2, 1

L	FOBS	FCAL
-6	0	-13
-5	527	515
-4	103	-84
-3	688	646
-2	212	163
-1	874	831
0	13	4
1	609	649
2	133	-107
3	517	506
4	27	29
5	406	373

H,K= 2, 2

L	FOBS	FCAL
-6	344	367
-5	63	-64
-4	534	499
-3	30	26
-2	814	759
-1	129	89
0	599	599
1	48	-42
2	650	677
3	68	-58
4	362	355
5	20	25

H,K= 2, 3

L	FOBS	FCAL
-6	18	10
-5	460	449
-4	76	-71
-3	428	394
-2	78	75
-1	767	742
0	0	-13
1	626	644
2	59	-55
3	350	361
4	21	25
5	318	313

H,K= 2, 4

L	FOBS	FCAL
-5	29	20
-4	410	389
-3	0	-6
-2	554	509
-1	126	-102
0	542	540
1	87	83
2	473	479
3	24	-32
4	268	285

H,K= 2, 5

L	FOBS	FCAL
-4	0	-7
-3	350	373
-2	26	-26
-1	479	456
0	32	-30
1	422	421
2	0	13
3	300	312

H,K= 2, 6

L	FOBS	FCAL
-3	0	6
-2	373	368
-1	71	-69
0	309	321
1	33	42
2	310	323

H,K= 3, 0

L	FOBS	FCAL
-5	377	390
-3	626	621
-1	712	683
1	681	620
3	353	335
5	309	296

H,K= 3, 1

L	FOBS	FCAL
-6	355	384
-5	0	2
-4	404	402
-3	97	-83
-2	819	776
-1	31	28
0	609	582
1	62	54
2	423	428
3	21	-28
4	406	370
5	0	-9

H,K= 3, 2

L	FOBS	FCAL
-6	35	41
-5	430	444
-4	47	-55
-3	588	543
-2	118	-92
-1	525	487
0	155	135
1	604	629
2	40	-46
3	346	341
4	0	-13

