being favored with increasing acidity. This is in agreement with the low ionization constant of nitric acid, which results in increasing concentrations of undissociated acid molecules at high molarities.[17] To investigate the effect of hydrogen ion, extractions were carried out from solutions of nitric acid and potassium nitrate, in which the formal nitrate ion concentration was held constant. The results (Fig. 3) again show D_{Hg} decreasing with increasing acid concentration. This behavior is as predicted from eq. 4, but the results do not rule out some other type of hydrogen ion effect.

Further evidence in favor of the formation of protonated species was, however, obtained from electrical migration experiments in nitric acid–potassium nitrate solutions under standard conditions. After an initial increase, the anionic fraction decreases with increasing acid concentration, as required by eq. 4. It is interesting that the cathode fraction increases smoothly with increasing acid concentration, which suggests that eq. 4 (or some analog) may be followed by eq. 5.

$$H_2[Hg(NO_3)_4] + HNO_3 \rightleftharpoons [H_3Hg(NO_3)_4]^+ + NO_3^- \quad (5)$$

Equations 4 and 5 imply that the mercury(II)–nitrate anionic species are stronger bases than nitrate ion itself; unfortunately there seems to be no data on the base strength of complexes against which to compare this conclusion.

TABLE I

MIGRATION OF TRACER MERCURY(II) IN AQUEOUS NITRIC ACID–POTASSIUM NITRATE SOLUTIONS

HNO_3 concn., *M*	KNO_3 concn., *M*	% Hg activity at anode after 4 hr.	% activity at cathode after 4 hr.
0.41	1.24	5.4	0.3
0.55	1.10	7.6	0.8
0.83	0.82	15.8	1.8
1.10	0.55	7.6	2.8
1.24	0.41	6.6	3.0
1.65	0	1.7	7.7

Acknowledgment.—We wish to thank the University of Nottingham for the award of a Research Studentship (to S. S. C.), and Mr. J. I. Bullock for carrying out the electrical migration experiments.

[17] See E. Hesford and H. A. C. McKay, *Trans. Faraday Soc.*, **54**, 573 (1958).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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Identification of Complex Ions of Niobium(V) in Hydrofluoric Acid Solutions by Raman and Infrared Spectroscopy

BY O. L. KELLER, JR.

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The Raman spectra of $K_2NbOF_5 \cdot H_2O$ dissolved in water and K_2NbF_7 dissolved in 1 to 50% HF are compared with the Raman spectra of crystalline $K_2NbOF_5 \cdot H_2O$ (which also can be considered as $K_2Nb(OH)_2F_5$), $CsNbF_6$, and K_2NbF_7 to show that the $NbOF_5^{2-}$ (or $Nb(OH)_2F_5^{2-}$) and NbF_6^- ions are present in these solutions. The Raman lines characteristic of the NbF_7^{2-} ion were not seen in any of the solutions. The infrared spectrum of $K_2NbOF_5 \cdot H_2O$ was recorded from 650 to 4000 cm.$^{-1}$ to gain information on whether the $NbOF_5^{2-}$ or $Nb(OH)_2F_5^{2-}$ ion is present in the crystals and the solutions. The infrared and Raman spectra are found to be consistent with the presence of $NbOF_5^{2-}$ ions in the crystals, but they are not found to be consistent with the presence of $Nb(OH)_2F_5^{2-}$ ions.

Introduction

The identification of ionic species in concentrated electrolytes presents a difficult problem. Thermodynamic methods cannot be used in many cases because applicable activity coefficients are not available. Kinetic methods, such as conductance, are less widely applicable than thermodynamic methods. Direct identification of complex ions by molecular spectroscopy often requires a detailed theoretical treatment. If some of the characteristic frequencies of the ion are too weak to be seen, or if there is a mixture of complex ions, such a treatment is difficult. Identification of species in solution can be accomplished simply, however, if direct comparison can be made between spectra of the solutions and spectra of crystals of known composition and structure.

Niobium double fluoride complexes found in 0 to 50% HF are identified in this investigation by comparing the Raman spectra of the solutions with Raman spectra of crystals of $CsNbF_6$, K_2NbF_7, and $K_2NbOF_5 \cdot H_2O$.

