spectrum of liquid $CF_3SO_2OCl$.

The band at 336 $cm^{-1}$ for $CF_3SO_2OCl$ is assigned to the $SCF_3$ wag by analogy to this same assignment for the bands at 333 and 340 $cm^{-1}$ in $CF_3SO_2F$ and $CF_3SO_2OH$, respectively.[43] The $SO_2$ twist for $CF_3SO_2OCl$ either is too weak to observe or is degenerate with the $SCF_3$ wag at 336 $cm^{-1}$. The $SO_2$ twist in $FSO_2OCl$ is assigned to a weak band at 389 $cm^{-1}$. The band at 302 $cm^{-1}$ for $CF_3SO_2OCl$ is assigned to the CS stretch by analogy to $CF_3SO_2F$ and $CF_3SO_2OH$ where the CS stretch is assigned at 301 and 312 $cm^{-1}$, respectively.[38,43] Then the band at 321 $cm^{-1}$ in $CF_3SO_2OCl$ can be assigned to the $CF_3$ rock of A′ symmetry for $C_s$. It would, of course, be possible to reverse our CS stretch and $CF_3$ rock assignments. The bands are of almost equal intensity (the third and fourth most intense bands in the Raman spectrum) with the 302-$cm^{-1}$ band being slightly more intense and having the lower depolarization ratio. It seems reasonable for the CS stretch,[38,43] which would be polarized in any case, to have a lower depolarization ratio than the $CF_3$ rock which is depolarized in $C_{3v}$ local symmetry but becomes polarized under $C_s$ local symmetry. Consequently, we have chosen this assignment.[51]

The band at 211 $cm^{-1}$ in $CF_3SO_2OCl$ seems too intense for a $CF_3$ rock of A″ symmetry under $C_s$ local symmetry and is assigned to the SOCl bend.[50] A band at 212 $cm^{-1}$ with very similar relative intensity is so assigned in $FSO_2OCl$.[50] Either the band at 184 $cm^{-1}$ or the shoulder at $\sim$198 $cm^{-1}$ must be the $CF_3$ rock. The shoulder on the Rayleigh line near 90 $cm^{-1}$ must surely be a torsion. Since no evidence for a band assignable to the $CF_3$ torsion was obtained for $CF_3SO_2F$ or $CF_3SO_2OH$, we assume the $CF_3$ torsion is too weak to observe and assign 90 $cm^{-1}$ as the OCl torsion. Although no OCl torsion has been found in $FSO_2OCl$, an OF torsion is assigned at 137 $cm^{-1}$ in $FSO_2OF$[3,42]. Since the 184-$cm^{-1}$ band is near twice 90 $cm^{-1}$ and $\Delta\nu = 2$ transitions for torsions may be more prominent than $\Delta\nu = 1$ transitions,[52] we tentatively assign the 184-$cm^{-1}$ band as 2 $\tau_{OCl}$. Then the shoulder near 198 $cm^{-1}$ remains to be assigned to the $CF_3$ rock of A″ symmetry for local $C_s$ symmetry of the $CF_3$ group in $CF_3SO_2OCl$.

**Acknowledgment.** Support of this research by the National Science Foundation is gratefully acknowledged. D.D.D. thanks the 3M Co. for a generous sample of $CF_3SO_2F$.

**Registry No.** $CF_3SO_2OCl$, 65597-24-2; $CF_3SO_2OBr$, 70142-16-4; $CF_3SO_2OCF_3$, 3582-05-6; $CF_3SO_2OSO_2OCF_3$, 72214-10-9; $CF_3SO_2F$, 335-05-7; $CF_3SO_2OH$, 1493-13-6.

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(51) In $CF_3SO_2OCl$, coupling could occur among three modes giving bands between 300 and 350 $cm^{-1}$ so the situation could be even more complex than in $CF_3SO_2F$ and $CF_3SO_2OH$. However, in the absence of further information we prefer to retain our description of $\delta(SCF_3)$ and $\nu$(C–S) with proper qualification of the later[38] as done in $CF_3SO_2F$ and $CF_3SO_2OH$[43] and list the band at 321 $cm^{-1}$ as a $CF_3$ rock.