H,K= 3, 3

L	FOBS	FCAL
-5	17	-8
-4	451	448
-3	0	-9
-2	528	490
-1	39	-38
0	485	469
1	0	16
2	431	446
3	0	-4
4	309	298

H,K= 3, 4

L	FOBS	FCAL
-4	0	15
-3	458	436
-2	24	-29
-1	382	367
0	0	1
1	467	472
2	30	-40
3	290	296

H,K= 3, 5

L	FOBS	FCAL
-3	51	57
-2	404	396
-1	53	-56
0	353	354
1	42	-32
2	284	309

H,K= 3, 6

L	FOBS	FCAL
-1	316	326
0	0	-4

H,K= 4, 0

L	FOBS	FCAL
-4	374	392
-2	411	417
0	672	610
2	329	314
4	263	261

H,K= 4, 1

L	FOBS	FCAL
-5	333	375
-4	50	48
-3	483	468
-2	81	-75
-1	489	451
0	0	-9
1	431	460
2	28	26
3	326	306
4	0	-11

H,K= 4, 2

L	FOBS	FCAL
-5	29	36
-4	400	422
-3	0	-9
-2	460	441
-1	67	-57
0	476	469
1	0	-1
2	291	305
3	0	18

H,K= 4, 3

L	FOBS	FCAL
0	291	315
1	0	-22
-4	26	30
-3	486	488
-1	384	364
0	0	-8
1	315	344
2	0	3
3	289	287

H,K= 4, 4

L	FOBS	FCAL
-4	304	345
-3	23	-6
-2	379	385
-1	21	24
0	335	340
1	52	-50
2	237	259

H,K= 4, 5

L	FOBS	FCAL
-2	15	-7
-1	298	308
0	0	4

H,K= 5, 0

L	FOBS	FCAL
-3	345	375
-1	344	347
1	281	294

H,K= 5, 1

L	FOBS	FCAL
-4	352	395
-3	29	31
-2	314	318
-1	13	-10
0	328	353
1	22	-23
2	262	272

H,K= 5, 2

L	FOBS	FCAL
-4	0	15
-3	319	353
-2	31	25
-1	374	370
0	51	-48
1	222	258
2	0	4

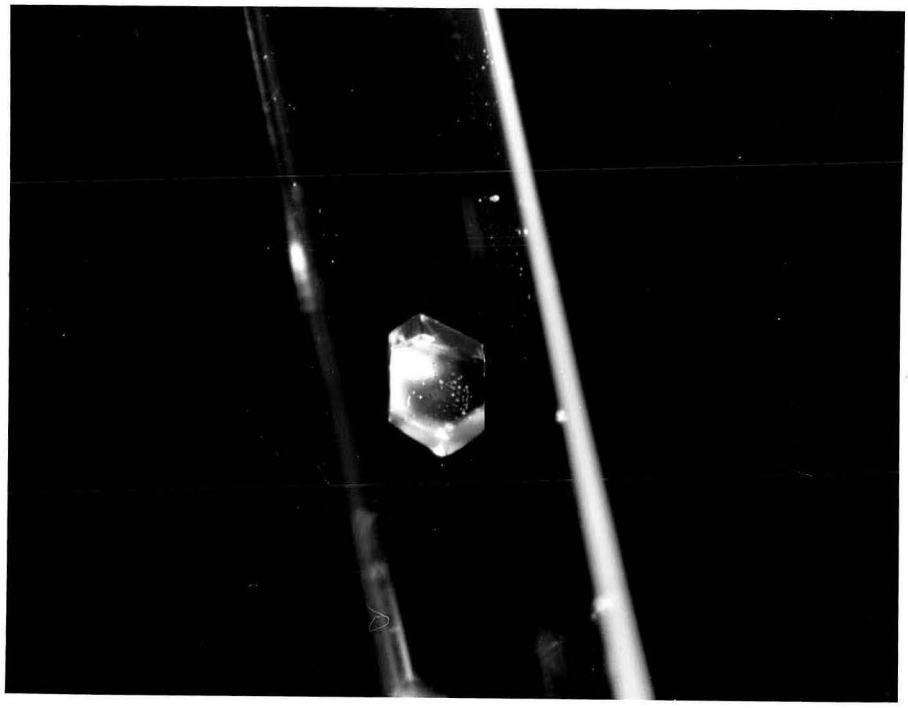
H,K= 5, 3

L	FOBS	FCAL
-3	0	-9
-2	314	333
-1	27	5

Table 3: Distances in XeF_4. The asterisked values are ~~inter-~~ intra-molecular distances.

Xe	-	2 F_1	1.91 ± .02 Å	*
		2 F_2	1.91 ± .02 Å	*
		2 F_2	3.22 ± .02 Å	
		2 F_1	3.27 ± .02 Å	
F_1	-	Xe	1.91 ± .02 Å	*
		F_2	2.71 ± .03 Å	*
		F_2	2.69 ± .03 Å	*
		F_2	3.03 ± .03 Å	
		F_2	3.08 ± .03 Å	
		F_2	3.09 ± .03 Å	
		2 F_1	3.16 ± .02 Å	
		F_2	3.22 ± .03 Å	
		F_1	3.24 ± .04 Å	
		F_2	3.26 ± .03 Å	
		Xe	3.27 ± .02 Å	
F_2	-	Xe	1.91 ± .02 Å	*
		F_1	2.71 ± .03 Å	*
		F_1	2.69 ± .03 Å	*
		2 F_2	3.02 ± .01 Å	
		F_1	3.03 ± .03 Å	
		F_1	3.08 ± .03 Å	
		F_1	3.09 ± .03 Å	
		F_1	3.22 ± .03 Å	
		F_1	3.26 ± .03 Å	
		F_2	3.32 ± .04 Å	
		Xe	3.22 ± .02 Å	

Figure 1: Two views of the crystal of XeF_4 used in this structure determination. The two views are approximately 75° rotation apart from each other. The a axis is approximately parallel to the long edge of the crystal.