Infrared spectra of $K_2NbOF_5 \cdot H_2O$ crystals also were obtained to gain information on whether the $NbOF_5^{2-}$ or $Nb(OH)_2F_5^{2-}$ ion is present in the crystals and the solutions.

Experimental

Raman spectra were obtained with a Cary Model 81 spectrophotometer. The 4358 Å. mercury line was isolated with a filter solution of Cyasorb U.V. 24[2] and ethyl violet in *n*-propyl alcohol solution.

The infrared spectra were obtained with a Perkin-Elmer Model 221 spectrophotometer equipped with the prism grating interchange. A polystyrene film was used for the calibration.

The cells used for the Raman crystal spectra of K_2NbF_7 and

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[2] American Cyanamid Company.

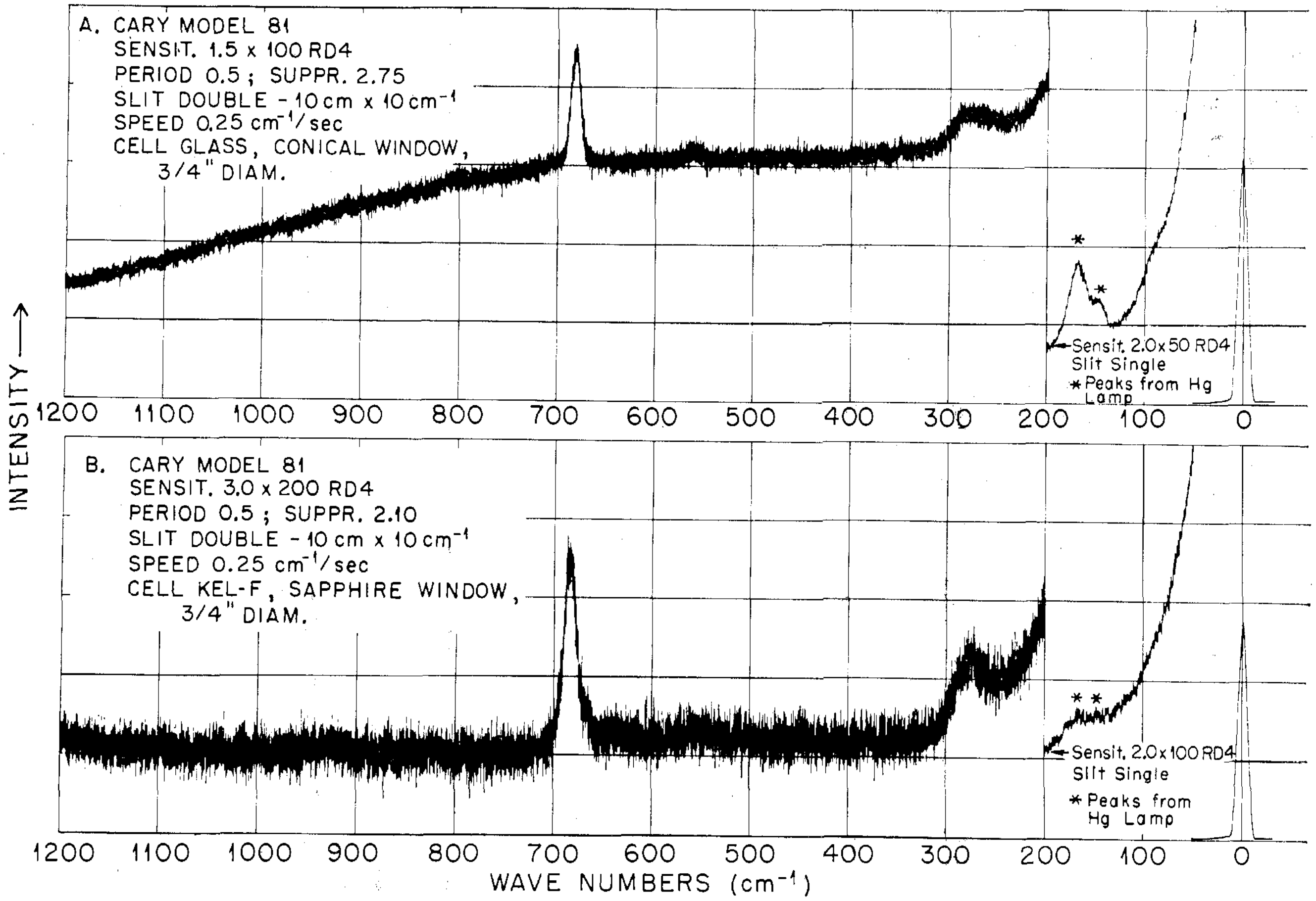

Fig. 1.—A: Raman spectrum of crystalline $CsNbF_6$. B: Raman spectrum of K_2NbF_7 in 40% HF solution.

$CsNbF_6$ had conical windows to allow more of the Raman scattered light to enter the monochromator.. The cell used for $K_2NbOF_5 \cdot H_2O$, which crystallizes in the form of thin plates, had a flat window.

For the HF solutions a Raman cell was made from Kel-F[3] and fitted with a sapphire end window. The wall of the tube was machined to a thickness of about 15 mils to make it more transparent. The dimensions of this cell were those of the Cary 19-mm. cell.

Analysis.—Analyses of all crystals and solutions were carried out by L. J. Brady and W. R. Laing of the ORNL Analytical Division. The fluoride analysis was made by pyrolyzing the sample with moist oxygen at 1000° using a tungstic oxide catalyst. The HF released was titrated. To analyze for oxygen, the compound was completely fluorinated with $KBrF_4$. The gases