(52) (a) Durig, J. R.; Bucy, W. E.; Carreira, L. A.; Wurrey, C. J. *J. Chem. Phys.* **1974**, *60*, 1754. (b) Durig, J. R.; Bucy, W. E.; Wurrey, C. J. *J. Chem. Phys.* **1974**, *60*, 3293. (c) Durig, J. R.; Bucy, W. E.; Wurrey, C. J.; Carreira, L. A. *J. Phys. Chem.* **1975**, *79*, 988.

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# Infrared and Raman Spectra of Ammonium, Potassium, Rubidium, and Cesium Metavanadates

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*Received August 31, 1979*

The infrared and Raman spectra of five metavanadates, $MVO_3$ (M = $NH_4$, $ND_4$, K, Rb, Cs), have been measured. The observed bands for $KVO_3$ in the aqueous solution were assigned to the vibrations of the $(VO_3)_n^{n-}$ ionic chain with $C_{2v}$ symmetry. The vibrational assignments to the chain in the crystalline salts were given tentatively by taking into consideration a different arrangement of atoms in the chain from that in aqueous solution. The internal vibrations of the ammonium ions in $NH_4VO_3$ and $ND_4VO_3$ at 77 and 100 K were also discussed. The rule of alternative inhibition has been adapted to the librations of the ammonium ions at 77 K.

In the previous paper,[1] the far-infrared spectra of five metavanadates, $MVO_3$ (M = $NH_4$, $ND_4$, K, Rb, Cs), were reported with the discussions concerning the bending vibrations of the $VO_3$ anion chain, the cation translations, and the $NH_4^+$ librations. It was suggested that these salts have similar force constants for the translational modes of the cations. According to the X-ray analyses of $NH_4VO_3$ and $KVO_3$,[2] the unit cell in a crystal with space group *Pmab*-$D_{2h}^{11}$ contains four $MVO_3$ molecules including four equivalent cations, and the $VO_3$ anions constitute a chain arrangement in which the $VO_4$ groups are tetrahedral. Few vibrational studies for the anion chain are found in the literature.[3,4]

In order to investigate the fundamental vibrations of the anion chain, we measured the infrared and Raman spectra of the powdered salts at room temperature. Since the stereochemical structure of the $VO_4$ tetrahedral chain in aqueous solution has been assumed to be different from that in crystal,[5] the spectra of the aqueous solution were also examined for $KVO_3$, which is soluble in water. This paper deals with the assignments for these observed bands. Internal motions and librations of the ammonium ions are also discussed for the spectra of $NH_4VO_3$ and $ND_4VO_3$ measured at room and low temperatures.

## Experimental Section

The materials measured were $NH_4VO_3$, $ND_4VO_3$, $KVO_3$, $RbVO_3$, and $CsVO_3$, all of which were prepared as previously reported.[1] Infrared spectra were measured with a Perkin-Elmer Model 125

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(2) Evans, H. T., Jr. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1960**, *114*, 257.

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(5) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; p 470.

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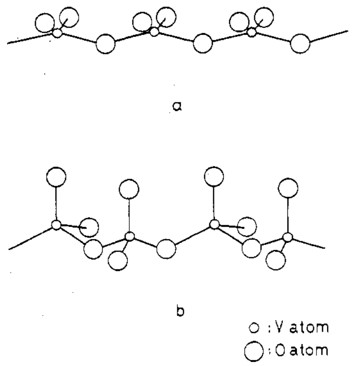

