

## Infra-red spectra and the solid state. III. Potassium bifluoride

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The infra-red spectrum of potassium bifluoride has been determined between 2 and  $8\mu$  at temperatures between 293 and 90° K. On passing from room temperature to that of liquid air, some of the absorption bands sharpen and split. The results have been analyzed with the object of assigning fundamental vibration frequencies to the  $(\text{HF}_2)^-$  ion, and also of deciding whether this ion has a symmetrical or unsymmetrical structure. Values assigned to the stretching vibration frequencies are 600 and 1450  $\text{cm}^{-1}$ , and to the deformation a pair at 1225/1274  $\text{cm}^{-1}$ . The spectrum can then be satisfactorily explained in terms of the selection rules which would be expected for a symmetrical  $(\text{HF}_2)^-$  ion lying in the particular crystal field suggested by X-ray work. Whereas the bending vibrations appear to involve little anharmonic character, there is an apparently large negative anharmonic coefficient for the overtone and combinations of the stretching vibration frequencies. This might be expected if the potential energy function for the antisymmetrical stretching vibration involved a higher power of the displacement co-ordinate than the second, and strengthens the interpretation in terms of a symmetrical ion. The molecular environment of the ion in the crystal state leads to a removal of the degeneracy of the deformational vibration, the latter being found to split, although one component is not noticed in absorption when the crystal is viewed along the c-axis.

Vibrational spectra of molecules in the solid state have recently been investigated with several objects. Shifts in frequency or changes of band contour which occur on solidification may lead to information about the intermolecular forces, while

a difference of the effective field symmetry due to changes of molecular environment may cause alteration in the selection rules. Further, if the spectra are also studied at low temperatures, decrease of band widths may lead to greater resolution, so that close-lying bands may be separated. When the symmetry of the force field in the crystal is such as to predict a splitting of degenerate modes, this may provide an important means of correlating the spectrum with the crystal structure. Changes in temperature may in any case lead to structural rearrangements in the solid state with consequent alteration of selection rules, resulting in marked variations of the band intensities. In some cases, a comparison of the effect of temperature upon different bands aids their assignment to particular modes and it may be possible to obtain special knowledge about complex ions in crystals. Such measurements have been made by Halford and his co-workers (Halford 1946, 1947, 1949, 1950) by Hornig (1948, 1949, 1950, 1951), by Smith, Keller & Johnston (1950, 1951), by King, Hainer & McMahon (1949) and by Richards & Thompson (1948).

The use of polarized infra-red radiation with crystals of simple molecules provides a further means not only of assigning vibration frequencies to normal modes, but alternatively of determining the crystal structures. Examples have recently been given by Mann & Thompson (1948), Crooks (1947), Brown & Corbridge (1948), Halverson & Francel (1949), Newman & Halford (1950).

#### EXPERIMENTAL PROCEDURE

In this paper we describe measurements on the spectra of potassium bifluoride crystals at different temperatures and in the succeeding paper similar work on some borofluorides. The spectra were measured with a Perkin Elmer 12C spectrometer using prisms of rock salt, potassium bromide, and lithium fluoride. The instrument was dried out by phosphorus pentoxide, and with the evacuated cell in position the absorption by atmospheric water vapour near  $6\mu$  was small. Carbon dioxide was removed by caustic potash. The effective slit widths are indicated in the diagrams below.

Two absorption cells were used, of the type illustrated in figure 1, and similar to those described by Wagner & Hornig (1950), and by Walsh & Willis (1950). A Pyrex glass tube about 10 mm. in diameter was joined at its lower end through a copper-glass seal to a silvered copper block. The copper tube was sunk into the block deep enough to leave a cavity so that the cooling agent made an effective contact with the main metal block. A rectangular or circular hole was made through the latter, with a rim at the middle. The plates of rock salt, potassium bromide or fluorite on which the sample was placed rested on this rim and were held in place by a silvered copper sleeve. Thermocouples were placed in the upper part of the block and also through a small hole drilled into the rock-salt plate. The whole unit was placed via a ground joint into an outer inverted T-shaped vessel with flanged ends, upon which suitable windows of rock salt or potassium bromide were fixed with Apiezon Q wax. The glass surfaces were silvered and the whole cell lagged outside with asbestos, so that when evacuated it formed a Dewar vessel. The lengths of the horizontal arms of the two cells were 10 and 20 cm. respectively. Experiments showed that with liquid