released were passed through liquid nitrogen traps, and the oxygen was measured manometrically. By passing the gases over heated copper turnings, the oxygen was removed to determine a blank. The water of hydration was determined by heating the sample in anhydrous Na_2CO_3 at 500° in a stream of nitrogen. To analyze for niobium, the sample was fumed with sulfuric acid, then heated with sulfurous acid to bring about complete hydrolysis. The Nb_2O_5 was filtered, ignited at 1000°, and weighed.

Materials.—All commercial chemicals employed were reagent grade.

$CsNbF_6$ was prepared[4] by adding an equivalent amount of CsF to Nb metal dissolved in 50% HF. The $CsNbF_6$ was recrystallized twice from 35% HF.

Anal. Calcd. for $CsNbF_6$: Nb, 27.3; F, 33.5. Found: Nb, 28.1; F, 32.4.

K_2NbF_7 was obtained from the Kawecki Chemical Company. The crystal sample run in the Raman was analyzed.

Table I

Vibrational Spectra of Crystals

Compound	Raman freq.[a] (Δ cm.⁻¹ from 4358 Å. Hg)		Infrared bands (cm.⁻¹)
$CsNbF_6$	280 (m)	$[\nu_5](F_{2g})$	
	562 (w)	$[\nu_2](E_g)$	
	683 (s)	$[\nu_1](A_{1g})$	
K_2NbF_7	388 (m)		
	630 (vs) (sharp)		
	782 (w)		
$K_2NbOF_5 \cdot H_2O$	295 (m)		738
	600 (vw)		932
	935 (m)		1083
			1626 $(\nu_2)^b$
			3572 $(\nu_1)^b$
			3643 $(\nu_3)^b$

[a] (vw), very weak; (w), weak; (m), medium; (s), strong; (vs), very strong. [b] Water of hydration.

Anal. Calcd. for K_2NbF_7: Nb, 30.6; F, 43.7. Found: Nb, 30.4; F, 42.1.

The $K_2NbOF_5 \cdot H_2O$ used for the Raman crystal spectra was obtained from Kawecki Chemical Company and recrystallized from 1% HF.

Anal. Calcd. for $K_2NbOF_5 \cdot H_2O$: Nb, 30.9; F, 31.6; O, 5.3; H_2O, 6.0. Found: Nb, 30.8; F, 32.7; O, 4.1; H_2O, 5.9.

