what lower than the P^+–O^- moment in contrast to the fact that the C=S moment is 0.3 higher than the C=O, which latter bonds contain large contributions from semipolar forms.[19]

Summary

The dielectric constants and densities of solutions of ethyl undecylate, palmitate and stearate in heptane, of *n*-propyl, *i*-butyl and *s*-butyl borate in benzene, and of triphenyl phosphite, phosphate and thiophosphate in benzene have been measured at 25° and used to calculate the dipole moments of the molecules of the solutes.

The small variation of polarization with concentration shows the intermolecular action to be very small in the three trialkyl borates and in triphenyl phosphite and to decrease with increasing molecular size in the long-chain fatty acid esters. The small intermolecular action is due to effective screening of the dipoles from one another by the hydrocarbon groups, while the large intermolecular action in the phosphate and thiophosphate is due to the presence of an imperfectly screened semipolar bond.

Ethyl undecylate, palmitate and stearate have dipole moments indistinguishable from one another and from those of ethyl propionate and butyrate, which shows that the long chains in these molecules do not affect the dipole moment of the molecule or hinder its free orientation at 25° in an alternating electric field of frequency as high as 520 kc. Equations are derived for the calculation of the resultant moments of the trialkyl borates and of triphenyl phosphite, phosphate and thiophosphate on the assumption of equal probabilities of all the positions of rotation around the B–O and P–O bonds. Strong steric repulsion between the alkyl groups in the borates lowers their moments to less than half of the values calculated on the basis of free rotation as well as on that of B–O bonds stiffened by double-bond character. Excellent agreement is obtained between the observed and the calculated values for triphenyl phosphite, where steric hindrance plays a minor role. The equations are used to calculate approximate moment values for three bonds as follows: P–O, 1.2; P^+–O^-, 3.5; P^+–S^-, 3.2.

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[19] Smyth, THIS JOURNAL, 60, 183 (1938).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 762]

A Redetermination of the Parameters in Ammonium Bifluoride

BY M. T. ROGERS AND L. HELMHOLZ

Introduction

The structure of ammonium bifluoride has been determined by Pauling,[1] who gave approximate values of the parameters obtained with the use of the data of Hassel and Luzanski.[2] He found a hydrogen-bonded structure with each nitrogen atom surrounded by four fluorine atoms at tetrahedral corners, the mean N–F distance being 2.76 ± 0.06 Å. and the F–F distance 2.37 ± 0.10 Å. The value we have found[3] for the F–F distance in KHF_2, 2.26 ± 0.01 Å., is equal to Pauling's value of the distance in NH_4HF_2 to within its limits of error, so it is not possible to say whether or not the distance has been increased by the formation of two additional hydrogen bonds in NH_4HF_2. For this reason a more accurate determination of this distance has been made. The unit translations found by Hassel and Luzanski[2] and the parameters given by Pauling[1] have been revised and the limits of error reduced. From these new values the F–F and N–F distances have been calculated to be F–F = 2.32 ± 0.03 Å. and N–F = 2.82 ± 0.03 Å. The weakening of the F–F bond in the formation of two hydrogen bonds in passing from KHF_2 to NH_4HF_2 is thus shown to exist; the increase in bond length amounts to 0.06 ± 0.04 Å. The space group D_{2h}^7 used by Pauling has been confirmed by the absence of reflections of the type $(h0l)$, h odd, observed by Hassel and Luzanski.

Experimental Method and Results

Oscillation photographs about the c and a axes were taken of crystals of orthorhombic NH_4HF_2 prepared by evaporation of solutions of NH_4HF_2 in glacial acetic acid.

The space group was shown to be D_{2h}^7 by the

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[1] L. Pauling, *Z. Krist.*, (**A**) **85**, 380 (1933).

[2] O. Hassel and N. Luzanski, *Z. Krist.*, **83**, 448 (1932).

[3] L. Helmholz and M. T. Rogers, THIS JOURNAL, **61**, 2590 (1939).

absence of reflections of type ($h0l$), h odd, and ($hk0$), h and k odd. The reflection (102) reported by Hassel and Luzanski, which would eliminate this group, was sought but not observed on any photographs. This justifies the choice made by Pauling. The unit cell contains four molecules and the dimensions of the unit were found to be

$$a_0 = 8.426 \pm 0.020 \text{ Å.}; \; b_0 = 8.180 \pm 0.020 \text{ Å.}; \; c_0 = 3.69 \pm 0.05 \text{ Å.}$$

The first two are from oscillation photographs, the third from layer line measurements. Data giving a_0 and b_0 are shown in Table I. These correspond to axial ratios $1:0.971:0.438 = a_0:b_0:c_0$ compared by goniometric values $1:0.977:0.444 = a_0:b_0:c_0$ (Groth).