air in the cooling enclosure, the sample could be maintained at a temperature not more than a few degrees above that of liquid air, and without significant fogging of the windows. It was also possible to maintain steady conditions at intermediate temperatures. The plate carrying the material was usually separated from the metal rim in the block by a thin film of soft silicone grease, but if too much of this grease is used there is a danger of cracking the plate due to a too rapid cooling when liquid air is used.

In some cases the spectrum of a sample was measured at room temperature both before and after measurement at the low temperature, with complete reproducibility.

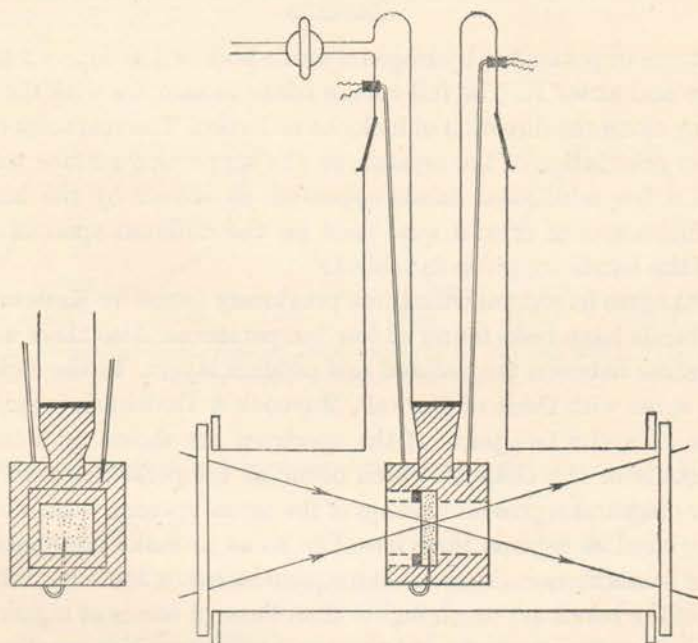


FIGURE 1. Low-temperature absorption cell.

#### PREPARATION OF BIFLUORIDE CRYSTALS

Potassium hydrogen fluoride was prepared by a method essentially similar to that of Pitzer & Westrum (1949). Solid potassium carbonate (70 g.) was added slowly with constant stirring to 40 g. aqueous hydrogen fluoride in a platinum dish. After filtering off the crystals of the bifluoride, they were redissolved in a little hot water and recrystallized by very slow cooling. In this way crystals of fairly large area were obtained, and about 0.1 mm. thick. Analysis for the fluorine content by the method of Vogel (1946) gave a value within 1% of the theoretical. A mosaic of such crystals was made on a plate of calcium fluoride by sticking the corners with a little adhesive wax. These relatively thicker layers were used for measurements of the overtone and combination bands between 2 and  $4\mu$ . For the longer wave-lengths thinner layers were necessary. These were made by slow evaporation of a dilute aqueous solution of the salt on a plate of calcium fluoride. Specimens were thus obtained with the crystal plates lying flat and parallel to the fluorite plate. In this

arrangement the *c*-axis of the crystal lies perpendicular to the fluorite surface. More rapid crystallization led to a random orientation in the layer, and the significance of this difference is discussed below.

In all these preparations it was impossible to use a base-plate of rock salt or potassium bromide, since these are attacked by the solution. Accordingly, measurements could not be made at wave-lengths greater than about  $9\mu$ . Also, the bifluoride appears to react with nujol and since the scattering with perfluorokerosene pastes was too great, the spectrum of suspensions in these materials could not be determined.

### RESULTS

The spectrum of potassium hydrogen fluoride is shown in figures 2 and 3 at room temperature and at  $90^\circ\text{K}$ . The full curves relate to samples with the *c*-axis of the crystals lying along the direction of incident radiation. The spectrum of a specimen with random orientation of the crystals on the supporting surface was also determined, and a few additional bands appeared, as shown by the broken curves. Different thicknesses of crystal were used for the different spectral regions. The positions of the bands are given in table 1.

