768. *Isotope and Crystal-field Effects in the Vibrational Spectrum of Potassium Tetrafluoroborate.*

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Comparison of the infrared spectra of normal and ^{10}B-enriched potassium tetrafluoroborate suggests that complexities in the vibrational spectrum of this compound arise both from an isotope doubling in the ν_3 and ν_4 fundamentals of the tetrahedral BF_4^- ion and from the removal of vibrational degeneracy of the ν_3 band as a result of interaction of the tetrahedral ion with a crystal field of lower symmetry. This distortion also permits the forbidden ν_1 symmetrical breathing mode to absorb weakly. Bands near 1310 and 1650 cm.$^{-1}$ are assigned as the combinations $(\nu_1 + \nu_4)$ and $(\nu_3 + \nu_4)$ respectively. The possibility of Fermi resonance between $2\nu_4$ and ν_3 is also considered.

A REGULAR tetrahedral ion MX_4^- has only two infrared-active fundamentals, ν_3 and ν_4, and these are both triply degenerate.[1] The infrared spectrum of potassium tetrafluoroborate was investigated in the region 555—1665 cm.$^{-1}$ by Duval and Lecomte [2] who found only two maxima, a strong, broad band near 990 cm.$^{-1}$ (assigned as ν_3) and a relatively

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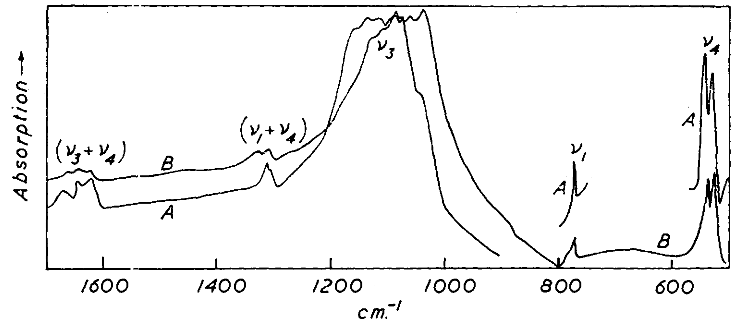
[1] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co. Inc., 1945.

[2] Duval and Lecomte, *Bull. Soc. chim. France*, 1947, **14**, 1057.

weak band at 1535 cm.$^{-1}$ ($\nu_3 + \nu_4$). By difference, ν_4 was obtained as 545 cm.$^{-1}$ though this band was not directly observed. Further work by Coté and Thompson[3] in the region 400—5000 cm.$^{-1}$, using both sublimed films and paraffin mulls at room temperature and at —183°, revealed that the strong, broad ν_3 band had two maxima and two shoulders between 1000 and 1100 cm.$^{-1}$. In addition, there was a weak band at 771 cm.$^{-1}$ (assigned as the Raman-active ν_1 vibration) and a doublet at 521, 534 cm.$^{-1}$, assigned as ν_4. Combination bands were observed at 1302, 1784, and 2148 cm.$^{-1}$. The complex structure of the fundamentals ν_3 and ν_4 was discussed in terms of the isotopic species boron-10 and boron-11, and in relation to the possibility of removing the vibrational degeneracy which which may arise when a tetrahedral ion is situated in a crystal field of lower symmetry. Various arguments were considered and it was concluded, at that time, that it was impossible to decide between the two alternative interpretations. These difficulties have now mainly been resolved by investigating the infrared spectra of normal potassium tetrafluoroborate and of potassium tetrafluoroborate isotopically enriched in boron-10.

FIG. 1. *Infrared spectra of (A) ^{10}B-enriched and (B) normal potassium tetrafluoroborate.*



EXPERIMENTAL and RESULTS

The absorption spectrum of potassium tetrafluoroborate was recorded in the range 375—4000 cm.$^{-1}$ by means of a Unicam SP.100 spectrometer. Both Nujol mulls and potassium bromide discs (1—4 mg. of KBF_4/400 mg. of KBr) were used; the results were very similar over most of the spectrum but resolution within the ν_3 band appeared to be somewhat better with the disc technique.

Potassium tetrafluoroborate with a stated isotopic abundance ratio $^{10}B : {}^{11}B$ of 9 : 1 was supplied by 20th Century Electronics, Ltd. The $^{10}B : {}^{11}B$ ratio in normal potassium tetrafluoroborate (B.D.H) is 1 : 4. Both compounds were dried at 120° before use.

