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Abstract

Full Text

PHYSICAL CHEMISTRY

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VIBRATIONAL SPECTRA OF ALKALI-METAL FLUOROBERYLLATES OF THE TYPE $M_2\mathrm{BeF}_4$

The crystal lattices of fluoroberyllates of the type $M_2\mathrm{BeF}_4$ are built from tetrahedral anions BeF_4^{2-}, linked by alkali-metal cations (^{1}). A regular tetrahedron BeF_4^{2-} should possess four normal vibrations, two of which (F_2) will be active in the absorption spectrum, and all four active in the Raman spectrum. One of the bands of the tetrahedral ion (A_1), appearing in the Raman spectrum, should be strongly polarized, while the other three (E and $2F_2$) should be depolarized.

Fig. 1. Infrared absorption spectra of fluoroberyllates in the region 300-400 cm^{-1} (CsI prism) (A), and in the region 400-1000 cm^{-1} (KBr and NaCl prisms) (B)

The vibrational spectra of fluoroberyllates $M_2\mathrm{BeF}_4$ have not previously been studied in detail. Pecok and Sharp (^{2}) recorded the infrared spectrum of $K_2\mathrm{BeF}_4$ in the region 400-1000 cm^{-1} and found an intense band near 800 cm^{-1}, which split into two components. They assigned it to the triply degenerate stretching vibration of BeF_4^{2-}. Woodward attempted to record the Raman spectrum of $K_2\mathrm{BeF}_4$ in solution (^{3}). However, he did not succeed in detecting bands corresponding to the BeF_4^{2-} ion.*

We studied the infrared absorption spectra of $\mathrm{Li_2BeF_4}$, $\mathrm{Na_2BeF_4}$, $K_2\mathrm{BeF}_4$, $\mathrm{Rb_2BeF_4}$, and $\mathrm{Cs_2BeF_4}$ in the region 300-1000 cm^{-1}. The substances were recorded in the solid state as suspensions in vaseline oil. In the region 300-400 cm^{-1} the spectra were recorded with an IKS-11 single-beam spectrometer with a CsI prism; in the region 400-1000 cm^{-1}, with an IKS-14 double-beam spectrometer with KBr and NaCl prisms. The infrared absorption spectra are

Fig. 2. Schematic cross section of the cuvette with the specimen for recording the Raman spectrum of solid K_2BeF_4

Figure 2: Fig. 2. Schematic cross section of the cuvette with the specimen for recording the Raman spectrum of solid K_2BeF_4

Fig. 3. Raman spectrum of K_2BeF_4

Figure 3: Fig. 3. Raman spectrum of K_2BeF_4

shown in Fig. 1.

In addition, we investigated the Raman spectrum of solid K_2BeF_4 using a spectrometer with gratings of the DFS-12 type. A low-pressure mercury lamp of the DRS-600 type was used as the source of the exciting line ($\lambda = 4358$ Å). During the recording, a liquid filter with a concentrated solution of KNO_2 was used. For recording the Raman spectrum, the following method of sample preparation was developed. Molten K_2BeF_4 was distributed along the walls of a quartz test tube by rotating the latter, so that upon cooling— of the melt an inner cone was formed (Fig. 2). The test tube was placed with its open end toward the condenser. This method makes it possible to obtain considerably better results than when recording in conical glass cuvettes with double walls. After completion of the recording, K_2BeF_4 was analyzed for beryllium and silicon content. The silicon content in the specimen did not exceed 0.1%; the beryllium content did not change and corresponded to that calculated for K_2BeF_4. The Raman spectrum of K_2BeF_4 is shown in Fig. 3.

Fig. 2. Schematic cross section of the cuvette with the specimen for recording the Raman spectrum of solid K_2BeF_4

Fig. 3. Raman spectrum of K_2BeF_4

As follows from Fig. 1, potassium fluoroberyllate has two intense bands in the absorption spectrum (386 cm^{-1} and about 800 cm^{-1}). Both of these bands (ν_4 and ν_3) should be assigned to triply degenerate vibrations (F_2), the first being a deformation-vibration band and the second a stretching one. In the Raman spectrum there is a single intense band at 560 cm^{-1} (Fig. 3), which without doubt should be assigned to the totally symmetric vibration (A_1). In addition, in the Raman spectrum a weak ν_4 band at 388 cm^{-1} is clearly observed. The other two theoretically possible bands are apparently very weakened; their intensities do not exceed the noise level. By repeated recording, a very weak triply degenerate ν_3 band is detected at 800 cm^{-1}. The doubly degenerate ν_2

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* Obukhov-Denisov and co-workers (4) likewise did not succeed in recording the Raman spectrum of glassy BeF_2. On this basis they conclude that the Be–F bonds are predominantly ionic.

band is located, possibly, at 260 cm^{-1}.