**Figure 1.** Two possible structures of the $(VO_3)_n^{n-}$ ions.[5]

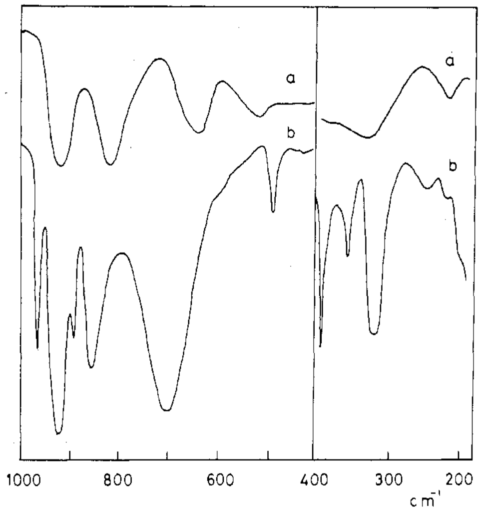

**Figure 2.** Infrared spectra of $KVO_3$: a, $KVO_3$ solution in $D_2O$ (2.2 mol/L, pH 7.8); b, $KVO_3$ solid (KBr disk and paraffin mull).

infrared spectrophotometer and with a Hitachi FIS-1 far-infrared spectrophotometer. A Kawaguchi Model KR-5 Raman spectrophotometer was used to measure Raman spectra, with 5145- and 4880-Å lines from a argon-ion laser as the exciting line. The powdered salts were directly irradiated to measure the Raman spectra. KBr and Nujol mulling methods were both used to obtain infrared spectra of the salts in solid state. Infrared and Raman spectra of the $(VO_3)_n^{n-}$ ion were measured for the solution of $KVO_3$ with the concentration of 2.2 mol/L and pH 7.8 in $D_2O$ and $H_2O$, respectively. Infrared spectra of the aqueous solution were measured with a polyethylene film cell.

## Results and Discussion

**Skeletal Vibrations of the $VO_3$ Anion Chain.** Two possible structures for the infinite-chain metavanadate anion are shown in Figure 1.[5] According to the X-ray analyses of ammonium and potassium metavanadate crystals, the $VO_3$ anion groups in a crystal constitute a chain arrangement depicted roughly in Figure 1b. On the other hand, the metavanadates in aqueous solution produce various vanadate ionic species as the function of the total vanadium concentration and the pH.[6] Existence of a cyclic tetramer or trimer was also proposed by Griffith and Wickins[4] for the solution with vanadium concentration of 2 mol/L and pH 8.2 on the basis of the Raman spectrum and the infrared spectrum higher than 700 cm$^{-1}$. In the present study, the infrared and Raman spectra of the metavanadate ion in aqueous solution were measured for the solution prepared by dissolving $KVO_3$ at room temperature so as to give the concentration of 2.2 mol/L and pH 7.8. The solution thus probably differs from that of Griffith and Wickins, who prepared the solution by boiling $NH_4VO_3$ with aqueous potassium hydroxide solution. The infrared and Raman spectra of the $KVO_3$ solution are shown in Figures 2 and 3, respectively, together with the spectra of the powder.

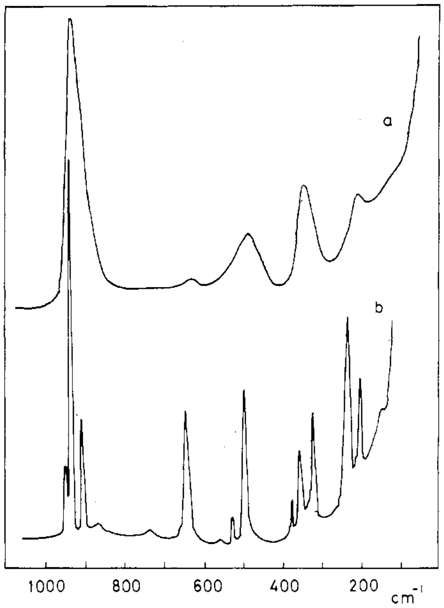

**Figure 3.** Raman spectra of $KVO_3$: a, $KVO_3$ solution in $H_2O$ (2.2 mol/L, pH 7.8); b, $KVO_3$ powder.

As seen from Figures 2 and 3, the solution spectra are substantially analogous to those of the crystal, which undergo the factor group splitting by the crystal field, and different from those reported by Griffith and Wickins. Therefore, the metavanadate ion in the present solution is assumed to have either structure a or b in Figure 1. The structure might be chosen in consideration of the vibrational freedom and the selection rule.