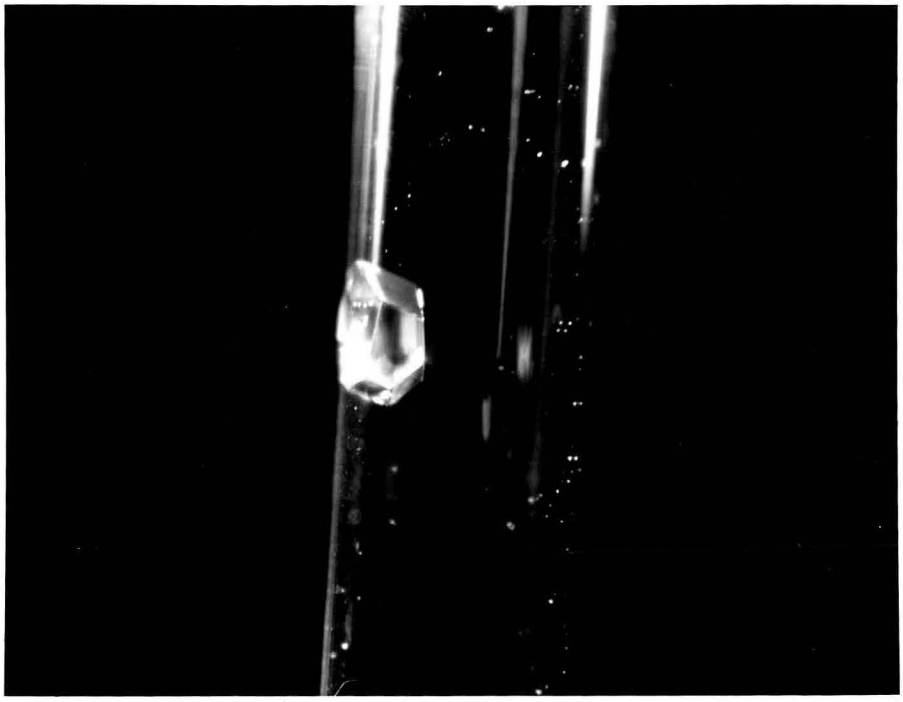


Figure 2: Molecular packing in XeF_4 as seen in projection down the b axis. The numbers on some of the atoms are b coordinates (x100).