The $K_2NbOF_5 \cdot H_2O$ used for the infrared spectra was from Kawecki Chemical Company. The crystals were ground in a mortar. Particle sizes between 44 and 74 μ were collected using standard sieves. The powder was dried at 35° in a vacuum oven for 30 min. to remove surface moisture. The Nujol mull technique was employed with KBr windows. The Nujol was dried with sodium metal. The powder was analyzed for water of hydration.

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[3] Minnesota Mining and Manufacturing Company.

[4] C. W. Balke and E. F. Smith, *J. Am. Chem. Soc.*, **30**, 1637 (1908).

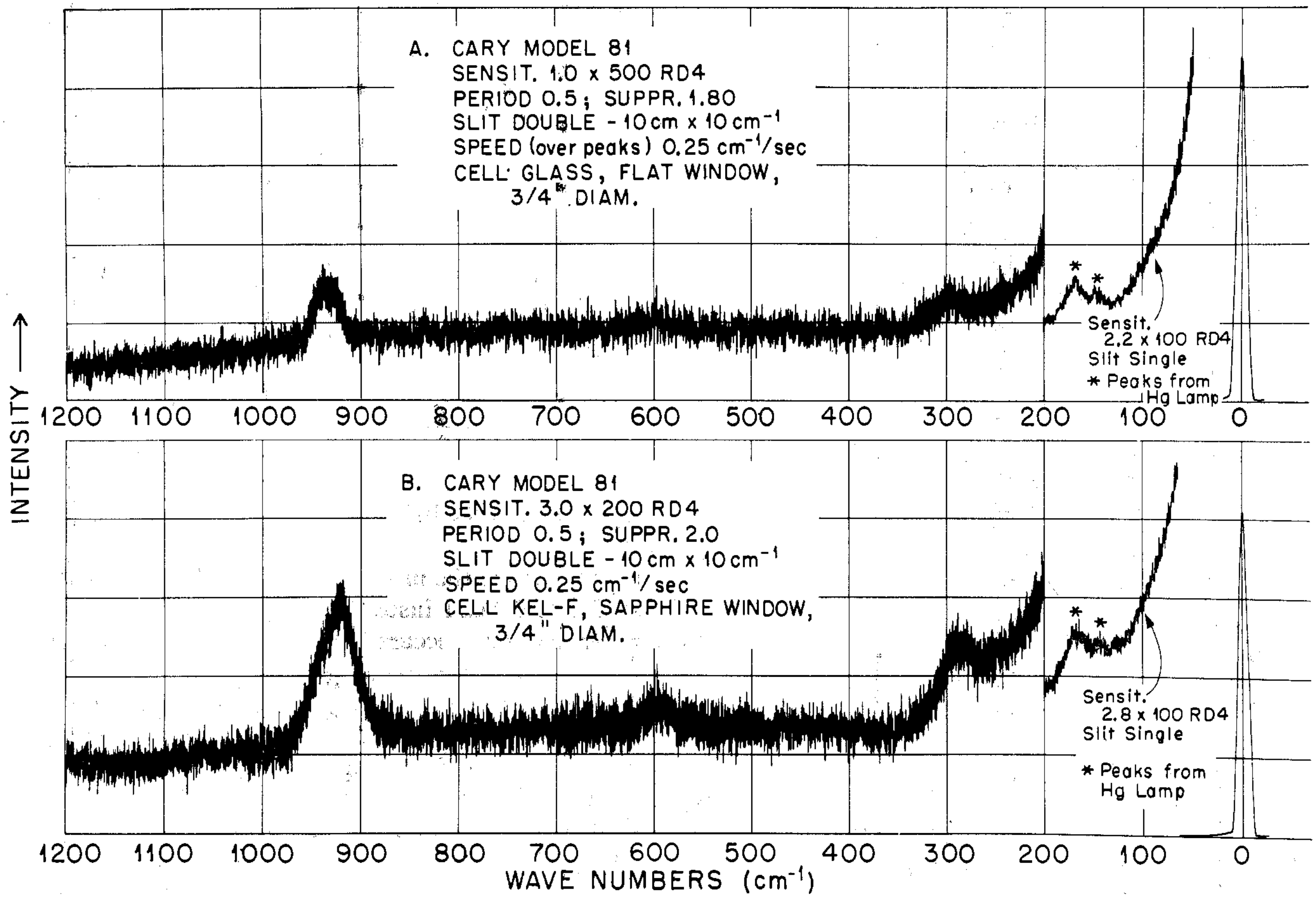

Fig. 2.—A: Raman spectrum of crystalline $K_2NbOF_5 \cdot H_2O$. B: Raman spectrum of K_2NbF_7 in 1% HF solution.

