Acta Cryst. (1971). B**27**, 1677

Nuclear magnetic resonance data on proton positions in solid HF.

S. P. Habuda, *Institute of Physics, Academy of Sciences of the USSR, Siberian Department, Krasnojarsk, USSR* and Yu. V. Gagarinsky, *Chemistry Division, F. E. Scientific Centre, Academy of Sciences of the USSR, Vladivostok, USSR*

(*Received* 12 *March* 1971)

The distance r(F–H) in the structure of solid HF was determined by analysing the second moment and shape of the fluorine nuclear magnetic resonance line. A correction was introduced for stretching and torsion vibrations of HF molecules, resulting in the value $r_{\text{corr}}(\text{F–H}) = (0{\cdot}95 \pm 0{\cdot}03)$ Å.

An X-ray study of solid HF (Atoji & Lipscomb, 1954) showed that HF molecules form chains whose links are coplanar zigzags. The shortest distance F–F in the chain is 2·49 Å, and the F–F–F angle 120·1°. Hydrogen atoms are, apparently, localized on the F–F bond lines, indicating the formation of F–H···F hydrogen bridges. Nevertheless data on proton positions in the HF structure have not been determined heretofore.

To determine the proton positions in the structure of solid HF, we used the opportunities offered by nuclear magnetic resonance(n.m.r.). Powder samples were obtained by freezing anhydrous HF, distilled twice in a polyethylene ampoule. ^{19}F n.m.r. spectra were recorded on a JNM-4H-100 spectrometer with a broad-line attachment at temperatures of −140°C up to almost melting point (−90°C). The spectra obtained were doublets characteristic of two-spin systems (Pake, 1948). In this case, the doublets were due to a pair of spins of fluorine and hydrogen nuclei in HF molecules.

Doublet splitting equalled $\Delta H = (26 \pm 1)$ oe, and the spectrum second moment (a correction for the modulation width was introduced) equalled $S_2 = (184 \pm 9)$ oe^2. These values were averaged from several spectra; noticeable temperature dependence was not observed.

The intermolecular interaction β to intramolecular interaction α ratio, equal to $0{\cdot}37 \pm 0{\cdot}03$, was determined on the basis of the absorption curve shape and by using computerized theoretical results for the spectra forms of powder two-spin systems (Pedersen, 1968). The full second moment equals (Pake, 1948).

$$S_2 = \tfrac{4}{5}\alpha^2 + \beta^2 , \tag{1}$$

where the two right-hand members present the intramolecular and intermolecular inputs into S_2. From the experimental values of S_2 and β/α the following values of α and β for HF are found:

$$\left.\begin{aligned} \alpha &= 14{\cdot}0 \pm 1{\cdot}5 \text{ oe} \\ \beta &= 5{\cdot}0 \pm 0{\cdot}5 \text{ oe}\,. \end{aligned}\right\} \tag{2}$$

The approximate value for α can also be determined from the experimental doublet split through $\Delta H = 2\alpha$. However, the asymmetry of the doublet components usually causes the α value to be less than its real value, the latter being best determined from the experimental values of S_2 and β/α in accordance with formula (1).

The magnitude of α is directly related to the distance r(H–F) between the hydrogen and fluorine nuclei in our twospin system (Pake, 1948)

$$\alpha = \mu_H \,.\, r^{-3}\,(\text{H–F}) \tag{3}$$

where $\mu_H = 1{\cdot}41 \times 10^{-23}$ erg. oe^{-1} is the proton magnetic moment.

