complex $(Me_2N)_3PO{:}Me_3SnCl$ ($K = 380\ M^{-1}$ in isooctane at 26 °C[21]) determined by ^1H NMR is consistent with the stronger donor characteristics of the phosphoramide base.

Chlorosilanes and chlorostannanes containing more than one chlorine exhibit complicated, concentration-dependent coordination shifts analogous to the behavior of $SiCl_4$, presumably due to the presence of several complexes along with the possibility of isomeric forms.[22] Further studies designed to determine K_2 values are currently under way.

It is worthwhile to note the substantial effect of added acetonitrile on the chemical shift of the $Ph_3PO{:}Me_3SiCl$ complex (Table I). Downfield resonance shifts exceed 3 ppm even with low concentrations (7% by volume) of MeCN. Since MeCN does not affect the chemical shift of Ph_3PO, the magnitude of the solvent-induced shift of the complex cannot be attributed solely to changes in the bulk susceptibility of the solvent. Some argument can be made for a shift due to magnetic anisotropy of the nitrilic moiety. Upon complexation with the metal, the highly polarized phosphoryl group may interact with the polarizable π electrons of MeCN thus inducing a shift owing to a nonzero orientational averaging of MeCN in proximity to the complex. Alternatively, acetonitrile may coordinate to phosphorus or, more likely, to silicon or tin, thus expanding the element's coordination number to 6. It appears that Δ increases upon further addition of the solvent, which suggests that the adduct is trimolecular ($Ph_3PO{:}Me_3SiCl{:}MeCN$). If indeed, coordination is to silicon, then these observations represent the first direct evidence for such a complex. Further quantitative investigations are currently being carried out to resolve this point.

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Registry No. 1, 791-28-6; **1·7**, 68307-43-7; **1·8**, 68307-44-8; **1·9**, 68332-32-1; **1·10**, 68307-45-9; **1·11**, 68307-46-0; **1·12**, 68307-47-1; **1·13**, 68307-48-2; **1·14**, 68307-49-3; **1·15**, 68307-50-6; **1·16**, 68307-51-7; **1·17**, 28176-41-2; **1·18**, 68307-52-8; **1·19**, 61646-57-9; **1·20**, 23209-03-2; $Ph_3PO{:}Me_3SiCl{:}MeCN$, 68307-53-9.

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Far-Infrared Spectra of Ammonium, Potassium, Rubidium, and Cesium Metavanadates

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The far-infrared spectra of NH_4VO_3, ND_4VO_3, KVO_3, $RbVO_3$, and $CsVO_3$ have been measured at room and low temperatures. The VO_2 and VOV bending vibrations were assigned to the bands in the regions 390–330 and 280–210 cm^{-1}, respectively. A linear relationship between the cation translations of these salts and $m^{-1/2}$ (m = mass of the cation) led to the suggestion that these salts have similar force constants for the translational modes. Temperature dependence of the librational absorption of the ammonium ion has also been discussed. The potential barrier of the restricted rotation was estimated to be 5.0 kcal/mol.

The crystals of metavanadates, MVO_3 (M = NH_4, K, Rb, and Cs), have a peculiar structure in which the tetrahedral VO_4 groups constitute a chain arrangement.[1] The space group is $Pmab$-$D_{2h}{}^{11}$ and the unit cell contains four molecules including four equivalent cations. Few vibrational studies for these crystals are found in the literature.[2] It is interesting for NH_4VO_3 that two librational bands of the NH_4^+ ion were found by the measurements of neutron scattering[3] while the four NH_4^+ ions are located at the equivalent sites in a cell. These two bands have been interpreted as arising from two- and threefold librational modes on the basis of the NMR relaxation times.[4]

In order to investigate the motions of the ions in metavanadates, far-infrared spectra of NH_4VO_3, ND_4VO_3, KVO_3, $RbVO_3$, and $CsVO_3$ powders were measured at room and low temperatures. This paper reports the assignments for the low-frequency absorptions with some discussions.

Experimental Section

Materials. NH_4VO_3 and KVO_3 were commercially obtained. ND_4VO_3 was obtained as the precipitate by the reaction $NaVO_3 + ND_4Cl \rightarrow ND_4VO_3 + NaCl$ (in D_2O). This powder showed a little absorption of the NH stretching due to the impurity. $RbVO_3$ (mp 673 °C) and $CsVO_3$ (mp 755 °C) were prepared, respectively, by the following reactions: $Rb_2CO_3 + V_2O_5 \rightarrow 2RbVO_3 + CO_2$ and $Cs_2CO_3 + V_2O_5 \rightarrow 2CsVO_3 + CO_2$.