Anal. Calcd. for $K_2NbOF_5 \cdot H_2O$: H_2O, 6.0. Found: H_2O, 5.9.

The solutions for Raman study were made by dissolving $K_2NbOF_5 \cdot H_2O$ in water or K_2NbF_7 in HF solutions. Dust was removed from solutions containing up to 10% HF by passing them through a Millipore filter with a pore size of 4500 Å. Solutions more concentrated in HF were centrifuged in polyethylene tubes for several hours.

Results and Discussion

The results of the Raman studies are given in Tables I and II. Figures 1 and 2 allow direct comparison of the spectra of crystalline $CsNbF_6$ and $K_2NbOF_5 \cdot H_2O$ with typical solution spectra. The spectra are somewhat obscured from about 130 to 210 cm.$^{-1}$ by lines from the mercury lamp.

We assume for the moment that crystalline $CsNbF_6$ and $K_2NbOF_5 \cdot H_2O$ contain the NbF_6^- and $NbOF_5^{2-}$ ions, respectively (see below). A comparison of the Raman lines characteristic of the crystals with the lines found for the solutions then shows that the $NbOF_5^{2-}$ ion is present in solutions containing up to about 35% HF, and that NbF_6^- ion is present in solutions containing at least about 25% HF.

No lines characteristic of K_2NbF_7 (Table I) appear in the solutions.

The $NbOF_5^{2-}$ line at 935 cm.$^{-1}$ in the crystals shifts with a change in environment. Since the 935 cm.$^{-1}$ line is infrared active (Fig. 3), the vibration involves a change in dipole moment. Therefore dipole–dipole interactions with the environment can cause a shift in the position of this band. In distinction, the vibrations of octahedral NbF_6^- active in the Raman are not active

TABLE II

RAMAN SPECTRA OF K_2NbF_7 IN HF SOLUTIONS

	Solvent								
Compounds	H_2O[a]	1% HF	10% HF	20% HF	25% HF	30% HF	35% HF	40% HF	50% HF
mg. of Nb/ml.	31.3	37.4	31.2	20.8	20.3	21.6	20.4	36.1	56.9
$NbOF_5^{2-}$	290 (m)[c]	290 (s)	285 (m)	280 (m)[b]	275 (m)[b] (br)	...	...	...	...
	595 (w)	595 (w)	595 (w)	...	...	...	...	...	...
	920 (s)	920 (s)	925 (s)	930 (m)	935 (m)	935 (w) (br)	935 (vvw) (br)	...	...
NbF_6^-	...	...	...	...	...	280 (m)[b]	275 (m)[b]	275 (m)	280 (s)
	...	...	...	...	...	...	...	...	...
	...	...	...	...	685 (w)	685 (m)	686 (m)	685 (vs)	685 (vs)

[a] $K_2NbOF_5 \cdot H_2O$ was dissolved in H_2O. [b] Appears only slightly above background of exciting line. [c] (vvw), very very weak; (w), weak; (m), medium; (s), strong; (vs), very strong; (br), broad.