The $VO_3$ chain in Figure 1a is composed of the $VO_3$ unit groups with $C_{2v}$ symmetry, while that of Figure 1b is constructed by two $VO_3$ groups with the same symmetry. The vibrational freedom of the $VO_3$ groups for the arrangement of Figure 1a is written by eq 1 and that for Figure 1b by eq

$$\Gamma_{VO_3} = 3\ A_1 + B_1 + 2\ B_2 \qquad (1)$$

2, where the longitudinal twisting vibrations of the chain,

$$\Gamma_{2VO_3} = 6\ A_1 + 3\ A_2 + 5\ B_1 + 3\ B_2 \qquad (2)$$

belonging to $B_2$ species, were excluded because the frequencies would be low compared with the skeletal vibrations of the chain. All species are infrared- and Raman-active modes except $A_2$ species which are infrared inactive, and $A_1$ species would be polarized. As seen in Figures 2a and 3a, the solution of $KVO_3$ has six infrared absorption bands and six Raman lines. A Raman line at 860 cm$^{-1}$ lies hidden behind a strong 945-cm$^{-1}$ line and is revealed by a polarized spectrum. Three polarized Raman lines at 945, 475, and 205 cm$^{-1}$ are assigned to $A_1$ species. Thus, the observed six frequencies are reasonably interpreted by eq 1, and this fact implies that the metavanadate ion in aqueous $KVO_3$ solution has the infinite-chain arrangement shown in Figure 1a. The coincidence of the infrared bands with Raman lines supports the $C_{2v}$ symmetric structure of the $VO_3$ chain. The difference between this result and that of Griffith and Wickins is ascribed to the fact that the cyclic metavanadate ion was formed by boiling ammonium metavanadate with potassium hydroxide solution; otherwise the saturated $KVO_3$ solution will conserve the chain structure in crystal.

The assignments for the observed frequencies of the $KVO_3$ solution tabulated in Table I are based on the results of the

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(6) Pope, M. T.; Dale, B. W. *Q. Rev., Chem. Soc.* **1968**, *22*, 527.

**Table I.** Vibrational Frequencies (cm$^{-1}$) and the Assignments for $(VO_3)_n^{n-}$ Ions in Aqueous Solution

| chain[c] | | | cyclic tetramer[a] | | |
|---|---|---|---|---|---|
| Raman[b] | IR | assignt | Raman[b] | IR | assignt |
| 945 (p) | 920 | $A_1$ $\nu_{VO_2}$(free) | 945 (p) | 952 | $\nu_{VO_2}$ (sym) |
| 860 | 820 | $B_2$ $\nu_{VO_2}$(free) | 905 | 905 | $\nu_{VO_2}$(asym) |
| 630 | 640 | $B_2$ $\nu_{VOV}$(bridged) | 630 | | ring mode |
| 475 (p) | 530 | $A_1$ $\nu_{VOV}$(bridged) | 540 (p)<br>490 (p) | | ring breathing |
| 345 | 326 | $B_1$ $\delta_{VO_2}$ | | | $\delta_{VO_2}$ |
| 205 (p) | 223 | $A_1$ $\delta_{VOV}$ | 330 | | ring def |

[a] Reference 4. [b] (p) indicates a polarized line. [c] Present work.

vanadate anions $HVO_4^{2-}$, $HV_2O_7^{3-}$, $V_2O_7^{4-}$, and $(VO_3)_n^{n-}$ reported by Griffith and Wickins.[4] The free $VO_2$ stretching frequencies agree with the cyclic metavanadate ion, while the VOV bending frequencies appearing at 205 cm$^{-1}$ (Raman) and 233 cm$^{-1}$ (IR) resemble those of $V_2O_7^{4-}$ at 288 cm$^{-1}$ and $HV_2O_7^{3-}$ at 210 cm$^{-1}$.