The results agree in general with those previously found by Ketelaar (1941), but additional bands have been found at low temperatures. Also there are important small differences between the ordered and random layers. In the region of  $3\mu$  the results also agree with those of Buswell, Maycock & Rodebush (1940).

In figures 4*a* and *b* two parts of the spectrum are shown on a larger scale to illustrate details of the changes which occur at temperatures between 293 and  $90^\circ\text{K}$ . These diagrams represent tracings of the actual spectral transmission records, suitably displaced as regards their base-line so as to make the splitting and displacement of bands more easily seen. At frequencies below  $2600\text{ cm.}^{-1}$  the absorption coefficients of the bands are much higher than those of bands at higher frequencies, and although no attempt was made to measure the intensities exactly, they agreed closely with those given by Ketelaar.

### DISCUSSION

The most important conclusions to be derived from these results concern the structure of the  $(\text{HF}_2)^-$  ion. This can be regarded either as symmetrical, the potential energy function for vibration of the central hydrogen atom having a single minimum, or as an unsymmetrical structure with a double minimum in the potential energy function. We think that the best interpretation of the vibrational spectrum favours the first of these alternatives.

Ketelaar (1941, 1948) has argued in favour of the unsymmetrical formula. He attributed the pair of bands at  $1223$  and  $1450\text{ cm.}^{-1}$  to a splitting of the 'antisymmetric' stretching mode of the  $(\text{F}-\text{H}-\text{F})^-$  ion which would arise with a double minimum function. He assigned values below  $600\text{ cm.}^{-1}$  to the 'symmetrical' stretching mode and deformational mode, and from the amount of splitting of the 'antisymmetric' frequency he estimated a potential barrier of about 7 kcal. between the two extreme structures of the ion.



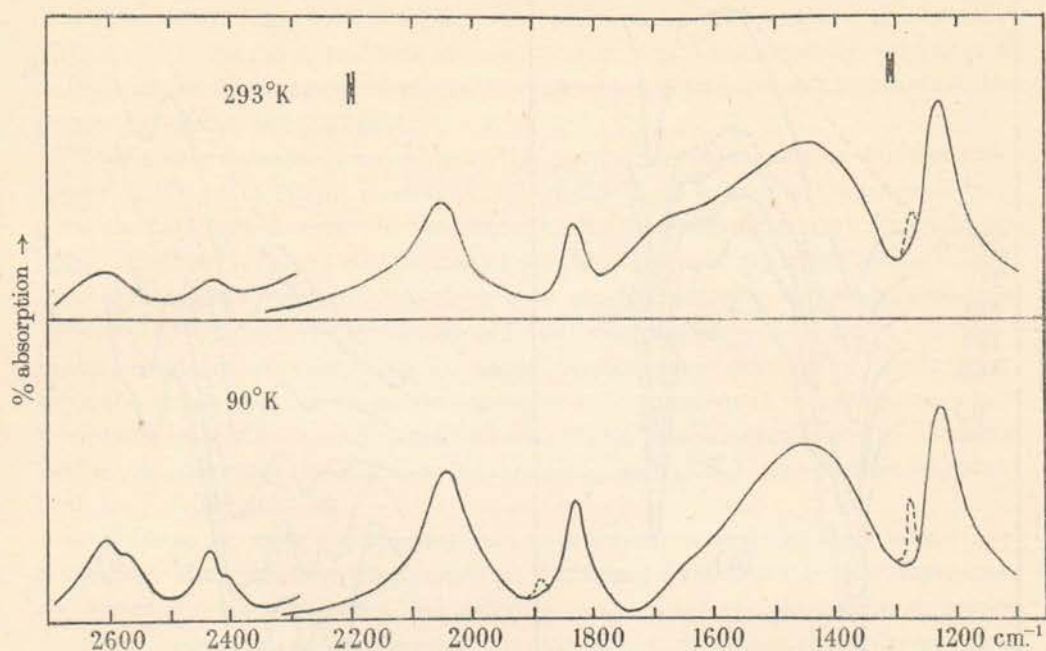


FIGURE 2. Potassium bifluoride crystals. Spectra at 293 and 90° K. The dotted curves relate to disordered layers.