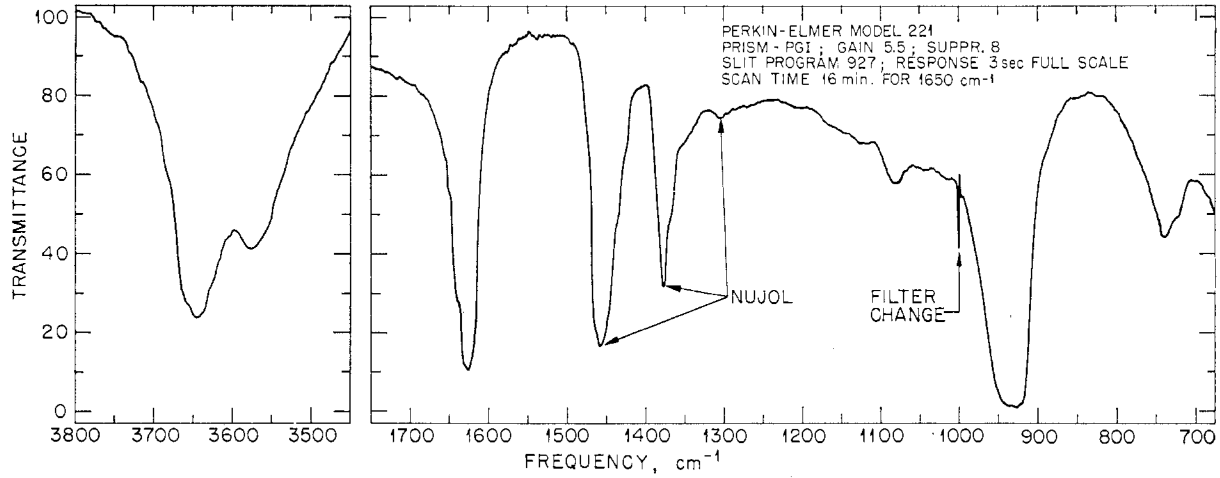

Fig. 3.—Infrared spectrum of crystalline $K_2NbOF_5 \cdot H_2O$.

in the infrared and the lines of NbF_6^- shift only a few wave numbers.

The presence of the complex ions NbF_6^- and $NbOF_5^{2-}$ in $CsNbF_6$ and $K_2NbOF_5 \cdot H_2O$, respectively, has not been established by X-ray analysis. Our spectra therefore will be analyzed to gain information about the complex ions present in these crystals.

The formula of $CsNbF_6$ established by chemical analysis suggests that these crystals contain NbF_6^- ions. The NbF_6^- ion would be expected to have the niobium atom at the center of a regular octahedron with the fluorine atoms at the corners. This structure belongs to point group O_h. Herzberg[5] gives diagrams of the normal vibrations. The $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$ vibrations are Raman active. The observed spectrum of NbF_6^- is similar to those of molecules of symmetry O_h. For example, MoF_6, which is isoelectronic with NbF_6^-, shows three frequencies in its Raman spectrum[6]: $\nu_1 = 741$, $\nu_2 = 645$, and $\nu_5 = 322$. Since Mo has an atomic number one higher than Nb, the MoF_6 frequencies are expected to be higher. The relative intensities of the three lines in the NbF_6^- spectrum are as expected for symmetry O_h.

Chemical analysis cannot decide between the alternate structures $K_2NbOF_5 \cdot H_2O$ and $K_2Nb(OH)_2F_5$. Since, however, $K_2NbOF_5 \cdot H_2O$ is isomorphous with $K_2TiF_6 \cdot H_2O$, it is believed[7] that the octahedral $NbOF_5^{2-}$ ion is present.

In order to gain further information on whether $NbOF_5^{2-}$ or $Nb(OH)_2F_5^{2-}$ is present in the crystals and the solutions, the infrared spectrum of $K_2NbOF_5 \cdot H_2O$ was taken from 650 to 4000 cm.$^{-1}$. The bands found are given in Table I and Fig. 3.

If $NbOF_5^{2-}$ ion is present in the crystals, then water of hydration also is present, and a frequency in the range characteristic for the bending mode (ν_2) of water should be seen. If, on the other hand, the $Nb(OH)_2F_5^{2-}$ ion is present, the mode ν_2 of H_2O will not appear, but an Nb–OH bend instead. The bending mode of the water molecule occurs in the vapor[8] at 1595 cm.$^{-1}$. In liquid water ν_2 occurs[9] at 1650 cm.$^{-1}$ and in hydrates[9-12] in the region 1585 to 1630 cm.$^{-1}$. If a heavier atom is substituted for one of the hydrogens in water, ν_2 is expected to occur at a lower frequency. For example, the bending mode[13] of HDO is 1403 cm.$^{-1}$ and for HTO it[14] is 1324 cm.$^{-1}$. Similarly, the bend[15] in $B(OH)_3$ is at 1196 cm.$^{-1}$ and that[16] of $In(OH)_3$ is at 1161 cm.$^{-1}$. Therefore the Nb–OH bend is expected to occur at frequencies considerably below 1600.

