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Abstract

Full Text

Physical Chemistry

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Investigation of the Vibrational Spectra of the Ions $Be(NH_3)_4^{2+}$ and $Be(H_2O)_4^{2+}$

Earlier we reported the results of an investigation of the vibrational spectra of crystalline fluoroberyllates of the type M_2BeF_4, containing tetrahedral BeF_4^{2-} ions (1). For this ion the following values of the normal-vibration frequencies were obtained: ν_1 (A_1) 560 cm^{-1}; ν_2 (E) 260 cm^{-1} (?); ν_3 (F_2) 800 cm^{-1} and ν_4 (F_2) 386 cm^{-1}; the force constant of the Be—F bond, calculated in the simple valence-force approximation, proved to be equal to: $k_{\text{Be–F}} = 3.5 \cdot 10^5$ dyn/cm.

Subsequently, one of the authors of the present work, together with K. N. Semenenko, investigated the vibrational spectra of chloroberyllates of the type M_2BeCl_4 (2). For the tetrahedral $BeCl_4^{2-}$ ion the following values of the normal-vibration frequencies were found: ν_1 (A_1) 294 cm^{-1}; ν_3 (F_2) 540 cm^{-1} and ν_4 (F_2) 210 cm^{-1}. The force constant of the Be—Cl bond proved to be equal to $1.81 \cdot 10^5$ dyn/cm. The force constants of the Be—F and Be—Cl bonds for the linear molecules $BeCl_2$ and BeF_2 (in the vapor), found by Büchler and Klemperer (3), have somewhat larger values; they are respectively equal to $2.9 \cdot 10^5$ dyn/cm and $5.0 \cdot 10^5$ dyn/cm. The decrease in the force constants of the beryllium—halogen bonds on going from the linear molecules Be $_2$ to the tetrahedral Be $^{2-}_4$ ions is evidently explained by a change in the hybridization of the valence orbitals of beryllium: instead of *sp*, *sp*^{3} orbitals are formed.

Fig. 1. Infrared absorption spectra of crystalline $Be(NH_3)_4Cl_2$ (a) and $Be(ND_3)_4Cl_2$ (b)

The present work is devoted to a further study of the vibrational spectra of tetrahedral beryllium ions: $Be(NH_3)_4^{2+}$ and $Be(H_2O)_4^{2+}$. The principal objects of investigation were crystalline beryllium chloride tetraammine and beryllium sulfate tetrahydrate.*

Beryllium sulfate was twice recrystallized from an aqueous solution. Crystals

Fig. 2. Combination-scattering spectrum of crystalline $Be(NH_3)_4Cl_2$

Figure 2: Fig. 2. Combination-scattering spectrum of crystalline $Be(NH_3)_4Cl_2$

of beryllium chloride tetraammine sufficiently large for recording combination-scattering spectra were obtained by slow evaporation of its solution in liquid ammonia at room temperature.

Infrared absorption spectra of crystalline $Be(NH_3)_4Cl_2$ and $Be(H_2O)_4SO_4$ were recorded in the region 1800–270 cm^{-1} on IKS-14 spectrometers with NaCl and KBr prisms and on an IKS-12 with a CsI prism. The preparations were made in the form of suspensions in vaseline oil. For the purpose of assigning frequencies, infrared absorption spectra of crystalline $Be(ND_3)_4Cl_2$ and $Be(D_2O)_4SO_4$ were also recorded in the region 1800–270 cm^{-1}. The absorption spectra are given in Figs. 1 and 3. Combination-scattering spectra of the crystalline preparations were recorded on a spectrometer with gratings of the DFS-12 type. As the excitation source ($\lambda = 4358$ Å), a mercury lamp of the type DRS-600; the filter was a saturated solution of KNO_2. The crystalline samples were placed in a conical cuvette with double walls, which was fastened by the base of the cone toward the condenser lens. The combination-scattering spectra of the crystalline substances are shown in Figs. 2 and 4. In addition, combination-scattering spectra were recorded for concentrated aqueous solutions of beryllium sulfate, chloride, and nitrite. The concentration of beryllium sulfate in solution was 3 moles, the concentration of chloride 5 moles, and the concentration of nitrate 4 moles per 1 liter. The solutions were recorded in cuvettes 20 mm in diameter and 100 mm long.