TABLE I

EQUATORIAL MEASUREMENTS

(hkl)	$d_{\text{obsd.}}$ Å.	a_0 obsd. Å.
400	2.105	8.421
600	1.405	8.434
800	1.053	8.424
1000	0.0842	8.423
	Average a_0	8.426
020	4.097	8.195
040	2.045	8.180
060	1.362	8.172
080	1.022	8.177
	Average b_0	8.180

The relative intensities of all observed reflections were estimated visually using a calibrated scale.

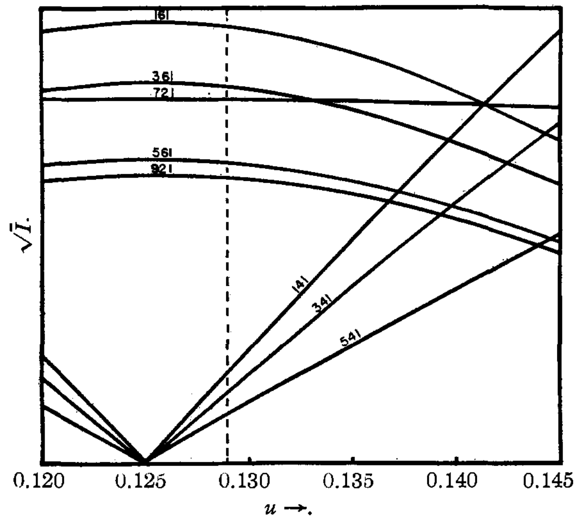

Fig. 1

Theoretical values for the relative intensities were calculated using the formula

$$I = C\frac{1 + \cos^2 2\theta}{\sin 2\theta} F^2 \exp -3.0 \left(\frac{\sin \theta}{\lambda}\right)^2$$

where F is the structure factor and $\exp -3.0 \left(\frac{\lambda}{\sin \theta}\right)^2$ the temperature factor. The structure factors for the four classes of planes are

I $F = 4f_F \sin 2\pi ku \sin 2\pi lv$ for h odd, k even

II $F = 4f_{NH_4} \cos 2\pi \left(\frac{h+k}{4} + lz\right) - 4f_F \sin 2\pi ku \sin 2\pi lv$ for h even, k odd

III $F = 4f_F(\cos 2\pi hw - \cos 2\pi ku \cos 2\pi lv)$ for h odd, k odd

IV $F = 4f_{NH_4} \cos 2\pi \left(\frac{h+k}{4} + lz\right) + 4f_F(\cos 2\pi kw + \cos 2\pi ku \cos 2\pi lv)$ for h even, k even

The f values used were those of Pauling and Sherman.[4] The intensities of reflections ($h00$) depend only on parameter w, and of reflections ($0k0$) only on parameter u, and a rough determination of these parameters might have been made using the observed ($h00$) and ($0k0$) intensities. The intensities of these reflections, however, are so sensitive to the choice of f values for F^- and NH_4^+ that little confidence was felt in the determination carried out from this starting point, and, indeed, the parameters thus obtained led to marked discrepancies between calculated and observed intensities for planes of different types.

To overcome this difficulty the determination was carried out in the following manner. The parameter u was determined first using observed intensities for planes of class I with $l = 1$. The factor $\sin v$ is known closely enough from Pauling's determination of $v = 0.135 \pm 0.01$ since it enters only as a common factor. The calculated intensities are plotted as functions of u in Fig. 1. The value $u = 0.131 \pm 0.002$ is found.

Accepting this value of u it is now possible to choose the f values for NH_4^+ which will account for the observed intensities of ($0k0$) planes. The appropriate f_{NH_4} values were found to be close to the values used by Pauling.[1] Experimental values of f_{NH_4} have been obtained by Wyckoff and Armstrong[5]; a comparison of these values with those we have used is shown in Table II.

TABLE II

Sin Θ/λ	0.1	0.2	0.3	0.4	0.5	0.6	0.7
f_{NH_4} (Pauling)	8.11	6.01	3.96	2.65	1.99	1.68	1.55
f_{NH_4} (Hartree)	6.7	4.4	3.1	2.50	2.0	1.65	1.65
f_{NH_4} (used)	7.7	5.64	3.70	2.43	2.00	1.68	1.55
f_{NH_4} (Wyckoff)	8.8	5.5	3.1	1.8	1.2		

We next obtained an approximate value of w, 0.137 ± 0.004, from reflections ($h00$). The value of v was obtained by comparing intensities of

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[4] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

[5] Wyckoff and Armstrong, *ibid.*, **72**, 319 (1930).

planes of Class I with varying values of *l*, using the value found for *u*. The calculated intensities plotted as functions of *v* are shown in Fig. 2. Planes with $k = 2, 6, 10$ were used since these vary negligibly with *u* in the allowed range for that parameter.