From equations (2) and (3)

$$r(\text{H–F}) = 1{\cdot}02 \pm 0{\cdot}03 \text{ Å} \tag{4}$$

The value obtained actually presents the upper limit of r(H–F), since, owing to libration and stretching vibrations of HF molecules, the local fields on the fluorine nuclei, determined by the 'measured' magnitude α, are slightly reduced compared with their idealized values in absence of vibrations. A more precise value for r_{corr} (H–F) may be obtained by introducing corrections for librating and stretching vibrations of HF molecules. For this purpose, one may make use of similar corrections accounting for stretching and torsional vibrations of O–H and H–H in water molecules (Pedersen, 1964) by using the formula:

$$\alpha = \mu H \,.\, r_{\text{corr}}^{-3}(\text{H–F}) \times 0{\cdot}98(1 - 3\langle\theta^2\rangle) \tag{5}$$

where r_{corr} is the corrected value of r calculated with consideration for stretching and libration variations. The mean square of the amplitude of libration vibrations determined by their frequency ν and the corresponding force constant f is

$$\langle\theta^2\rangle = \frac{h\nu}{f}\left[\tfrac{1}{2} + h\nu\left(\exp\frac{h\nu}{\kappa T} - 1\right)^{-1}\right] \tag{6}$$

where h and κ are the Planck and Boltzmann constants, and T is the absolute temperature.

According to the investigation data for the molecule vibration spectrum in solid HF, the libration vibration frequency in the zigzag plane was $\sim 3 \times 10^3$ Hertz ($f = 0{\cdot}199 \times 10^{-3}$ dyne.rad^{-2}) and perpendicular to the plane $\sim 1{\cdot}5 \times 10^{13}$ Hertz ($f = 0{\cdot}061 \times 10^{-3}$ dyne.rad^{-2}).

Taking into account that formula (6) involves ν/f, one may conclude that the amplitude of the libration vibrations of the HF molecules, both in the zigzag plane and perpendicular directions, is approximately the same, its mean square at −130°C being equal to $\langle\theta^2\rangle = 0{\cdot}01$ rad^2. From this value, we have found by means of (5) that

$$r_{\text{corr}}(\text{H–F}) = 0{\cdot}95 \pm 0{\cdot}03 \text{ Å}\,. \tag{7}$$

According to some investigators (El Saffar, 1966), equation (5) slightly exaggerates the input of libration vibrations on specifying r. Hence, (7) may rather be taken for the lower limit of the H–F distance in solid HF.

Comparing the values obtained with $r(\text{H–F}) = 0{\cdot}9175$, measured for free HF molecules in gas (Sutton, 1958), one may infer that the increase of r(H–F) in solid HF is, ostensibly, the result of the formation of a hydrogen bond .This conclusion is directly confirmed by the experimental value for the intermolecular part of the second moment $\beta^2 = 25 \pm 5$ oe^2. Calculations after Van Vleck (1948) lead to

$\beta^2 = 24{\cdot}4$ oe^2 when the protons are situated on F–F lines. Proton deviation from F–F directions (the magnitude of the intramolecular distance r(F–H) being preserved) lessen the theoretical values for β^2 so that with H–F–F angles exceeding 20° β^2 becomes less than the lower limit of its possible values. To summarize, it may be said that, according to the n.m.r. data, the protons in solid HF are situated at a distance of $(0{\cdot}95 \pm 0{\cdot}03)$ Å from the F atoms, involving a possible deviation from the F–F line not exceeding 10°.

It is also worthy of mention that according to the empirical formula of Pimentel & McClellan (1960), with F–F equal to 2·49 Å, the F–H bond length should approximately equal 1·02 Å, which is in agreement with our r(H–F) value in solid hydrogen fluoride.

The authors are grateful to Dr L. M. Avkhutsky for his aid in recording the spectra.

References

Atoji, M. & Lipscomb, W. H. (1954). *Acta Cryst.* **7**, 173.
El Saffar, Z. M. (1966). *J. Chem. Phys.* **45**, 4643.
Pake. G. (1948). *J. Chem. Phys.* **16**, 327.
Pedersen, B. (1964). *J. Chem. Phys.* **41**, 122.
Pedersen, B. (1968). *Acta Chem. Scand.* **22**, 444.
Pimentel, G. C. & McClellan, A. L. (1960). *The Hydrogen Bond.* San Francisco: Freeman.
Sutton, L. E. (1958). *Interatomic Distances,* Special Publication No. 11. London: The Chemical Society.
Van Vleck J.F. (1948). *Phys. Rev.* **74,** 1168.