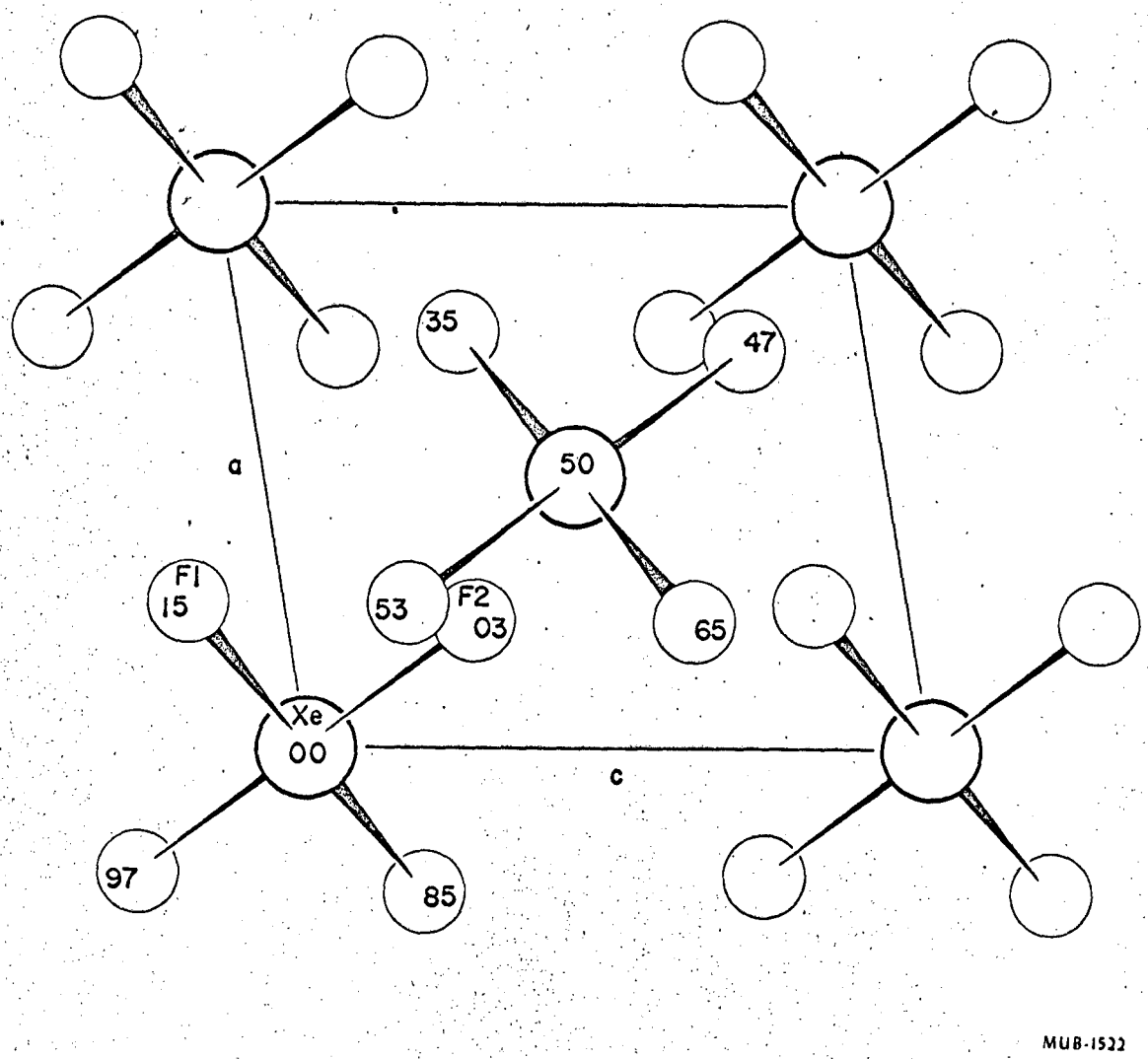
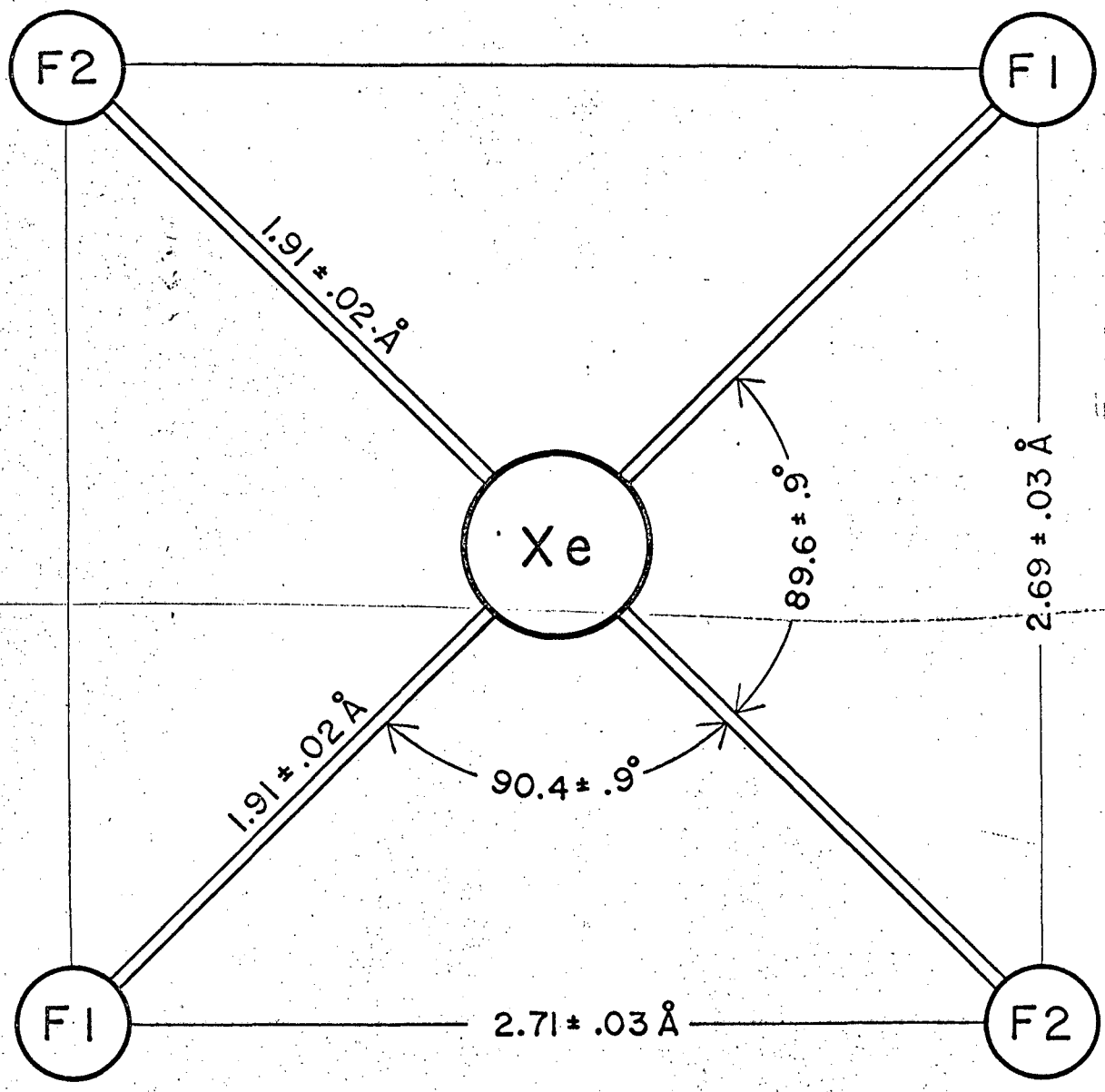


Figure 3: Molecular dimensions in XeF_4. Distances have not been corrected for thermal vibrations in this figure.



XeF_4

MUB-1521