The value $v = 0.131 \pm 0.003$ was obtained in this way. A more accurate value of *w* was then found using intensities of reflections of type III with $l = 0$, which depend only on *u* and *w*. Plots were made of the calculated intensities as functions of both *u* and *w* for these planes and values of these parameters giving the best agreement with observed intensities were taken. To account for the observed intensity ratios of 910:930:350:530 it was found necessary to use the lower limit for *u* ($u = 0.129$). The value of *w* chosen was $w = 0.137 \pm 0.002$. This choice was confirmed by plotting calculated intensities for reflections of type III with $l = 1$ as functions of *w* using previously obtained values of *u* and *v*.

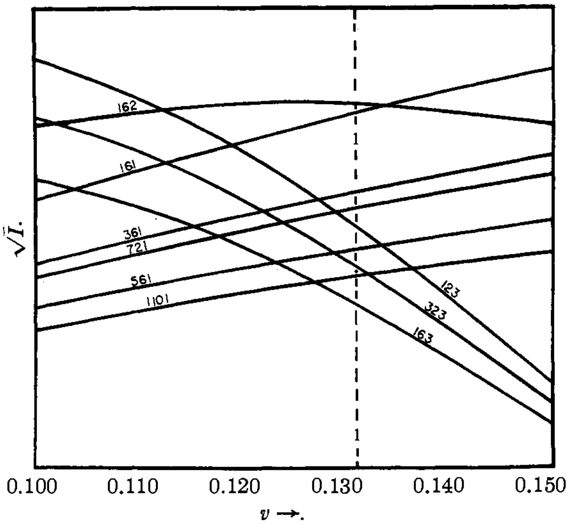

Fig. 2

TABLE III

TYPE I PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
121	32	33	921	5.4	4.5
141	1.9	2.3	122	20.5	14
161	8.4	7.4	142	1.4	1.2
181	1.2	abs.	162	8.5	6.7
1,10,1	5.0	4.1	322	12.5	14
321	20.5	20	342	1.1	abs.
341	1.4	1.8	362	7.8	4.0
361	6.8	6.6	123	7.0	5.4
521	11.2	14	143	0.8	1.0
541	1.0	abs.	163	4.7	4.1
561	5.6	4.5	323	5.6	4.4
721	6.4	5.7	343	0.5	abs.
741	0.6	abs.	363	4.6	2.5
761	5.3	4.0			

TABLE IV

TYPE II PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
011	20.4	18.7	012	27.7	30
031	22	26.5	032	7.9	7.9
051	12.6	10	052	4.6	4.2
071	2.2	abs.	072	7.5	8.2
211	31	36	092	9.2	10
231	9	11	212	7.8	6.1
251	5.7	7.1	232	15.6	17.8
271	5.2	6.3	252	11.7	11.6
291	6.1	4.4	272	1.4	abs.
411	8.9	7.1	013	0.2	abs.
431	11.3	14.1	033	8.5	10
451	8.1	9.2	053	7.9	8.5
471	1.8	2.0	073	1.1	5
611	8.5	10.0	213	9.7	11
631	3.3	3.1	233	0	abs.
651	3.2	3.1	253	0.8	abs.
671	4.6	3.6	273	6.6	7.1
811	2.8	1.1	014	4.1	7.5
831	5.2	5.1	034	5.2	4.1
851	6.2	3.4	054	5.5	5.4
10,1,1	5.3	5.0	214	4.4	1.4
			234	4.1	5.2

TABLE V

TYPE III PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
110	3.7	4.2	931	4.6	4.9
310	67	61	151	17.7	23
510	22.5	30	351	5.6	7.7
710	2.6	3.3	551	0.2	abs.
910	4.4	3.3	751	10.5	8.6
130	63	61	171	0.2	abs.
330	2.6	4.0	371	12.4	11
530	5.5	5.8	571	8.3	8.1
730	15.2	17	771	2.0	abs.
930	6.6	7.3	191	1.6	3.6
150	25	37	391	9.6	7.4
350	3.6	4.3	112	16.8	16.7
550	2.0	abs.	312	13.9	14
750	11.7	11.5	132	10.6	14
950	5.2	5.0	332	11.0	7.5
170	1.6	abs.	152	6.7	5.8
370	14.5	15.3	352	6.7	5.8
570	9.4	10.2	172	5.4	2.5
770	0.3	abs.	372	5.7	5.8
190	0.9	abs.	113	12.8	13
390	10.3	8.4	313	2.8	4
590	w+	6.0	133	0.6	2.5
111	10.4	14.0	333	11.7	7
311	42.5	45	153	1.5	abs.
511	12.6	14	173	9.5	3.5
711	4.6	5.9	114	10.2	5.8
911	3.4	2.5	314	1.2	2
131	37	43	134	0.6	abs.
331	7.3	7	334	10.5	6
531	1.5	abs.	552	3.4	vvw
731	12.3	15	553	6.5	vvw

The reflections of type II, *h* even and *k* even, with different values of *l* were used to obtain a value of *z*. Intensities which were very sensitive to *u*, *v*, or *w* were not used. As before, calculated intensities were plotted as a function of *z* and the best value chosen; $z = 0.540 \pm 0.005$ was found.

