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The Crystal Structure of Hydrogen Fluoride

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Hydrogen fluoride forms orthorhombic crystals in the space group D_{2h}^{17}–$Bmmb$, with four molecules in a unit cell of dimensions $a = 3{\cdot}42$, $b = 4{\cdot}32$ and $c = 5{\cdot}41$ Å. Infinite zigzag chains of hydrogen bonds exist parallel to (100). The FH · · · F hydrogen-bonded distance is $2{\cdot}49 \pm 0{\cdot}01$ Å, and the hydrogen-bond angle about fluorine is 120·1°. The anisotropic thermal motion of fluorine shows larger amplitudes of vibration perpendicular to the y axis, the direction of the hydrogen bonds.

Introduction

Solid hydrogen fluoride has been studied previously by the X-ray diffraction method by Gunther, Holm & Strunz (1939), who indexed powder photographs on a tetragonal unit cell with $a = 5{\cdot}45$ and $c = 9{\cdot}95$ Å. These results, as well as their hydrogen-bond distance of 2·7 Å and bond angle of 134°, are incorrect. The presence of a hydrogen-bonded structure, however, is demanded by a variety of physical data. In an electron-diffraction study (Bauer, Beach & Simons, 1939) an FH · · · F distance of 2·55 Å and a bond angle of 144° about fluorine are reported. Our distance of 2·49 Å and bond angle of 120·1°, obtained as described below, are considerably more precise and suggest that a re-investigation by the electron-diffraction method should be made to decide if the differences between the solid and the gas are real.

In addition our Fourier maps provide some support to the unsymmetrical nature of the hydrogen bond in hydrogen fluoride.

Methods and results

Anhydrous hydrogen fluoride, 99·0% pure, was obtained from the Matheson Company, East Rutherford, New Jersey. The material was distilled through copper and Teflon tubing into thin-walled Fluorothene capillaries about 0·5 mm. in diameter, which were then sealed with the use of heated pliers. The observed melting point of our sample was within ±0·5° of the expected value of −83·4° C. (Hu, White & Johnston, 1953).

Precession photographs were taken of a single crystal at −125° C. with the use of Mo $K\alpha$ radiation and a precession angle of 28°. Successive, timed exposures were made of each zone, and intensities were estimated visually with the aid of standard, timed scales prepared from single-crystal reflections. Lorentz and polarization factors (Waser, 1951) were applied, and the structure factors were then obtained.

The symmetry of the reciprocal lattice is D_{2h}–mmm, and the dimensions of the orthorhombic unit cell are

$$a = 3{\cdot}42,\ b = 4{\cdot}32 \quad \text{and} \quad c = 5{\cdot}41 \text{ Å},$$

all within ±0·01 Å. If four molecules are assumed in this unit cell the calculated density is 1·663 g.cm.$^{-3}$ at −125° C., in very good agreement with the measured value of 1·658 g.cm.$^{-3}$ at −97·2° C. (Biltz, Boucher & Fischer, 1932). Systematic extinctions of hkl when $h+l$ is odd, $hk0$ when either h or k is odd lead to the possible space groups D_{2h}^{17}–$Bmmb$, C_{2v}^{16}–$B2mb$ or C_{2v}^{12}–$Bm2_1b$.

The structure was obtained by trial. The normal decline of $hk0$ reflections indicated special x and y coordinates, while the $0kl$ reflections indicate a general z coordinate to be determined from the relative intensities. Thus the fourfold positions for fluorine

$$0,\ \tfrac{1}{4},\ z;\quad 0,\ -\tfrac{1}{4},\ -z;\quad \tfrac{1}{2},\ \tfrac{1}{4},\ \tfrac{1}{2}+z;\quad \tfrac{1}{2},\ -\tfrac{1}{4},\ \tfrac{1}{2}-z$$

in D_{2h}^{17}, or identical positions in C_{2v}^{16} or C_{2v}^{12}, are indicated. The weakness or absence of $0kl$ when k is even and $l = 4n+2$, of $0kl$ when k is odd and $l = 4n$, of $2k2$ when k is even, and of $2k4$ when k is odd all lead to, approximately, $z = \frac{1}{8}$. From the Fourier projection along a (Figs. 1 and 2) the value is $z = 0{\cdot}117$, while a similar synthesis from the use of calculated structure factors as coefficients indicated a backshift of $-0{\cdot}002$. Thus the final, corrected parameter is $z = 0{\cdot}115$.