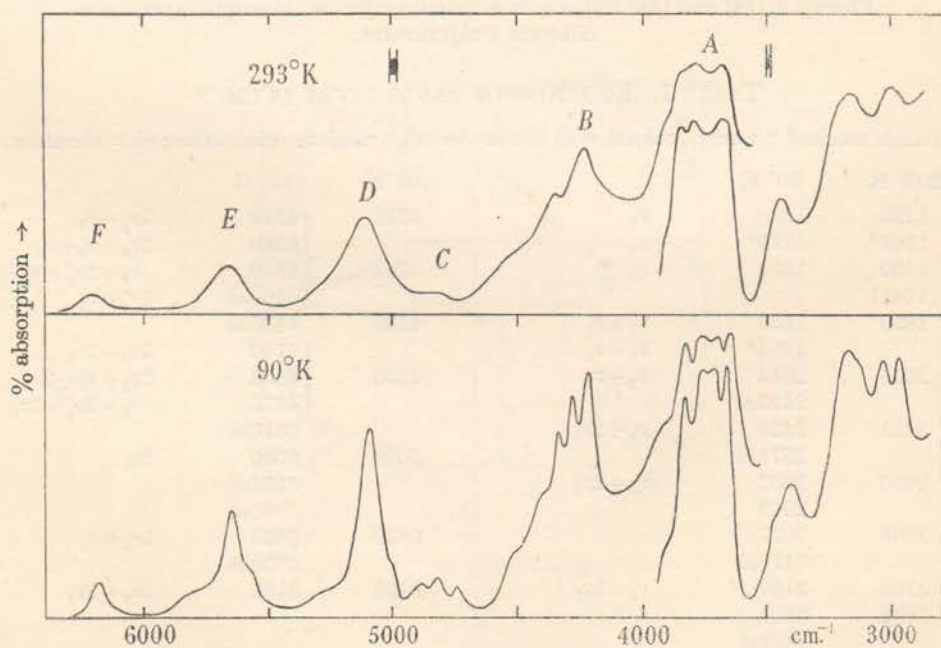


FIGURE 3. Potassium bifluoride crystals: spectra at 293 and 90° K.