The crystal structure of $KVO_3$ has an inverse arrangement of two $VO_3$ groups alternately as shown previously. The space group is $D_{2h}$, and the unit cell contains four molecules. The site symmetry of the $VO_3$ chain in the crystal is $C_{2v}$, and the fundamental vibration of the chain is given by eq 2. The spectra of Figures 2b and 3b do not give all the frequencies, and 11 Raman lines and 12 infrared bands can be read from the spectra as listed in the first column of Table II. The observed frequencies can be roughly assigned by comparing them with the frequencies observed in aqueous solution, but the exact assignments cannot be given because no spectra of the single crystal have been measured. Since the VO stretching frequencies in solution are close to those in the crystal, as seen in Tables I and II, the bridged VO and free VO bonds of the $VO_3$ chain in solution have similar bond lengths to those in $KVO_3$ crystal, in which the bond lengths are 1.80 and 1.66 Å, respectively. The infrared and Raman spectra of other metavanadates are sketched in Figure 4, and the observed frequencies are summarized in Table II. Figure 4 indicates that the spectra in this region are little influenced by the kind of cation, implying the similar $VO_3$ chain structures in five metavanadate crystals. Another point noticeable in Figure 4 is that almost all of the fundamental vibrations appear correspondingly in both infrared and Raman spectra. Since the rule of alternative inhibition would originally be applied to the skeletal vibrations of the $VO_3$ chain under the influence of the $D_{2h}$ space group, the release from the inhibition rule should be explained by a significant effect of the $C_{2v}$ site symmetry to the $VO_3$ anion chain. This may be supported by the fact that the lattice constant in the direction of the long-

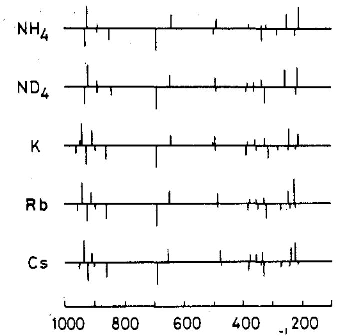

**Figure 4.** Vibrational spectra of the $VO_3$ chain in five metavanadates. Upward lines show Raman scattering and downward lines show infrared absorption. Length of the bar shows relative intensity of the band.