The two spectra are reproduced in Fig. 1. The vertical axis has been adjusted to give

Vibration bands of potassium tetrafluoroborate (R.I. = *relative intensity*)

	KBF_4 (20% ^{10}B)		KBF_4 (90% ^{10}B)		
Ref. 3	ν (cm.$^{-1}$)	R.I.	ν (cm.$^{-1}$)	R.I.	Assgt.
521	525	8·3	530	14·2	ν_4^{11}
534	536	7·4	542	16·1	ν_4^{10}
771	773	2·3	773	0·8	ν_1 *
1032	1038	26·5	1042	16·0	†
1058	1063	25·6	—	—	
1072	1078	25·5	1073	25·1	
(1090)	1088	26·2	1086	25·2	
—	1107	23·9	1115	25·2	
—	1128	22·5	1135	25·2	
—	—	—	1158	23·8	

	KBF_4 (20% ^{10}B)		KBF_4 (90% ^{10}B)		
Ref. 3	ν (cm.$^{-1}$)	R.I.	ν (cm.$^{-1}$)	R.I.	Assgt.
1302	1312	1·4	1305	1·9	$(\nu_1 + \nu_4)$
(1305)	1330	1·3	1312	2·2	
1784	1623	0·9	1622	2·4	$(\nu_3 + \nu_4)$
	1644	1·1	1644	2·0	
	1671	0·7	1668	1·1	
2148	2340	1·1	2335?	0·3	‡
—	2925	1·3	2930	1·4	?

* Forbidden. † ν_3^{11} and ν_3^{10} with triple degeneracy removed; possibly also some $2\nu_4$. ‡ Possibly $2\nu_3$, $(2\nu_4 + \nu_3)$.

[3] Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

comparable peak heights in the region of the ν_3 absorption. A different scale was used to plot the spectrum of the ^{10}B-enriched sample below 900 cm.$^{-1}$ in order to avoid congestion of the diagram. Enrichment in ^{10}B enhances the relative peak height of the high-frequency component of the ν_4 doublet and has a similar effect on the shape of the ν_3 band. The position and shape of the forbidden ν_1 singlet remains unaltered. The frequencies and relative intensities of the absorption maxima are given more precisely in the Table which also compares the present results with those of Coté and Thompson.[3]

DISCUSSION

A molecule or ion containing n atoms has $3n-6$ normal modes of vibration. For a regular tetrahedral ion (symmetry T_d), there are nine modes distributed as follows: (1) a single vibration ν_1 of symmetry class A_1, Raman-active only; (2) a doubly degenerate deformation ν_2 of class E, Raman-active only; (3) a triply degenerate vibration ν_3 (class F_2), active in both Raman and infrared regions; and (4) a triply degenerate deformation ν_4 (class F_2) active in both Raman and infrared regions. These modes are illustrated in Fig. 2.

An isolated BF_4^- ion has zero dipole moment. As the ν_1 and ν_2 modes leave this moment unchanged they are forbidden infrared vibrations. The two triply degenerate modes ν_3 and ν_4, however, confer a resultant dipole on the ion and are thus infrared-active. Moreover, since the central atom moves in both these modes the frequency of ν_3 and ν_4 should, in principle, depend on the isotopic mass of the boron atom, though the shift in frequency might be too small to be resolved. If the tetrahedral ion is placed in a crystal field of lower symmetry the symmetrical ν_1 breathing frequency might be sufficiently distorted to permit weak absorption. Similarly, in a non-cubic field the co-ordinates x, y, and z in Fig. 2 are no longer arbitrarily interchangeable since motion along each axis is subject to a different potential field, *i.e.*, the vibrations are no longer degenerate. Potassium tetrafluoroborate has orthorhombic crystal symmetry, D_{2h}^{16}–*Pnma* with $a = 7{\cdot}85$, $b = 5{\cdot}68$, and $c = 7{\cdot}37$ Å,[4] and it is of interest to establish whether this reduction in symmetry is sufficient to remove the threefold degeneracy of the ν_3 and ν_4 modes.

Coté and Thompson [3] pointed out that the observed splittings of the ν_3 and ν_4 bands were consistent with the Teller–Redlich product rule for isotope effects,[1] but that the ν_3 band appeared to be split into at least four components and that the peak heights of the two ν_4 components were not in the ratio 1 : 4 as expected from the isotopic abundance ratio of boron-10 and -11. Difficulties were also encountered in attempting to explain the appearance of the bands exclusively in terms of removal of vibrational degeneracy and they were unable to decide between the two alternative interpretations. The present results resolve this difficulty by indicating that the two effects occur simultaneously. This leads to the following interpretation of the infrared spectrum of potassium tetrafluoroborate:

(1) The intense, polarized Raman line observed [5] at 769 cm.$^{-1}$ clearly corresponds to the ν_1 mode. This is a forbidden transition in the infrared region but is weakly [1] permitted in crystalline potassium tetrafluoroborate because of the perturbing influence of the crystal field on the tetrahedral BF_4^- ion. As the boron atom does not move in this mode (Fig. 2) its isotopic mass is unimportant and the absorption occurs as a single, narrow band at 773 cm.$^{-1}$ independently of the abundance ratio ^{10}B : ^{11}B.

(2) The doubly degenerate ν_2 mode has been observed [5] as a weak Raman line at 353 cm.$^{-1}$. It falls outside the wavelength region investigated here and, in the absence of a distorting crystal field, is forbidden in the infrared region. No overtones or combinations of this band were observed.