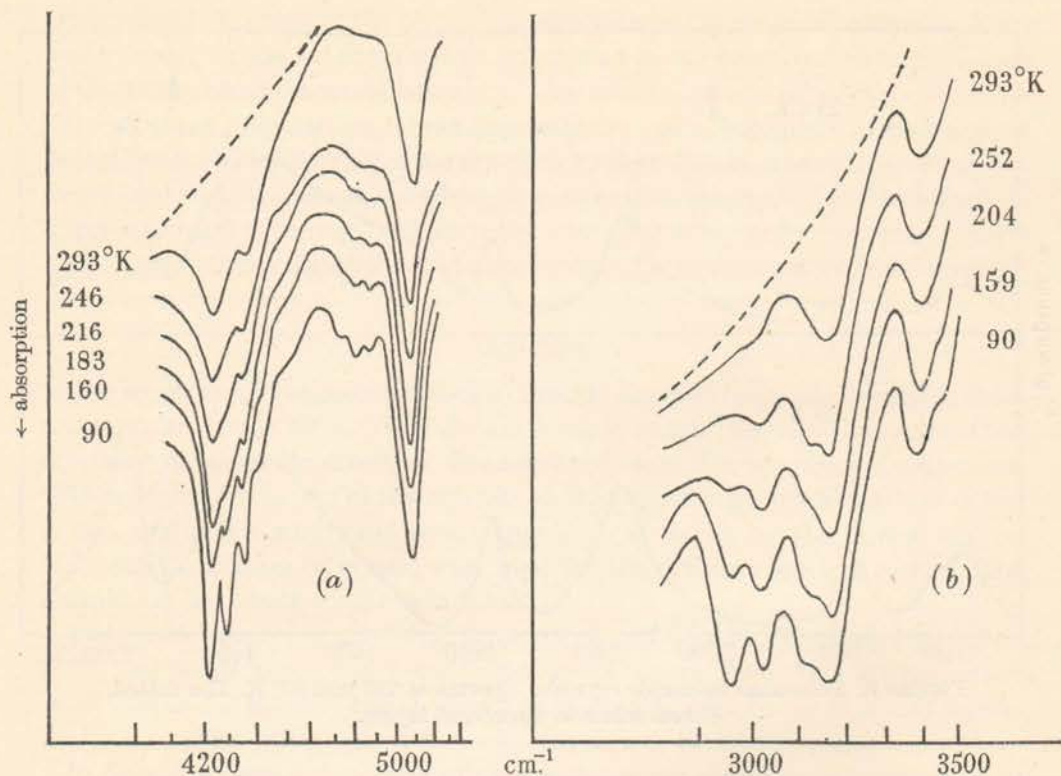


FIGURE 4. (a) and (b). Potassium bifluoride crystals. Absorption occurs at different temperatures.

TABLE I. POSITIONS OF BANDS GIVEN IN  $\text{cm}^{-1}$

Bands marked \* were obtained with the layers with random orientation; *sh* = shoulder.

293° K	90° K		293° K	90° K	
1223	1225	$\nu_2$	4232	4218	$3\nu_2 + \nu_1$
1267*	1274*	$\nu_2'$		4280	$2\nu_2 + \nu_2' + \nu_1$
1450	1450	$\nu_3$	4342	4340	$\nu_2 + 2\nu_2' + \nu_1$
(1648)				4400 <i>sh</i>	$3\nu_2' + \nu_1$
1830	1833	$\nu_2 + \nu_1$	4508	4495 <i>sh</i>	
	1884*	$\nu_2' + \nu_1$		4740	$3\nu_2 + 2\nu_1$
2055	2044	$\nu_3 + \nu_1$	4830	4803	$2\nu_2 + \nu_2' + 2\nu_1$
	2403 <i>sh</i>			4875	$\nu_2 + 2\nu_2' + 2\nu_1$
3421	2426	$\nu_2 + 2\nu_1$		5010 <i>sh</i>	
	2571 <i>sh</i>		5099	5090	$3\nu_3$
2610	2602	$\nu_3 + 2\nu_1$		5254 <i>sh</i>	
	2962			5565 <i>sh</i>	
3001	3027		5650	5643	$3\nu_3 + \nu_1$
	3119 <i>sh</i>			5790 <i>sh</i>	
3166	3166	$\nu_3 + 3\nu_1$	6196	6185	$3\nu_3 + 2\nu_1$
3432	3401				
	3459 <i>sh</i>				
3665	3651	$3\nu_2$			
	3700	$2\nu_2 + \nu_2'$			
3778	3765	$\nu_2 + 2\nu_2'$			
3829	3828	$3\nu_2'$			
	3898 <i>sh</i>				

Buswell *et al.* (1940) studied only the region of  $3\mu$  and assigned the band at  $3600\text{ cm.}^{-1}$  to the antisymmetric stretching vibration. This band also appeared to be double, and it was again concluded that there is a double minimum function, the barrier calculated being 32 kcal.

Other measurements do not support the unsymmetrical structure. For example, Pitzer & Westrum (1949) measured the specific heat over a wide range of temperature and thus determined the entropy. No discontinuities were found in the specific heat curve, and a comparison of the third-law entropy with that calculated by other methods indicated that there is no residual entropy at the absolute zero. This strongly suggested a symmetrical formula for the ion, with a single minimum in the potential energy function. The same conclusion was reached by Polder (1947) from the result that the dielectric constant is independent of temperature, which would not be so for an unsymmetrical ion. Polder also showed that the vibration frequencies suggested by Ketelaar for the  $(\text{HF}_2)^-$  and  $(\text{DF}_2)^-$  ions were inconsistent with the double minimum.