Fig. 2. Combination-scattering spectrum of crystalline $Be(NH_3)_4Cl_2$

If the ions $Be(NH_3)_4{}^{2+}$ in the lattice of $Be(NH_3)_4Cl_2$ are regular tetrahedra, then in the absorption spectrum of $Be(NH_3)_4Cl_2$ two frequencies should appear, corresponding to vibrations of the BeN_4 tetrahedron, namely two frequencies of triply degenerate vibrations (F_2). In addition, bands corresponding to internal vibrations of the coordinated ammonia molecule should appear in the absorption spectrum. There should be three such vibrations with frequency below 1800 cm^{-1}. On the basis of the calculation carried out by Mitsuzima (^{5}) and of numerous experimental data obtained for various coordination compounds of ammonia (^{6}), in the absorption spectrum of $Be(NH_3)_4Cl_2$ the following bands can be assigned to the indicated three internal vibrations of ammonia: 1608 cm^{-1} $\delta(E)$;

Fig. 3. IR absorption spectrum of crystalline $BeSO_4 \cdot 4H_2O$ (*a*) and $BeSO_4 \cdot 4D_2O$ (*b*)

Table 1

* The structure of beryllium sulfate tetrahydrate was investigated by X-ray diffraction (^{4}).

Fig. 3. IR absorption spectrum of crystalline $BeSO_4 \cdot 4H_2O$ (a) and $BeSO_4 \cdot 4D_2O$ (b)

Figure 3: Fig. 3. IR absorption spectrum of crystalline $BeSO_4 \cdot 4H_2O$ (a) and $BeSO_4 \cdot 4D_2O$ (b)

Frequency values in the IR absorption spectra of $Be(NH_3)_4Cl_2$ and $Be(ND_3)_4Cl_2$ (cm^{-1})

Compound	δ(E)	δ(A)	δ(Rock)	ν_1(A)	ν_2(E)	ν_3(F_2)	ν_4(F_2)
	NH_3 bands	**NH_3 bands**	**NH_3 bands**	**BeN_4 tetrahedron bands**	**BeN_4 tetrahedron bands**	**BeN_4 tetrahedron bands**	**BeN_4 tetrahedron bands**
$Be(NH_3)_4Cl_2$	1608	1305	625	493	–	914	290
$Be(ND_3)_4Cl_2$	1176	1012	520	–	–	838804	278 (?)
νH/νD	1.37	1.29	1.20	–	–	1.09	1.04

1305 cm^{-1} δ(A) and 625 cm^{-1} δ(Rock). This assignment is confirmed by the observed magnitude of the isotopic shift. The ratio νH/νD for the ammonia bands under consideration is usually 1.30–1.37. As can be seen from the data of Table 1, the experimentally obtained values of νH/νD for the frequencies δ(E) and δ(A) fit well within these limits. The value of νH/νD for the frequency δ(Rock) is somewhat smaller than should have been expected; nevertheless, it is considerably greater than the maximum permissible value of νH/νD for the vibration frequencies of the BeN_4 tetrahedron (1.09 on going from ${Be(NH_3)_4}^{2+}$ to ${Be(ND_3)_4}^{2+}$).

The remaining two intense bands in the absorption spectrum of $Be(NH_3)_4Cl_2$ (914 and 290 cm^{-1}) should evidently be assigned to the triply degenerate vibrations of the BeN_4 tetrahedron. The magnitude of the isotopic shift ν_H/ν_D of the triply degenerate stretching vibration $\nu_3(F_2)$ is 1.09.

The only intense band observed in the Raman spectrum, 488 cm^{-1}, must evidently be assigned to the totally symmetric vibration of the BeN_4 tetrahedron. In the absorption spectrum this band corresponds to a very weak band at 493 cm^{-1}, which appears, apparently, as a result of a slight distortion of the tetrahedron in the crystal lattice. This phenomenon is matched by the asymmetric appearance of the $\nu_3(F_2)$ band in the IR spectrum of $Be(NH_3)_4Cl_2$. In the IR spectrum of $Be(ND_3)_4Cl_2$ this band is clearly split into two maxima (838 and 804 cm^{-1}).

The force constant of the Be—N bond, calculated in the simple valence-force approximation when each ammonia molecule is considered as a single mass ($M = 17$), is: $k_{\text{Be—N}} = 2.38 \cdot 10^5$ dyn/cm.

Fig. 4. Raman spectra of crystalline $BeSO_4 \cdot 4H_2O$ (a), aqueous solutions of $BeSO_4 \cdot 4H_2O$ (b), $BeCl_2 \cdot 4H_2O$ (c), and $Be(NO_3)_2 \cdot 4H_2O$ (d).

Figure 4: Fig. 4. Raman spectra of crystalline $BeSO_4 \cdot 4H_2O$ (a), aqueous solutions of $BeSO_4 \cdot 4H_2O$ (b), $BeCl_2 \cdot 4H_2O$ (c), and $Be(NO_3)_2 \cdot 4H_2O$ (d).

The Raman spectrum of $Be(H_2O)_4SO_4$, presented in Fig. 4, agrees satisfactorily with the spectrum of this compound studied earlier (^{7}). The authors of that study assign all the more or less intense bands of the spectrum to vibrations of the SO_4^{2-} ion (symmetry V_d). The absence in the spectrum of a sufficiently intense band that could be assigned to the totally symmetric vibration of the Be—O bonds of the $Be(H_2O)_4^{2+}$ tetrahedron was explained by the authors as a considerable weakening of it due to strong hydrogen bonds. At the same time, they found in the spectrum several weak bands that they could not assign to any definite type of vibration, including the bands 337, 571, and 698.5 cm^{-1}. Weak bands close in value are also observed in the spectrum we obtained: 335, 563, and 697 cm^{-1}.