The band at 1626 cm.$^{-1}$ seen in the spectrum of $K_2NbOF_5 \cdot H_2O$ therefore arises from the bending mode of water of hydration rather than an Nb–OH bend.

Further evidence on the structure of $K_2NbOF_5 \cdot H_2O$ may be obtained by comparing the observed infrared and Raman spectra of this compound with the spectra expected for an octahedral $NbOF_5^{2-}$ ion and the spectra expected for two probable structures for $Nb(OH)_2F_5^{2-}$ ion.

An $NbOF_5^{2-}$ ion of octahedral structure would belong to point group C_{4v}. For this symmetry there are four normal vibrations in species A_1, none in A_2, two in B_1, one in B_2, and four (doubly degenerate) in E. A_1 and E are both infrared and Raman active whereas B_1 and B_2 are Raman active only. Symmetry considerations therefore allow eleven Raman fundamentals to appear. In fact, only three Raman lines are observed. It is readily noted, however, that these three lines form a spectrum which bears a marked resemblance to the spectrum of NbF_6^-.

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[5] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 122.

[6] T. G. Burke, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952); K. N. Tanner and A. B. F. Duncan, *J. Am. Chem. Soc.*, **73**, 1164 (1951).

[7] J. L. Hoard and W. J. Martin, *ibid.*, **63**, 11 (1941).

[8] H. H. Nielsen, *Phys. Rev.*, **59**, 565 (1941); E. K. Plyler and W. W. Sleator, *ibid.*, **37**, 1493 (1931); ref. 5, p. 281.

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[12] E. Hartert and O. Glemser, *Z. Elektrochem.*, **60**, 746 (1956).

[13] E. F. Barker and W. W. Sleator, *J. Chem. Phys.*, **3**, 660 (1935).

[14] P. A. Staats, H. W. Morgan, and J. H. Goldstein, *ibid.*, **24**, 916 (1956).

[15] D. F. Hornig and R. C. Plumb, *ibid.*, **26**, 637 (1957).

[16] O. Glemser and E. Hartert, *Naturwiss.*, **40**, 552 (1953).

$NbOF_5^{2-}$ would be formed by replacing one of the fluorines of NbF_6^- by an oxygen, the octahedral structure being retained. It therefore is reasonable to suppose that the vibrations which are analogous to those which produce a change in polarizability of NbF_6^- will produce the largest change in polarizability of $NbOF_5^{2-}$. These are therefore the most intense lines in the Raman, and they are the only ones detected in the spectrum given in Fig. 2.

The analogy with symmetry O_h gives information on the species of the vibrations appearing in the $NbOF_5^{2-}$ spectrum; The correlation tables in Wilson, Decius, and Cross[17] show that Raman-active species $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $F_{2g}(\nu_5)$ of O_h go, respectively, into species A_1, $(A_1 + B_1)$, and $(B_2 + E)$ for C_{4v}. The lines at 935, 600, and 295 cm.$^{-1}$ of $NbOF_5^{2-}$ therefore are identified as belonging to species A_1, (A_1 and/or B_1), and (B_2 and/or E), respectively. Since A_1 is both infrared and Raman active, the 935 cm.$^{-1}$ vibration should appear in both spectra as it does. Since A_1 and E are both infrared and Raman active whereas B_1 and B_2 are Raman active only, a more thorough study of the infrared might allow an assignment of the 600 and 295 cm.$^{-1}$ lines.

Although the spectra are consistent with an octahedral $NbOF_5^{2-}$ ion, it is helpful to see whether they also are consistent with probable structures for the $Nb(OH)_2F_5^{2-}$ ion. Three different structures have been reported for seven-coördinated complex ions. Two of these structures allow the OH groups in $Nb(OH)_2F_5^{2-}$ to be placed in positions such that they are equivalent to each other, but not to any fluorine. These structures are shown in Fig. 4 with the hydrogens left off.

