NOV 8 1963

The Nature of the Hydrogen Bond in the Bifluoride Ion*

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CONF-232-2

Neutron diffraction data, obtained from single crystals of NaHF_2 and NaDF_2 , have been analyzed in terms of several models for the bifluoride ion geometry. In sodium acid fluoride the bifluoride ion must be linear and the two fluorine atoms equivalent. The F-H-F distance is 2.264 ± 0.003 A, the F-D-F distance is 2.265 ± 0.007 A. The neutron diffraction data obtained by Peterson and Levy from a single crystal of KHF_2 have been refined in an attempt to settle the question of the geometry of the bifluoride ion in KHF_2 . The F-H-F distance is 2.277 ± 0.006 A. In neither sodium acid fluoride nor potassium acid fluoride is it possible from the diffraction data alone to distinguish between a symmetric model for the bifluoride ion and one in which the potential for the hydrogen (or deuterium) along the bond has two equal minima on either side of the center, even when these minima are 0.15 A or so from the center. However, in both cases from a comparison between the differences in mean-square amplitudes of vibration along the bond of hydrogen (or deuterium) and fluorine as obtained from the analysis of the diffraction data and as calculated from the spectroscopic frequencies it is concluded that the bifluoride ion is indeed symmetric.

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Introduction

The literature on the F-H-F ion in KHF_2 is extensive¹. The principal reason for this is the interest in strong hydrogen bonds; the F-H-F ion contains one of the strongest hydrogen bonds known. Although the simplest interpretation of the spectroscopic and bulk measurements on the bifluoride ion in KHF_2 is that the ion is linear and symmetric, there remain certain difficulties involving the divergence of the energy levels and the isotopic dependence of the frequencies which Blinc² has called attention to.

We undertook the present diffraction study of the bifluoride ion in sodium acid fluoride and the present refinement of the earlier data³ on potassium acid fluoride with the hope of obtaining more accurate information not only on the position of the hydrogen atom, but also on the vibrations of the ion. We felt that it would be through the combination of information on the motions of the system from diffraction and spectroscopic studies that the question of the symmetry of the ion could be settled. In this paper we summarize briefly⁴ the results of our diffraction study and show that these data, in combination with the spectroscopic data, provide new, and we feel convincing, evidence that the F-H-F ion is linear and symmetric.

Unit Cells and Possible Space Groups

In a series of precession and Weissenberg photographs taken with $\text{MoK}\alpha$ radiation it was confirmed that NaHF_2 and NaDF_2 have Laue symmetry $\bar{3}m$, with systematic absences of the hexagonal indices⁵ corresponding to the trigonal system. The cell dimensions, based on $a_{\text{NaCl}} = 5.6402$ at 27°C , are

$$\text{NaHF}_2: \quad a = 3.476 \pm 0.002\text{\AA}, \quad c = 13.76 \pm 0.01 \text{\AA}$$

$$\text{NaDF}_2: \quad a = 3.474 \pm 0.002\text{\AA}, \quad c = 13.75 \pm 0.01 \text{\AA}.$$

The density calculated for three molecules of NaHF_2 in the triply primitive hexagonal cell is 2.14 g/cm^3 versus that of 2.08 g/cm^3 measured by Andersen and Hassel.⁶

The space groups consistent with the diffraction symbol $\overline{R3m}$ are $D_{3d}^5-\overline{R3m}$, C_{3v}^5-R3m , and D_3^7-R32 . As a result of calculations described elsewhere⁴ models for these structures based on the non-equivalence of the fluorine atoms (i.e., $R3m$) are improbable. Accordingly we shall consider only two possible models for the $NaHF_2$ structure: Na at (0,0,0), F at $\pm(0,0,z_F)$ with $z_F \approx 0.41$ ⁶, and $\frac{1}{2}H$ (or $\frac{1}{2}D$) at $\pm(0,0,z_H)$. If $z_H = \frac{1}{2}$, the H atom is centered (model 1); if $z_H \neq \frac{1}{2}$, the H atom is distributed randomly but symmetrically on either side of the center (model 2, a double minimum potential well with the ground level below the barrier).

From both x-ray studies and the neutron diffraction study³ it is known that KHF_2 is tetragonal, with four molecules in a cell of dimensions $a = 5.67$, $c = 6.81$ Å. The space group is $D_{4h}^{18}-I4/mcm$. The potassium atoms occupy the positions $(4a) \pm (0,0,\frac{1}{4})$ (+ body centering). The fluorine atoms occupy the positions $(8h) \pm (x, \frac{1}{2}+x, 0)$, $\pm(\frac{1}{2}+x, \overline{x}, 0)$ with $x_F \approx 0.14$ ⁷. Half-hydrogen atoms also occupy position (8h); for $x=0$ we obtain model 1, for $x \neq 0$ we obtain model 2.