In order to reconcile the spectral data with a symmetrical ion, Halverson (1947) reassigned the vibration frequencies at  $1225$  and  $1450\text{ cm.}^{-1}$  to the degenerate deformational mode, which would split due to the non-isotropic crystal structure, shown in figure 5. In the two mutually perpendicular directions the hydrogen atom would move in a markedly different ionic field.

Perhaps the only unambiguous assignment of the vibration frequencies so far suggested is that of the symmetrical stretching mode, found by Couture-Mathieu & Mathieu (1949, 1950) in the Raman spectrum near  $600\text{ cm.}^{-1}$ .

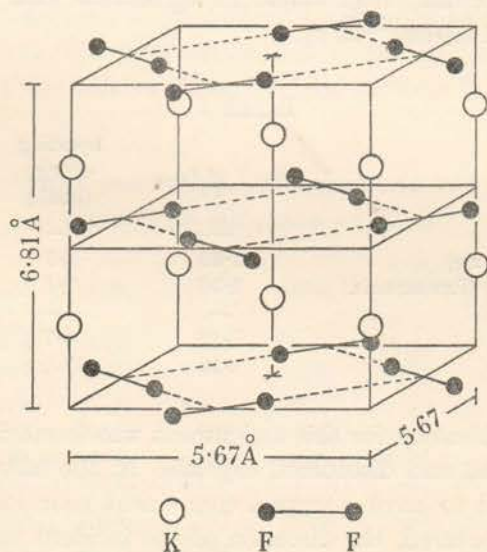


FIGURE 5. Potassium biferuoride: crystal structure. See Halverson (1947).

On the basis of our experimental results, it is possible not only to make a more satisfactory vibrational assignment, but also to provide strong evidence for



regarding the  $(\text{HF}_2)^-$  ion as symmetrical. The three normal modes of this ion will be denoted as follows:

- symmetrical stretching vibration  $\nu_1$   
 antisymmetrical stretching vibration  $\nu_3$   
 deformational vibration (degenerate)  $\nu_2$

$\nu_3$  will be expected to have a value much lower than  $3400 \text{ cm.}^{-1}$  for the following reason. When a linkage such as H—F or O—H is affected by the bonding of another atom to the hydrogen, the stretching vibration frequency of the link is lowered. The greater the bonding energy of the association process, the greater will be the lowering of the vibration frequency. Table 2 summarizes data which exemplify this. The very considerable bonding energy in the  $(\text{HF}_2)^-$  ion will be expected to lead to a much lower vibration frequency of the 'original' H—F bond, and, indeed, if in the ion the two bonds are equivalent or approximately so, there will be stretching vibration frequencies of the triatomic system widely different from any 'modified' H—F link vibration.

On the basis of the observed band intensities, as well as from a general consideration of the overtones and combinations, it seems certain that the frequencies at  $1225$  and  $1450 \text{ cm.}^{-1}$  should be attributed to fundamental vibrations. This conclusion was also drawn by Ketelaar and has been generally accepted. Both these bands are strong in the reflexion spectrum. Approximate calculations by Pitzer & Westrum (1947, 1949) suggested that the two frequencies  $\nu_2$  and  $\nu_3$  may not differ much in magnitude, the strong nature of the bonding raising the deformation frequency to an abnormally high value. In agreement with this, we shall adopt  $1225 \text{ cm.}^{-1}$  as  $\nu_2$  and  $1450 \text{ cm.}^{-1}$  as  $\nu_3$ .

TABLE 2

	$\nu_{\text{O—O}}$ or $\nu_{\text{F—F}}$ ( $\text{\AA}$ )	bonding energy (kcal.)	frequency ( $\text{cm.}^{-1}$ )
free O—H	—	—	3650
O—H—O (ice)	1.38	4.5	3250
O—H . . . . O (formic acid)	1.33	7.1	3030
free H—F	—	—	3960
$(\text{HF})_2$	1.26	6.7	3440
$(\text{HF}_2)^-$	1.13	27	?