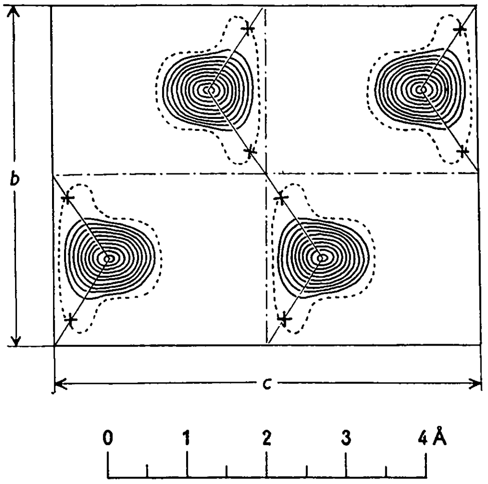

Fig. 1. Electron-density projection along the a axis. Each contour line represents a density increment of 1 e.Å^{-2}, the two-electron line being broken. The cross symbols, showing the possible positions of the hydrogen atoms, are based upon the HF distance of 0·92 Å in the gas phase.

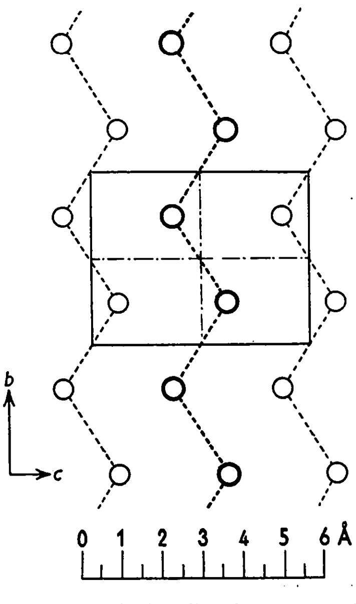

Fig. 2. Arrangements of the fluorine atoms in the a-axis projection. Atoms represented by heavy and light circles are at $x = \frac{1}{2}$ and 0, respectively. Hydrogen bonds are indicated by broken lines.

The $0kl$ data, however, lead equally well to $z = 0{\cdot}135$, for which the structure factors are identical in magnitude. This ambiguity, which results in two different structures with $z = \frac{1}{8}-0{\cdot}010$ (correct) or $z = \frac{1}{8}+0{\cdot}010$ (incorrect), can be resolved by those reflections for which l is odd. The value of $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ is 0·079 (observed reflections only) and 0·098 (all reflections) for the correct structure, and is 0·134 (observed reflections only) and 0·153 (all reflections) for the incorrect structure. For those reflections for which $l = 3$ we find $R = 0{\cdot}05$ for the correct structure and $R = 0{\cdot}34$ for the incorrect structure. Specific examples, showing the worst disagreements with the observed data (Table 1), are $F_{101} = 15{\cdot}7$, $F_{103} = -9{\cdot}7$, $F_{113} = -6{\cdot}1$ and $F_{123} = 7{\cdot}3$ for the incorrect structure.

The marked ellipticity of the contours of $\varrho(y, z)$ (Fig. 1) and of $\varrho(x, y)$, as well as the marked decline of intensities with increasing h and l indices, indicate an anisotropic temperature factor. The amplitude of oscillation is greatest perpendicular to the b axis, which is the direction of hydrogen bonding. The constants $B_1 = 0{\cdot}08_1$, $B_2 = 0{\cdot}01_8$ and $B_3 = 0{\cdot}03_2$ in the expression $\exp(-B_1h^2-B_2k^2-B_3l^2)$ were determined from a comparison of observed and calculated structure factors (Table 1). These values lead to mean square amplitudes $\overline{\Delta X^2} = \overline{\Delta Z^2} = 0{\cdot}048$ Å^2 and $\overline{\Delta Y^2} = 0{\cdot}017$ Å^2. A similar anisotropy was observed in methanol (Tauer & Lipscomb, 1952).

Discussion

The closest F · · · F distance of 2·49 Å undoubtedly contains the hydrogen bond. The probable error is estimated as low as ±0·01 Å, because the distance is chiefly dependent upon the lattice parameter, b. Next closest F · · · F distances are 3·12 and 3·20 Å, both larger than the expected van der Waals contact,* because of the abnormally large thermal vibrations. The most interesting F · · · F · · · F bond angle is that of 120·1° along the chain of hydrogen bonds.