Comparison of calculated and observed intensities for reflections of type II (Table III) served as a check on all these parameters. The calculated and observed intensities for all reflections observed are listed in Tables III to VI. Intensities of reflections observed by Hassel and Luzanski[2] and not by us are designated by letters rather than numbers.

TABLE VI

TYPE IV PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
020	7.3	7.9	081	7.2	8.6
040	25.9	19.4	082	13	12
060	6.7	8.1	0,10,1	11.4	14.1
080	22	15.8	201	61	70
0,10,0	0	abs.	202	14.1	14.1
200	0	abs.	203	4.1	abs.
220	35.8	40	204	12.5	w
240	27.0	43	221	30	44
260	9.1	8.6	222	13.5	10.6
280	1.0	abs.	223	6.0	6.1
400	27	27	224	2.5	3.3
420	42	31.5	241	4.4	4.5
440	20.2	19	242	10.5	12.3
460	14.6	13	243	7.9	7.2
480	5.5	3.4	261	7.4	5.9
600	10.8	13	262	4.0	8
620	16	14	263	5.9	4.4
640	12.8	12	281	9.7	8.2
660	9.6	7.7	282	5.5	5
680	4.4	2.6	401	21.2	28
800	20.8	20	421	6.8	10.5
820	1.4	2.2	441	12.4	19.4
840	4.7	5.3	461	1.4	3.6
860	1.9	2.0	481	7.6	5.2
10,0,0	3.3	2.5	601	22.4	20
003	0	abs.	621	2.7	3.8
004	3.0	vvw	641	3.4	5.5
021	78	75	661	1.1	abs.
022	9.7	9.3	801	7.0	8.3
023	15.7	14.7	821	11.8	10
024	5	3.3	841	4.9	3.3
041	7.1	10.5	404	11.5	w
042	21.7	21	402	6.3	vw
043	10.4	8.3	403	18.9	m
044	17.8	10	802	10.7	m
061	21.3	16.4	442	2.7	vw(w)
062	3.3	5.6	443	5.5	vw(m^-) (m^+)
063	10.8	10.5	662	8.1	m^{++}

Conclusions.—The values of the F–F distance calculated using these parameters are

$$F_1\text{–}F_1 = 2.31 \pm 0.035 \text{ Å.}$$
$$F_2\text{–}F_2 = 2.320 \begin{matrix} +0.03 \text{ Å.} \\ -0.02 \text{ Å.} \end{matrix}$$

The lower limit is less in the latter case since the value chosen for *u* was the lower limit (0.129) given it in the determination above; probably *u* cannot be less than 0.129.

Comparing these values with the value F–F 2.26 ± 0.01 Å. for KHF_2 it is seen that there is a slight increase in the distance in NH_4HF_2, amounting to between 0.03 and 0.08 Å., due to the weakening of the bond by the two extra hydrogen bonds formed in NH_4HF_2.

The N–F distances found are $N\text{–}F_1 = 2.80 \pm 0.02$ Å., and $N\text{–}F_2 = 2.80 \pm 0.03$ Å. This value is larger than the average found by Pauling (2.76 Å.) and is 8% larger than the value N–F = 2.63 Å. for NH_4F. We thus confirm the observation of Pauling that the hydrogen bond in NH_4HF_2 is weaker than that in NH_4F. The longer ammonium ion to fluorine contacts are: $N\text{–}F_I = 3.02$ Å. and $N\text{–}F_{II} = 3.40$ Å.

Summary

The unit translations for the orthorhombic crystal NH_4HF_2 have been revised to $a_0 = 8.426$ Å., $b_0 = 8.180$ Å., $c_0 = 3.69$ Å. The space group and structure given by Pauling have been confirmed and the parameters redetermined:

$$z = 0.540 \pm 0.005 \text{ Å.} \qquad u = 0.129 \begin{matrix} +0.003 \text{ Å.} \\ -0.001 \text{ Å.} \end{matrix}$$
$$w = 0.137 \pm 0.002 \text{ Å.} \qquad v = 0.131 \pm 0.003 \text{ Å.}$$

The four smallest N–F distances are all equal to 2.80 ± 0.025 Å. and the F–F distances in the two non-equivalent HF_2^- ions are found to be 2.32 ± 0.03 Å.

PASADENA, CALIFORNIA RECEIVED MARCH 13, 1940