In $Nb(OH)_2F_5^{2-}$ the hydrogens are expected to move with the oxygens in the motions of the heavier atoms. These motions are called the "skeletal" vibrations. Hornig and Plumb,[15] for example, found that the "skeletal" vibrations of $B(OH)_3$ give rise to a spectrum which resembles that of BF_3. Similarly, the spectrum[18] of $Te(OH)_6$ resembles that[19] of TeF_6.

The structure in Fig. 4(b) is the pentagonal bipyramid found[20] for $UO_2F_5^{3-}$. This structure, which belongs to point group D_{5h}, is probably the form that $Nb(OH)_2F_5^{2-}$ would take since this structure allows the oxygens to be shielded from each other by the niobium in the same way that the uranium does this in $UO_2F_5^{3-}$. Point group D_{5h} allows no coincidences between the infrared and Raman spectra even though it does not have a center of symmetry. Since the 935 cm.$^{-1}$ line of the Raman occurs as a strong line in the infrared, an $Nb(OH)_2F_5^{2-}$ ion of symmetry D_{5h} is not present in the crystals. It might be that perfect D_{5h} symmetry is distorted in the crystals. Any distortion, however, must be slight since the Raman spectra of the crystals and solutions are so similar. Furthermore, employing the rule that the most intense line in the Raman is the symmetrical stretch, the 935 cm.$^{-1}$ line is identified. Then, if the pentagonal bipyramid is distorted slightly, a small change in dipole moment would occur during the symmetrical stretch leading to a weak line in the infrared. Since in fact a strong line appears, it is reasonable to suppose that this line does not arise from a slightly distorted pentagonal bipyramidal $Nb(OH)_2F_5^{2-}$ ion and that such an ion is therefore not present in the crystals.

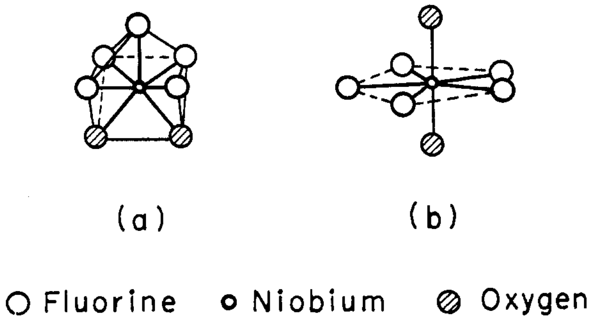

Fig. 4.—*cis* and *trans* forms for a $Nb(OH)_2F_5^{2-}$ ion.

Figure 4(a) shows an $Nb(OH)_2F_5^{2-}$ ion of symmetry C_{2v}. This structure is the type found by Hoard[21] for NbF_7^{2-}. Such an $Nb(OH)_2F_5^{2-}$ ion therefore would be expected to have a spectrum similar to K_2NbF_7. Comparison of the two observed spectra, given in Table I, shows that they are not similar. Therefore, $Nb(OH)_2F_5^{2-}$ ion of symmetry C_{2v} is not present in the crystals.

The third form of complex ions with seven-coördination is that found by Williams and Hoard[22] for $NbOF_6^{3-}$. This ion has a distorted octahedron of fluorines around the niobium with the oxygen off one face. The symmetry is C_{3v}. For $Nb(OH)_2F_5^{2-}$ to have this structure at least one of the OH groups must be placed in a position equivalent to a fluorine. Both a *cis* and a *trans* structure which place the OH groups in equivalent unique positions are available (Fig. 4) as structures for this ion. It therefore appears reasonable to suppose that an unsymmetrical structure would be unstable relative to them or to octahedral $NbOF_5^{2-}$, particularly in solution.

The Raman and infrared spectra of $K_2NbOF_5 \cdot H_2O$ therefore are consistent with the presence of water of hydration and an octahedral $NbOF_5^{2-}$ ion, but they are not consistent with an assignment based on an Nb–OH bend or the presence of the two most probable structures for an $Nb(OH)_2F_5^{2-}$ ion.

Acknowledgment.—Appreciation is expressed to A. Chetham-Strode, G. M. Begun, and W. H. Fletcher for helpful discussions throughout the course of this work.

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