Acta Cryst. (1971). B27, 1678

The crystal structure of $POBr_3$: space group and refinement by least squares.*

By Lieselotte K. Templeton and David H. Templeton, *Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California* 94720, *U.S.A.*

(*Received* 4 *December* 1970)

Contrary to an earlier report, the X-ray diffraction data for $POBr_3$ are consistent with space group *Pnma*.

Olie & Mijlhoff (1969) (referred to below as OM) reported a crystal structure for phosphoryl bromide, $POBr_3$, which had been refined in space group $Pn2_1a$, but which deviated from *Pnma* by no more than 0·08 Å. OM stated that refinement in *Pnma* (with a block-diagonal least-squares program) 'proved to be disastrous' and that 'R did not drop below 36%', whereas (with anisotropic thermal parameters) R was reduced to 11·3% in $Pn2_1a$. We found it incredible that one could not get approximately as good agreement in space group *Pnma* as in $Pn2_1a$ with such slight deviations from the higher symmetry. Indeed, calculations we have made with the data of OM have reduced R below 11·3% in both space groups. We must conclude that there was some defect in the program used by OM or some error in using it.

Dr Olie kindly gave us a list of 432 non-zero structure factors. We refined the structure using the CDC-6600 computer and the full-matrix least-squares program of Dr Allan Zalkin of this laboratory. Scattering factors for neutral atoms were taken from Cromer & Waber (1965) with dispersion corrections for Br and P from Cromer (1965). OM used slightly different scattering factors and apparently neglected the dispersion corrections, but this difference certainly is not the origin of the divergence of our results. We assigned equal weights to the reflections for lack of knowledge of the experimental accuracies. The cell dimensions of OM were used: $a = 9{\cdot}467(6)$, $b = 9{\cdot}938(6)$, $c = 6{\cdot}192(3)$ Å.

Starting with coordinates similar to those reported by OM (but naturally with Br(1) and Br(3) equivalent), four cycles of refinement in *Pnma* with individual isotropic thermal parameters reduced $R = \sum|\Delta F|/\sum|F_o|$ to 0·192 Further cycles yielded no significant improvement. With individual anisotropic thermal parameters, eight cycles reduced R to 0·110 and $R_2 = [\sum(\Delta F)^2/\sum F_o^2]^{1/2}$ to 0·128. The final shifts in no case exceeded 10^{-3} times the respective estimated standard deviation. The resulting parameters are listed in Table 1 and the molecular dimensions are compared in Tables 2 and 3 with those found with the other space group. Observed and calculated structure factors (multiplied by 6) are listed in Table 4.

Table 1. *Final parameters in space group Pnma*

	Br(1)	Br(2)	P	O
x	0·3469 (4)	0·4801 (6)	0·3102 (10)	0·174 (3)
y	0·0790 (3)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
z	0·1799 (5)	0·6096 (8)	0·3799 (14)	0·494 (4)
B_{11}*	7·1 (2)	5·0 (3)	2·5 (4)	4 (1)
B_{22}	2·6 (1)	5·8 (2)	2·2 (3)	6 (2)
B_{33}	4·2 (1)	3·3 (2)	2·4 (3)	3 (1)
B_{12}	−0·5 (1)	0	0	0
B_{13}	0·8 (2)	−1·6 (2)	0·5 (4)	2 (1)
B_{23}	−1·2 (1)	0	0	0

* The temperature factor is $\exp(-\sum_i \sum_j h_i h_j b_i b_j B_{ij}/4)$.

Table 2. *Bond distances*

	Pnma	$Pn2_1a$	
	This work	This work	OM
P–Br(1)	2·131 (6) Å	2·118 (21) Å	2·131 (11) Å
P–Br(2)	2·147 (10)	2·148 (11)	2·140 (6)
P–Br(3)	(2·131)	2·147 (17)	2·150 (11)
P–O	1·470 (29)	1·445 (32)	1·442 (18)
O---Br*	3·065 (27)	3·092 (29)	3·08 (2)

* Atom in adjacent molecule.

---

* Work done under the auspices of the U.S. Atomic Energy Commission.