An important justification for this assignment was found in the comparison of the spectra of ordered and disordered crystals. In the latter case the band at  $1225 \text{ cm.}^{-1}$  was found to have a second component near  $1274 \text{ cm.}^{-1}$ . When the ordered crystal is measured, the direction of the incident radiation is along the *c*-axis, which is also the direction of electric moment change of one component of the 'degenerate' deformation. The slight split arises because of the lack of equivalence of the field in the two perpendicular directions. The splitting of about  $50 \text{ cm.}^{-1}$  is roughly what might be expected by analogy with other cases such as the deformational vibrations of the  $(\text{NH}_4)^+$  ion in crystalline ammonium salts. If this



assignment is adopted, together with a value for  $\nu_1$  of about  $600 \text{ cm.}^{-1}$ , the spectrum as a whole can be satisfactorily explained in terms of the selection rules expected.

According to Helmholtz & Rogers (1939) the space group in crystalline potassium bifluoride is  $D_{4h}^{18}$ . If the ion is symmetrical, a consideration of the site symmetry of the different atoms by the methods of Halford and Hornig leads to the following selection rules:

- (1)  $\nu_3, \nu_2$  and  $\nu_1'$  will be active as fundamentals,
- (2) all binary combinations and overtones will be inactive except those involving  $\nu_1$  with an active fundamental,
- (3) the second overtones (i.e.  $3\nu$ ) of  $\nu_2, \nu_2'$  and  $\nu_3$  will be active, and triple combinations of these frequencies except  $(\nu_2 + \nu_2' + \nu_3)$ , and
- (4) third overtones will be inactive and fourth overtones active.

In considering the interpretation of the absorption bands, it may be preferable to deal with the spectrum measured at low temperatures, since the bands are usually sharper and multiple components are resolved. First, the first overtone of the fundamental vibrations at  $1225/1274$  and  $1450 \text{ cm.}^{-1}$  do not appear. At first sight, the band at  $2426 \text{ cm.}^{-1}$  might have been attributed to the harmonic of  $1225 \text{ cm.}^{-1}$ , but this would involve the assumption of a larger anharmonicity factor than is consistent with the next higher overtone at  $3651 \text{ cm.}^{-1}$ . Moreover, the band at  $2426 \text{ cm.}^{-1}$  falls well into line with a series of multiples of  $\nu_1$  coupled with  $\nu_2$ , as indicated in table 3. It should be noted that in this and other series in which multiples of  $\nu_1$  are coupled with another frequency, there seems to be a large coupling factor which leads to a combined frequency substantially different from that which might normally be expected from the numerical values of the fundamentals concerned. The band at  $1274 \text{ cm.}^{-1}$ , interpreted as the second component of the perturbed degenerate deformation, has an analogue at  $1884 \text{ cm.}^{-1}$  which is attributed to  $(\nu_2' + \nu_1)$ . The bands at  $2044, 2602$  and  $3166 \text{ cm.}^{-1}$  are similarly explained as a progression.

TABLE 3. VIBRATION BANDS AND INTERVALS FOR POTASSIUM HYDROGEN FLUORIDE AT  $90^\circ \text{ K}$

			$+\nu_1$		$+2\nu_1$		$+3\nu_1$
$\nu_2$	1225	(608)	1833	(593)	2426	{(536) (596)}	{2962? 3027?
$\nu_2'$	1274	(610)	1884	—	—	—	—
$\nu_3$	1450	(594)	2044	(558)	2602	(564)	3166
$3\nu_2$	3651	(567)	4218	(522)	4740	—	—
$2\nu_2 + \nu_2'$	3700	(580)	4280	(523)	4803	—	—
$\nu_2 + 2\nu_2'$	3765	(575)	4340	(535)	4875	—	—
$3\nu_2'$	3828	(572)	4400	—	—	—	—
$3\nu_3$	5090	(553)	5643	(558)	6185	—	—
	5010	(555)	5565	—	—	—	—
	5254	(536)	5790	—	—	—	—