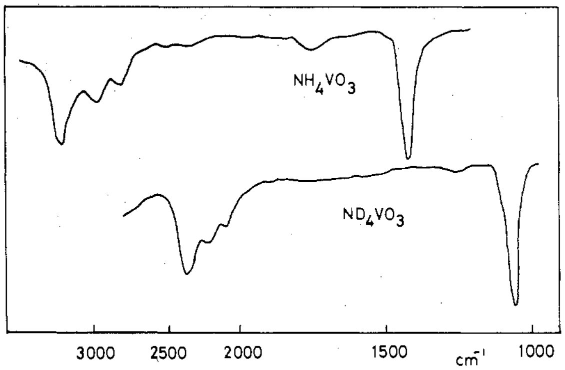

**Figure 5.** Infrared spectra of $NH_4VO_3$ and $ND_4VO_3$ at 100 K.

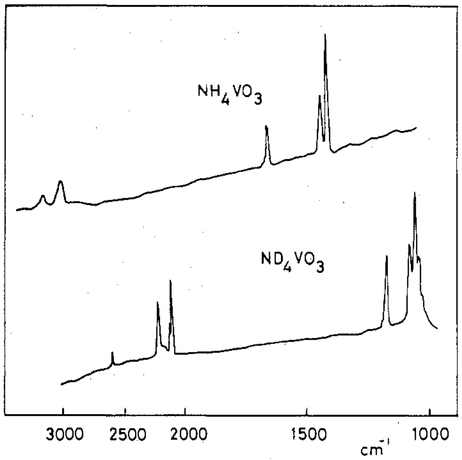

**Figure 6.** Raman spectra of $NH_4VO_3$ and $ND_4VO_3$ at 77 K.

**Table II.** Observed Frequencies (cm$^{-1}$) and Intensisties[a] for the $VO_3$ Chain in $MVO_3$ at Room Temperature

| K | | Rb | | Cs | | $NH_4$ | | $ND_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Raman | IR | Raman | IR | Raman | IR | Raman | IR | Raman | IR | assignt |
| 950 w | 960 w | | 957 w | | 948 w | | | | | $\nu_{VO_2}$(sym) |
| 940 s | 935 s | 942 s | 935 s | 935 s | 920 s | 925 s | 935 s | 925 s | 940 s | |
| | 890 w | | 895 w | | 905 w | | 895 w | | 890 w | |
| 910 m | 850 s | 908 m | 863 s | 912 m | 860 s | 895 m | 850 s | 895 m | 845 s | $\nu_{VO_2}$(asym) |
| 648 m | 693 s | 648 m | 685 s | 652 m | 690 s | 643 m | 690 s | 647 m | 690 s | $\nu_{VOV}$(asym) |
| 520 w | | | | | | | | | | |
| 498 s | 495 w | 485 s | 485 w | 475 s | 475 w | 497 s | 495 w | 495 s | 498 w | $\nu_{VOV}$(sym) |
| 383 w | 385 m | 375 w | 382 m | 375 w | 379 m | 380 w | | 375 w | 389 w | $\delta_{VO_2}$ |
| 362 m | 352 w | 357 m | 347 w | 355 w | 337 w | 342 w | | 360 w | 365 w | |
| 322 m | 318 s | 330 m | 318 s | 332 w | 328 s | 315 w | 333 s | 330 w | 327 s | |
| | 262 w | | 267 w | | 269 w | | | | | $\delta_{VOV}$ |
| 230 s | 231 w | 242 m | 238 w | 230 m | 249 w | 255 m | 223 w[b] | 250 m | 220 w[b] | |
| 205 m | 219 w | 222 s | 210 w | 222 s | 217 w | 205 s | | 205 s | | |

[a] Abbreviations: s = strong, m = medium, w = weak. [b] At 50 K.

**Table III.** Observed Internal Frequencies ($cm^{-1}$) for the Ammonium Ions in $NH_4VO_3$ and $ND_4VO_3$

| $NH_4VO_3$ | | $ND_4VO_3$ | | |
|---|---|---|---|---|
| Raman[a] | IR[b] | Raman[a] | IR[b] | assignt[c] |
| 3050 | 3190 | 2220 | 2340 | $\nu_3$ |
| | 2980 | | 2180 | $\nu_2 + \nu_4$ |
| | 2800 | | 2100 | $2\nu_4$ |
| 2920 | | 2100 | | $\nu_1$ |
| 1650 | | 1180 | | $\nu_2$ |
| 1440 | | 1075 | | |
| 1420 | 1412 | 1060 | 1067 | $\nu_4$ |
| 1370 | | | | |

[a] At 77 K. [b] At 100 K. [c] Key: $\nu_1$, NH symmetrical stretching; $\nu_2$, HNH doubly degenerate bending; $\nu_3$, NH triply degenerate stretching; $\nu_4$, HNH triply degenerate bending.

itudinal chain axis ($a$ axis) is little affected by the cation for four metavanadate crystals.[2]

**Internal Vibrations of the $NH_4^+$ Ion in $NH_4VO_3$.** Infrared and Raman spectra of $NH_4VO_3$ and $ND_4VO_3$ in the frequency region where the internal vibrations are expected are shown in Figures 5 and 6. The observed frequencies are listed in Table III. It may be assumed that the factor group splitting of a tetrahedral $NH_4^+$ ion removes all the vibrational degeneracies. The Raman spectrum exhibits the splitting lines of $\nu_4$ vibration ($F_2$), but no splittings are observed for $\nu_3(F_2)$ and $\nu_2(E)$ in both Raman and infrared spectra. It has been pointed out by the study of X-ray analyses[2] that the thermal motion of the $NH_4^+$ ion in $NH_4VO_3$ is more constrained than that of the $K^+$ ion in $KVO_3$, leading to the suggestion that there is hydrogen bonding between the $NH_4^+$ ion and the $VO_3$ groups in the anion chain. Existence of the hydrogen bond is supported by the comparatively high librational frequency of the ion at 375 $cm^{-1}$ and also by the fact that the potential barrier of the restricted rotation (5.0 kcal/mol[7]) is higher than those of other ammonium salts,[8] such as $NH_4ClO_4$ (0.1–0.2 kcal/mol) and $NH_4NO_3$ (2.4 kcal/mol). The $\nu_1$ and $\nu_3$ frequencies (2920 and 3190 $cm^{-1}$, respectively) lower than those of $NH_4ClO_4$ (3206 and 3290 $cm^{-1}$) and $NH_4NO_3$ (3130 and 3250 $cm^{-1}$) can be explained by the formation of the N–H···O hydrogen bonding.