Collection and Reduction of the Neutron Diffraction Data

Data were collected at room temperature from single crystals of $NaHF_2$ and $NaDF_2$ on one of the Brookhaven single crystal spectrometers. The neutron wavelength was 1.073 Å. The values of I and $\sigma(I)$ were reduced in the usual way to values of F_0^2 and $\sigma(F_0^2)$. Estimated standard deviations $\sigma(I)$ were obtained from a combination of the usual errors based on the counting statistics with the factor $(0.05 \times I)$ which attempts to allow for errors inherent in the crystals, for example for those factors which give rise to differences between the intensities of hkl and $\overline{hkl}$. In all there were 52 non-zero independent F_0^2 values for $NaHF_2$ and 44 for $NaDF_2$. For KHF_2 the values of F_0 and $\sigma(F_0)$ given by Peterson and Levy³ were used without further modification, except for rescaling. There were 43 non-zero values of F_0 .

Analysis of the Diffraction Data

Because of the limited number of data, the reliable error estimates for these data, and our desire to obtain easily the thermal parameters of the atoms, we chose to analyze the data by least-squares rather than by Fourier techniques. All least-squares calculations were carried out on an IBM 7094 computer, using the local modification of the Busing-Levy ORFLS program. For sodium acid fluoride refinements were carried out on F^2 ; for potassium acid fluoride refinements were carried out on F .

In all refinements the thermal motions of the atoms were taken to be anisotropic. For the sodium salt the appropriate form of the temperature factor (which modifies the scattering amplitude b_i of atom i) is, for the general harmonic oscillator

$$T_i = \exp(-2\pi^2 \{ (4/(3a^2))(h^2 + hk + k^2) \langle u_{\perp}^2 \rangle_i + (1/c^2) \ell^2 \langle u_{\parallel}^2 \rangle_i \})$$

where $\langle u_{\perp}^2 \rangle_i$ and $\langle u_{\parallel}^2 \rangle_i$ are the mean-square amplitudes of vibration of atom i normal to and along the F-H-F bond. For the potassium salt it is more convenient to write the temperature factor as

$$T_i = \exp(-(\beta_{11}h^2 + \beta_{11}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk)).$$

The mean-square amplitudes of vibration for each atom are then

$$\langle u_{\parallel}^2 \rangle = (a^2/2\pi^2)(\beta_{11} + \beta_{12})$$

$$\langle u_{\perp 1}^2 \rangle = (a^2/2\pi^2)(\beta_{11} - \beta_{12})$$

$$\langle u_{\perp 2}^2 \rangle = c^2 \beta_{33}/2\pi^2$$

where $\langle u_{\perp 1}^2 \rangle$ is normal to the bond in the plane $z = 0$ and $\langle u_{\perp 2}^2 \rangle$ is normal to the bond along c . For the potassium atom $\beta_{12} = 0$, by symmetry.

Least-squares refinements for both the sodium and potassium salts diverge if the positional parameter of the $\frac{1}{2}H$ is allowed to vary. This is because as the models tend toward model 1 the matrix of normal equations is nearly singular and spurious shifts occur. Accordingly it is most convenient to carry out the least-squares refinements for fixed values of the $\frac{1}{2}H$ parameters.

Thus with z_H (or z_D) constrained there are for NaHF_2 eight parameters, the fluorine positional parameter, the two thermal parameters for each of the three atoms, and the scale factor to be determined from the 52 observations. There is in addition the deuterium scattering amplitude (i.e., the percentage deuteration) to be determined from the 44 observations for NaDF_2 . We find for both NaHF_2 and NaDF_2 that there is no significant change in the agreement between F_o^2 and F_c^2 as z_H or z_D ranges from $\frac{1}{2}$ to 0.48, that is as the hydrogen or deuterium is allowed to move up to 0.2 Å from the center. Only the mean-square amplitude of vibration along the bond of the hydrogen or the deuterium changes significantly as z_H or z_D is changed (Fig. 1); the other parameters are virtually independent of the value of z_H or z_D . Thus it is impossible in the diffraction experiment to distinguish between models 1 and 2.