After a discussion of the anomalous properties of the symmetrical hydrogen bond in $(FHF)^-$ ion, Westrum & Pitzer (1949) conclude that the more nearly normal hydrogen bond in HF is probably unsymmetrical. Our Fourier projection (Fig. 1) perhaps provides some support for this conclusion, for the hydrogen-like bulge† occurs in the correct position

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* Although 2·7 Å (Pauling, 1948, p. 189) is the proper F · · · F distance in primarily ionic crystals, the distance of 3·0 Å is more consistent with our present values in HF, and with recent more reliable values in less dominantly ionic or molecular crystals. Some of these values are 3·09 Å in KHF_2 (Helmholz & Rogers, 1939), 3·11 Å in K_2GeF_6 (Hoard & Vincent, 1939), 3·0 Å in NH_3BF_3 (Hoard, Geller & Cashin, 1951), and 3·03 Å in SiF_4 (Atoji & Lipscomb, 1954).

† This bulge was not present in a similar Fourier projection in which the coefficients were those calculated from F on y. A difference Fourier gave H peaks of height 1·7 e.Å^{-} in positions indicating unsymmetrical hydrogen bonds, statisti-

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	14·6	16·2	024	7·0	6·6	151	3·8	−3·2
400	1·8	3·2	034	1·0	1·3	212	9·0	−9·1
020	20·8	−20·9	044	4·3	−3·8	222	< 1·3	−1·0
040	8·5	8·6	016	3·4	2·6	232	5·4	5·8
002	3·4	2·8	026	1·0	0·9	242	< 1·3	0·5
004	8·9	−8·4	036	3·8	−2·0	313	2·6	−2·9
006	1·0	−1·1	101	18·4	17·8	323	1·8	1·7
220	10·0	−9·7	202	1·2	1·2	333	1·9	2·1
240	4·4	5·2	303	2·4	−2·0	214	< 1·4	−1·1
420	1·5	−2·1	204	4·4	−4·6	224	3·7	3·5
012	18·5	−20·1	103	6·6	−6·6	234	< 1·4	0·7
022	1·2	−1·9	206	< 1·1	−0·7	113	8·9	−9·0
032	9·0	10·1	111	14·3	−14·0	123	5·3	5·0
042	< 1·0	0·9	121	11·0	−11·5	133	4·9	5·5
052	4·9	−4·6	131	7·4	7·0	143	2·8	−2·7
014	2·1	−2·0	141	5·0	5·4	216	2·1	1·6

for an unsymmetrical hydrogen bond, statistically distributed throughout the crystal. These results seem incompatible with the assumption of a symmetrical hydrogen bond. Even so, this statistical distribution would not lead to a measurable residual entropy in HF because the number of configurations is only two for each nearly-infinite chain, assuming no F^- or H_2F^+, but only HF molecules. The hydrogen bond system is thus very similar to those systems in methanol, hydrazine, and hydrogen peroxide, all of which have zero residual entropy.

In view of the small dispersion forces between the chains, it is remarkable that no disordered phase occurs in which parallel chains exist with random orientation. We suggest that the coplanarity of the chain might be due to the nature of the bonding within the chain, as well as to the ordering forces in the crystalline solid. That much planarity persists in the gas phase polymers is questionable (Oriani & Smyth, 1948), and indeed, there is disagreement between our bond angle of 120·1° with that of 144° obtained by the electron diffraction method. Hence it would probably be unwise to generalize our results to the gas phase, but clearly a reinvestigation of the gas at various temperatures by the electron diffraction method would be of some value.

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cally distributed. One false peak of height 1·2 e.Å^{-2} occurred in the asymmetric unit of the assumed space group D_{2h}^{17}.

Because the space group D_{2h}^{17} requires the statistical distribution if the hydrogen bridge is unsymmetrical, we also carried out a refinement of H positions in the polar sub-group C_{2v}^{12} (4H in $0, y, z$ etc.), but the difference synthesis giving hydrogen contributions refined to the statistical distribution of unsymmetrical hydrogen bonds already found in D_{2h}^{17}. On the other hand, placement of the four hydrogen atoms at $0, y, z$; $\frac{1}{2}, \bar{y}, \frac{1}{2}-z$; $0, y+\frac{1}{2}, \bar{z}$; $\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$ with $y = 0{\cdot}066$ and $z = 0{\cdot}030$ in the space group D_{2h}^{16}–*Pmnb* leads to no violations of the *B* centering, within the limits of our observations. Even though the worst disagreement is for $F_{20)} = 19\ 6$, this non-polar structure must also be regarded as almost as satisfactory as the random structure.