The bands above  $3500 \text{ cm.}^{-1}$  must all be due to overtones or combinations. In disentangling these, a guide may be found in their behaviour with change of temperature. It can be seen that the groups marked *A*, *B* and *C* in figure 3 show



a marked splitting at low temperatures, closer details of which are given in figures 4*a* and *b*. By contrast, the bands *D*, *E* and *F* do not show corresponding behaviour, although weak shoulders occur with *D* and *E*. Further, the intervals between *A*, *B* and *C* suggest again a coupling with multiples of  $\nu_1$ , and the same holds for the series *D*, *E* and *F*. We have already given strong arguments for assigning  $\nu_2$  and  $\nu_1$ , but the multiplet nature of the groups *A*, *B* and *C* probably implies again that there is no fundamental near  $3600 \text{ cm.}^{-1}$ , since it would be difficult then to explain the observed splitting of bands either by Fermi resonance or any other means. These bands are interpreted in table 3. There is some doubt about the interpretation of the bands at  $2962$  and  $3027 \text{ cm.}^{-1}$ , but that suggested is not unreasonable. Two bands due to  $(\nu_2 + 3\nu_1)$  and  $(\nu_2' + 3\nu_1)$  will be expected here, but on grounds of intensity and exactness of frequency fit there is some ambiguity. It is possible that Fermi resonance could disturb the frequencies. There is also a band of medium intensity near  $3401 \text{ cm.}^{-1}$  for which no satisfactory explanation can be given. This might be a ternary combination in which there is a strong coupling or anharmonicity factor.

One interesting feature of the whole spectrum is that the effect of temperature upon the various bands is least with the fundamentals. As the complexity of the combinations and overtones increases, the band shape, extent of splitting, and small displacements of frequency become more marked.

Perhaps the most important point about the overtone bands relates to the anharmonic character of the fundamentals  $\nu_2$  and  $\nu_3$ , and provides further evidence for believing that the barrier in any double minimum potential function of the  $(\text{HF}_2)^-$  ion must be very low indeed, if present at all. The observed and calculated positions of overtones and combinations of the bending vibrations  $\nu_2$ ,  $\nu_2'$  are given in table 4. It is seen that the anharmonic and coupling factors are small. This is not so, however, with  $3\nu_3$  which lies at  $5090 \text{ cm.}^{-1}$ , the calculated position being  $4350 \text{ cm.}^{-1}$ . This result implies a high negative anharmonic coefficient. Such a divergence of the vibrational levels of the stretching mode might well be expected, as Pitzer & Westrum (1947, 1949) have pointed out, if the potential energy varies as a higher power of the displacement co-ordinate than the second. This latter circumstance is to be expected if the two fluorine atoms in the ion come very close together, and the effect on the potential energy curve and vibrational levels is depicted in figure 6. The results are therefore adequately explained by assuming that if a double minimum exists at all, the intervening barrier potential must be very small and may well be zero.

TABLE 4

	obs.	calc.
$3\nu_2$	3651	3675
$2\nu_2 + \nu_2'$	3700	3724
$\nu_2 + 2\nu_2'$	3765	3773
$3\nu_2'$	3828	3822

Similar measurements with deuterated potassium bifluoride might give confirmatory evidence for the above interpretation, and this work is in progress. It is hoped also to carry out appropriate studies with polarized infra-red radiation.



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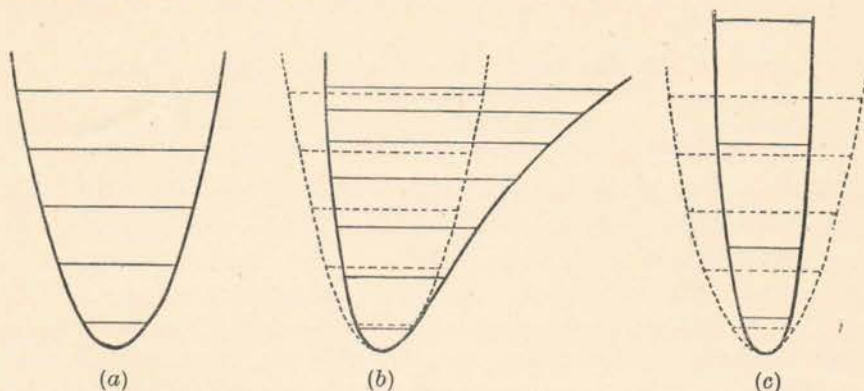


FIGURE 6. Potential energy curves and vibrational energy levels for different laws of force.

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