Fig. 4. Raman spectra of crystalline $BeSO_4 \cdot 4H_2O$ (a), aqueous solutions of $BeSO_4 \cdot 4H_2O$ (b), $BeCl_2 \cdot 4H_2O$ (c), and $Be(NO_3)_2 \cdot 4H_2O$ (d).

The latter band appears in the IR absorption spectrum as a fairly intense band (690 cm^{-1}, see Fig. 3, Table 2), together with an even more intense band at 771 cm^{-1}. Both of these bands may be regarded as components of the triply degenerate stretching vibration of the Be—O bonds in the $Be(H_2O)_4^{2+}$ tetrahedron, which is possibly split as a result of lowering of the symmetry of the regular tetrahedron. The band at 335 cm^{-1} likewise corresponds to a band in the absorption spectrum (312 cm^{-1}). This band may be assigned to the triply degenerate deformation vibration of the Be—O bonds. The absence of splitting of this band in the spectra may be connected either with the poorer resolving power of the instrument (in the case of the IR spectrum, recorded on a single-beam IKS-12 spectrometer), or with the low intensity of the band (in the case of the Raman spectrum).

It should be noted that the 335 cm^{-1} band also appears in the Raman spectra of concentrated aqueous solutions of various beryllium salts, in which $Be(H_2O)_4^{2+}$ ions are also evidently present.

Along with this band, in the spectra of solutions there is always also a band near 550 cm^{-1}, found in the Raman spectrum of crystalline $Be(H_2O)_4SO_4$. In the spectra of beryllium nitrate and chloride solutions this band lies somewhat lower (533 cm^{-1}) than in the spectra of cry-

Table 2

Frequency values in the spectra of $Be(H_2O)_4SO_4$ and $Be(D_2O)_4SO_4$ (cm^{-1})

	H_2O bands	H_2O bands	SO_4-ion bands	SO_4-ion bands	SO_4-ion bands	SO_4-ion bands	BeO_4 tetrahedron bands	BeO_4 tetrahedron bands	BeO_4 tetrahedron bands	BeO_4 tetrahedron bands
	δ_{OH}	δ(Rock)	$\nu_1(A)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	$\nu_1(A)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
$Be(H_2O)_4SO_4$ (i-k)	1678 1660	670 651 —— 520	975	–	1121 1058	–	–	–	859 771	612 690
$Be(H_2O)_4SO_4$ (r.r.)	–	–	1000	505 412	1120 1063	618 593	563	–	781?697	735
$Be(D_2O)_4SO_4$ (i-k)	1240	490 440	962	507 412	1142 1067	613 589	–	–	850 767	660 602
ν_H/ν_D	1.35	1.20 —— 1.35	–	–	–	–	–	–	1.00 —— 1.05	1.03

crystalline and dissolved beryllium sulfate (563 and 550 cm^{-1}, respectively). This difference can be explained by the fact that in the spectra of the sulfate the indicated band is partly overlapped on both sides by very intense and broad bands of the sulfate ion, which makes it difficult to determine its position accurately. This same superposition of bands apparently considerably reduces its apparent intensity. Evidently, the indicated band can be assigned to the totally symmetric vibration of the $Be(H_2O)_4^{2+}$ tetrahedron. In the absorption spectra this band does not appear. It is noteworthy that in the spectrum of a beryllium nitrate solution, alongside the band at 533 cm^{-1}, another, less intense band appears (472 cm^{-1}). Its appearance in the spectrum evidently corresponds to the splitting of the doubly degenerate stretching vibration of the nitrate ion (1432 and 1341 cm^{-1}). Apparently, the bands at 472 and 1341 cm^{-1} belong to the ions $[Be(H_2O)_3NO_3]^{1+}$, which are present in the solution along with the ions $[Be(H_2O)_4]^{2+}$.

The force constant of the Be–O bond, calculated by considering the water molecules as a single mass for $\nu_1(A) = 533$ cm^{-1}, is $3.04 \cdot 10^5$ dyn/cm.

Thus, the values we have found for the force constants of the Be–N, Be–O, and Be–F bonds in the series of tetrahedral ions increase regularly: $2.38 \cdot 10^5$; $3.04 \cdot 10^5$; and $3.50 \cdot 10^5$ dyn/cm. On going from BeF_4^{2-} to $BeCl_4^{2-}$, the force constant of the bond decreases from $3.50 \cdot 10^5$ to $1.81 \cdot 10^5$ dyn/cm. Such behavior of the force constants corresponds to the regularity of the change in bond force constants observed upon successive change of the group number or period of one of the two atoms forming the bond (^{8}).

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Note: Figure translations are in progress. See original paper for figures.