The band of the triply degenerate stretching vibration (ν_3) in the absorption spectrum of K_2BeF_4 is noticeably asymmetric. In addition to the principal maximum at 805 cm^{-1}, it has a second maximum at 835 cm^{-1}. Such splitting of a triply degenerate band can apparently be explained by some lowering of the symmetry of the BeF_4^{2-} ion in the crystal field: namely, from the symmetry of the group T_d to the symmetry C_{3v}. In accordance with this, a weak band is found at 560 cm^{-1}, exactly corresponding to the totally symmetric band ν_1 in the Raman spectrum of K_2BeF_4. An analogous splitting of the frequency ν_3 probably also exists in the spectra of cesium and rubidium fluoroberyllates. These compounds also show weak bands (ν_1) in the region of 560 cm^{-1} (551 cm^{-1} for Rb_2BeF_4 and 540 for Cs_2BeF_4).

The asymmetry of the ν_4 band (deformation vibration F_2) in the spectra of potassium, rubidium, and cesium fluoroberyllates (Fig. 1) is not as sharply expressed as in the case of the ν_3 bands; this is possibly explained by the lower intensity of the ν_4 bands, as well as by the lower quality of recording on the single-beam spectrometer. The point group of symmetry C_{3v} for the BeF_4^{2-} ion is consistent with the results of X-ray determinations of the space group of the crystal lattices of fluoroberyllates. According to these determinations, the fluoroberyllates of K, Rb, and Cs are built according to the type β-K_2SO_4 (H_{16}); the space group is D_{2h}^{16} (Pnma) and $z = 4$ (5–7). In the case of such a space group, in the unit cell there are two groups of "sites" (special positions) with symmetry C_i and multiplicity 4, and one group of sites with symmetry C_s and multiplicity 4 (8). Thus, the BeF_4^{2-} ions can occupy in the lattice only positions with the point group C_s, which is a subgroup of the group C_{3v}.

In the lattice of sodium fluoroberyllate there occurs, in all probability,

a more substantial distortion of the BeF_4 tetrahedron than in the lattices of the fluoroberyllates of K, Rb, and Cs (see Fig. 1b). However, in the case of Na_2BeF_4 as well (olivine structural type, space group D_{2h}^{16}, $z = 4$ (5,9)), the symmetry of the BeF_4^{2-} ion apparently belongs to the point group C_{3v}, since the ν_3 band is split into only two peaks, although both are very intense.

It is interesting that in the spectrum of Na_2BeF_4 a splitting of the totally symmetric band ν_1 into two bands of equal intensity is also observed (Fig. 1). Such splitting may occur as a result of Fermi resonance if, for example, the doubly degenerate vibration ν_2 in this compound lies near 280 cm^{-1}, and its overtone $2\nu_2$ near 560 cm^{-1}, i.e., coincides with the frequency (in K_2BeF_4 ν_2 is assumed to be at 260 cm^{-1}).

In the spectrum of Li_2BeF_4 the frequency ν_3 clearly shows three maxima: 785 cm^{-1}, 809 cm^{-1}, and 864 cm^{-1}. Consequently, in the lithium fluoroberyllate lattice the BeF_4^{2-} ion has lower symmetry than in the lattices of the other fluoroberyllates, namely C_{2v}, C_s, or C_1.

The frequencies appearing in the spectra of fluoroberyllates M_2BeF_4 are collected in Table 1.

Table 1

Vibrational frequencies of BeF_4^{2-} in the spectra of fluoroberyllates of the type M_2BeF_4

	ν_1 (A_1)	ν_2 (E)	ν_3 (E_2)	ν_4 (F_2)	ν_5 $(\nu_3 + \nu_1)$	ν_6	ν_7 (?)
Li	(616)		785, 809, 864	364, 330			
Na	550, 567		767, 859	376			975
K	560	(260)	805, 835	386	951	914	
Rb	551		797, shoulder	379	937	891	977
Cs	540		780, shoulder	372	920	892	972

In addition to the frequencies of normal vibrations considered above, several weak frequencies in the region 900—1000 cm^{-1} also appear in the IR absorption spectra of the fluoroberyllates; these are evidently overtones or combination frequencies. The most intense of them, the frequency ν_5, which appears in the spectra of potassium, rubidium, and cesium fluoroberyllates, is well interpreted as the combination frequency $\nu_3 + \nu_1$.

As follows from the data of Table 1, the positions of the normal-vibration frequencies of the BeF_4^{2-} ion change little in going from Cs to Li.

A calculation in the simple valence-force approximation (starting from the frequency ν_1) gives for the valence-force constant of the Be—F bond the value: $K_{\text{Be–F}} = 3.5 \cdot 10^{-5}$ dyn/cm. This value may be compared with the corresponding values of the valence-force constants obtained by the same method for the tetrahedra BF_4^{1-} and CF_4: $6.91 \cdot 10^{-5}$ dyn/cm and $9.14 \cdot 10^{-5}$ dyn/cm, respectively ([3]). It is noteworthy that the change in the force constants of the M—F bonds in the series beryllium—carbon occurs almost linearly with the change in the formal charge of the central atom.

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