**The $NH_4^+$ and $ND_4^+$ Librations.** It was suggested in our previous paper[1] that the librational infrared absorption at 362 $cm^{-1}$ at room temperature was understood as an average of $NH_4^+$ librations about $C_2$ and $C_3$ rotational axes. The corresponding band of $ND_4^+$ ion has been observed at 267 $cm^{-1}$. These frequencies are located in the region of the skeletal bending vibrations, so that the assignments in this region are often confused. Figure 7 shows the Raman spectra of $NH_4VO_3$ and $ND_4VO_3$ at room and low temperatures. Both spectra of $NH_4VO_3$ and $ND_4VO_3$ at room temperature have broad bands around 360 and 220 $cm^{-1}$, respectively. The broad band at 360 $cm^{-1}$ is probably due to the superposition of $NH_4^+$ libration and $VO_2$ bending vibration and that at 220 $cm^{-1}$ consists of $ND_4$ libration and VOV bending vibration. At 77 K, these broad bands disappeared, while the infrared librational absorption at 362 $cm^{-1}$ shifted gradually toward 375 $cm^{-1}$ with a lowering of the temperature below 50 K, accompanying an increase in intensity. Thus, the rule of alternative inhibition can be adapted to the $NH_4^+$ and $ND_4^+$ librations as lattice vibrations at 77 K. Four $NH_4^+$ ions are situated at the $C_2$ site in the unit cell. Under the influence of $D_{2h}$ space group, the librations of the ion are split into the 12 modes

$$\Gamma_{NH_4^+}(\mathrm{lib}) = A_g + 2\,B_{1g} + B_{2g} + 2\,B_{3g} + A_u + 2\,B_{1u} + B_{2u} + 2\,B_{3u} \quad (3)$$

where $B_u$ species are infrared active and $A_g$ and $B_g$ are Raman-active modes. Therefore, the twofold rotation ($C_2$ libration) appearing in the infrared spectra at 375 $cm^{-1}$ in $NH_4VO_3$ will be any one of the $B_{1u}$, $B_{2u}$, and $B_{3u}$ species which are inactive in the Raman spectrum. A rise in temperature causes the loosening in the crystal field of $D_{2h}$, leading to an appearance of the $C_3$ librations. The librations thus become active modes in both infrared and Raman spectra at room temperature.

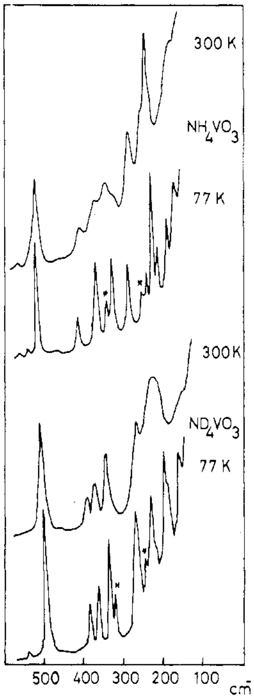

**Figure 7.** Raman spectra of $NH_4VO_3$ and $ND_4VO_3$ at room temperature and 77 K. The peaks denoted by asterisks in the spectra are unfiltered argon II laser fluorescence lines.

**Registry No.** $NH_4VO_3$, 7803-55-6; $ND_4VO_3$, 68683-01-2; $KVO_3$, 13769-43-2; $RbVO_3$, 13597-45-0; $CsVO_3$, 14644-55-4.

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