(3) The triply degenerate ν_3 mode occurs in the Raman spectrum [5] as a doublet at 984, 1016 cm.$^{-1}$. The structure of the band is more complex in the infrared region and appears to have about six incompletely resolved components. Increase in the ^{10}B : ^{11}B ratio decreases the absorption near 1038 and 1063 cm.$^{-1}$ and increases it near 1135 and

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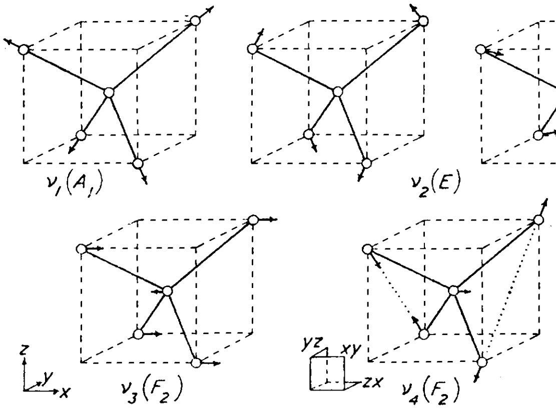
[4] Hoard and Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985.

[5] Goubeau and Bues, *Z. anorg. Chem.*, 1952, **268**, 221.

1158 cm.$^{-1}$. Some of the structure is therefore due to isotope doubling. Superimposed on this is the effect of the crystal field in removing the vibrational degeneracy so that a total of six components is expected. It is unlikely that the intensities of the originally degenerate modes will be equal since this depends on the extent of the distortion due to the field in each direction. For this reason it may well prove impossible to increase the resolution within the band or to observe all three modes and their isotopic doublets as individual maxima.

A further complicating factor must be considered, *viz.*, the accidental degeneracy between $2\nu_4$ and ν_3. The values of ν_4 in the Table being used, the calculated values for $2\nu_4$ are 1050 or 1060 and 1072 or 1084 cm.$^{-1}$. There is thus the possibility that some of the structure in the ν_3 band is due to enhanced absorption of the ν_4 overtone. Should these frequencies coincide exactly with any of the three pairs of originally degenerate ν_3 vibrations then there is also the possibility of Fermi resonance since the symmetry class of the upper state of $2\nu_4$ is $(F_2 + A_1 + E)$.

FIG. 2. *Normal modes of vibration for a tetrahedral ion* MX_4^-.



$\nu_3(F_2)$ is three degenerate modes involving displacements along the *x* axis or the *y* axis or the *z* axis.
$\nu_4(F_2)$ is three degenerate modes involving displacements along diagonals in the *yz* or the *xy* or the *zx* face.

(4) The ν_4 mode, observed at 524 cm.$^{-1}$ in the Raman spectrum,[5] occurs as a doublet in the infrared region. Enrichment in ^{10}B increases the peak height of the high-frequency component and establishes that the doublet arises from an isotope effect. Mixtures of normal and enriched potassium tetrafluoroborate have relative peak heights intermediate between the two extremes shown in Fig. 1. The separation is 11—12 cm.$^{-1}$ (cf. Coté and Thompson,[3] 13 cm.$^{-1}$). The fact that the ratio of peak heights (or band areas) is not 1 : 4 for the normal compound and 9 : 1 for the enriched sample does not conflict with the assignment of the doublet as an isotope effect for, even with a simple compound such as gaseous boron trifluoride, the intensity ratio of doublets in the unenriched compound is not 1 : 4 but is similar to that shown for ν_4 in Fig. 1.

The symmetrical contours of each component of the doublet indicates that there is no removal of vibrational degeneracy for this mode. This is presumably because each of the deformations involves displacements along parallel faces of the circumscribing cube but in diagonally opposite directions so that the *x*, *y*, and *z* components of the crystal field become, in a sense, averaged out. On the other hand, the three ν_3 vibrations can be considered as involving displacement along the *x*, or the *y*, or the *z* direction of the crystal field so that each is affected differently from the other two.

(5) The bands near 1300 cm.$^{-1}$ are assigned as $(\nu_1 + \nu_4)$, the agreement between calculated and observed frequencies being particularly good for the enriched sample:

1303 and 1315 cm.$^{-1}$, compared with the observed 1305 and 1312 cm.$^{-1}$. Enrichment in ^{10}B enhances the peak height of the high-frequency component as expected. The bands near 1650 cm.$^{-1}$ can be assigned to the combination ($\nu_3 + \nu_4$). Thus, for the enriched sample, the averaged frequency for ν_4 is 535 cm.$^{-1}$; subtraction of this from the frequencies near 1650 gives for the three ν_3 bands 1086, 1115, and 1135 cm.$^{-1}$, which are close to three of the observed ν_3 frequencies. Agreement for the normal sample is less satisfactory because of the poor resolution of the peaks near 1650 cm.$^{-1}$. The weak absorption at about 2340 cm.$^{-1}$ can be assigned either as $2\nu_3$ or as ($\nu_3 + 2\nu_4$).

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