With x_H constrained there are for KHF_2 eleven parameters, the fluorine positional parameter, the three thermal parameters for F, the three thermal parameters for H, the two thermal parameters for K, and two scale factors, to be determined from the 43 non-zero values of F_o . As in the sodium problem as the hydrogen is moved off center there is no change in the agreement between F_o and F_c and the only variable which changes significantly is the mean-square amplitude of vibration of the hydrogen along the bond, $\langle u_{||}^2 \rangle_H$. In Figure 2 we show the variation of $\langle u_{||}^2 \rangle_H$ (proportional to $\beta_{11} + \beta_{12}$) with distance of H from the center. Again we are forced to conclude that from the neutron diffraction data alone it is impossible to distinguish models 1 from 2 over a reasonable range of values of x_H .

Combination of Diffraction and Spectroscopic Data

The thermal vibrational amplitudes determined from the neutron diffraction data are the sum of all motions undergone by these atoms. In the absence of a complete analysis of the vibrations of the crystal it is

an impossible task to calculate these amplitudes from theory. If one makes the reasonable assumption that the vibrational amplitude of hydrogen (or deuterium) along the bond must be less than that of fluorine, then the restrictions indicated in Fig. 1 can be placed on the distance of the light atom from the center of the bond. However, the differences in amplitudes of hydrogen and fluorine along the bond arise only from those motions in which the hydrogen and fluorine do not move together, that is only from the stretching vibrations along the bond, and these are essentially zero-point vibrations. Assume then the simple linear symmetric F-H-F ion. It is then easy to derive from a normal-coordinate treatment that

$$\Delta = \langle u_H^2 \rangle_H - \langle u_F^2 \rangle_F = \frac{h}{16 \pi^2 m_F} \left\{ \frac{2m_F - m_H}{m_H \nu_3} - \frac{1}{\nu_1} \right\}$$

where ν_3 is the asymmetric and ν_1 the symmetric stretching frequency. With the values $\nu_3(\text{H}) = 1577 \text{ cm}^{-1}$ and $\nu_3(\text{D}) = 1150 \text{ cm}^{-1}$ for NaHF_2 and NaDF_2 ,⁸ $\nu_3(\text{H}) = 1450 \text{ cm}^{-1}$ for KHF_2 ⁹ and the value $\nu_1 = 600 \text{ cm}^{-1}$ for KHF_2 ¹⁰ (and assumed for NaHF_2 and NaDF_2) we obtain for the calculated values of 0.0097, 0.0062, and 0.0106 Å² for NaHF_2 , NaDF_2 , and KHF_2 . These calculated values are compared with the experimentally derived values in Figures 3 and 4. The agreement between the calculated values (where a linear symmetric bond is assumed) and those obtained from the neutron diffraction data for model 1 is excellent. This agreement, we feel, provides the most powerful evidence that the F-H-F and F-D-F bonds are symmetric.

The final positional parameters for F in these compounds are 0.41772 ± 0.00009 , 0.41760 ± 0.00024 , and 0.1420 ± 0.0003 and lead to F-H-F lengths of 2.264 ± 0.003 , 2.265 ± 0.007 , and 2.277 ± 0.006 Å in NaHF_2 , NaDF_2 , and KHF_2 .

Footnotes

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

1. Reference 2 contains references to many of these studies.
2. R. Blinc, Nature 182, 1016 (1958).
3. S. W. Peterson and H. A. Levy, J. Chem. Phys. 20, 704 (1951).
4. This work is described in greater detail in two papers in press in J. Chem. Phys.
5. Throughout this paper we refer the structure of NaHF_2 to the triply primitive hexagonal cell.
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8. Unpublished results of R. G. Snyder.
9. G. L. Côté and H. W. Thompson, Proc. Roy. Soc. A210, 206 (1951).
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Figure 1. The variation of $\langle u_{\parallel}^2 \rangle$ for H and D with distance of H and D from the center of the bond in NaHF_2 and NaDF_2 .

Figure 2. The variation of β_{11} , β_{12} , and derived quantities for KHF_2 with distance of the hydrogen atom from the center of the bond. Note that $\langle u_{\parallel}^2 \rangle_{\text{H}}$ is proportional to $\beta_{11} + \beta_{12}$.

Figure 3. The differences in mean-square amplitude of vibration along the bond of H or D and F versus the distance of H or D from the center of the bond in NaHF_2 and NaDF_2 .

Figure 4. The difference in mean-square amplitude of vibration along the bond of H and F versus the distance of H from the center in KHF_2 .