Measurements. A Hitachi FIS-1 far-infrared spectrophotometer was used to record the spectra. Each salt was mulled with paraffin wax on a 0.5 mm thick polyethylene sheet. Low-temperature spectra

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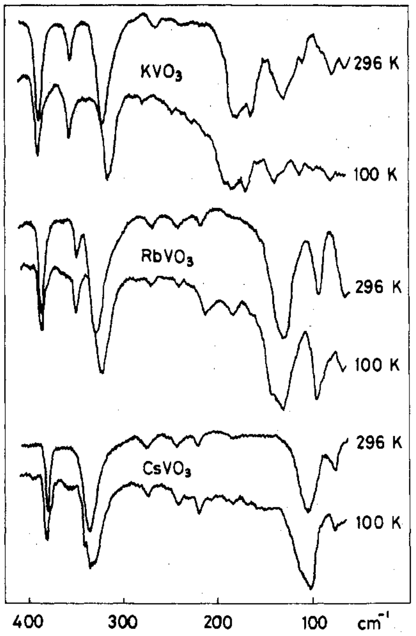

Figure 1. Far-infrared spectra of KVO_3, $RbVO_3$, and $CsVO_3$.

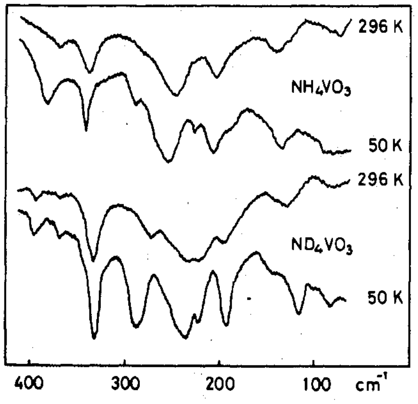

Figure 2. Far-infrared spectra of NH_4VO_3 and ND_4VO_3.

were measured with a liquid-helium cryostat[5] for the temperature ranges 50–296 K for NH_4VO_3 and ND_4VO_3 and 100–296 K for KVO_3, $RbVO_3$, and $CsVO_3$.

Results and Discussion

Bending Vibrations of the VO_4 Tetrahedral Chain. The far-infrared spectra of KVO_3, $RbVO_3$, and $CsVO_3$ at room and low temperatures are shown in Figure 1. In these spectra, strong absorption bands in the region of 390–330 cm^{-1} and weak bands in the region of 280–210 cm^{-1} appear independently of the kind of cation. This implies that the bands in both regions are originated from the intramolecular vibrations. According to the infrared and Raman spectral data,[6,7] the VO_4^{3-}, $HV_2O_7^{3-}$, $V_2O_7^{4-}$, and $(VO_3)_n^{n-}$ ions in aqueous solutions exhibit the VO_2 bending modes at around 360 cm^{-1} and the VOV bending modes at around 220 cm^{-1}. With the assumption that the bending frequencies of such a free $(VO_3)_n$ ion in aqueous solution is presumably close to those in solid, three bands in the region of 390–330 cm^{-1} in each spectrum in Figure 1 (two bands and one shoulder for $CsVO_3$) are tentatively assigned to the VO_2 bending vibrations and two bands in the region of 280–210 cm^{-1} to the VOV bendings. The three VO_2 bendings correspond to the infrared-active modes B_{1u}, B_{2u}, and B_{3u}, which are predictable by the factor group analysis for a unit VO_4 group.

Far-infrared spectra of NH_4VO_3 and ND_4VO_3 shown in Figure 2 would be interpreted similarly for the bands in the above regions, but the exact bending frequencies cannot be indicated because the regions are covered by broad absorptions due to librations and translation of ammonium ion, as will be mentioned later.

Table I. Frequencies (cm^{-1}) for the Cation Translations in Metavanadates, MVO_3

	band A		band B	
M	at 100 K	at 296 K	at 100 K	at 296 K
NH_4^+	250	242	203	199
ND_4^+	235	224	191	192
K^+	183, 168	178, 161	138	130
Rb^+	129	127	95	93
Cs^+	105	105	76	79

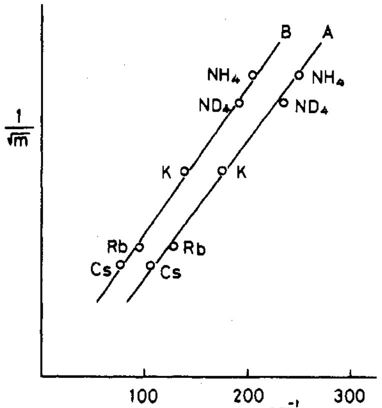

Figure 3. Relationship of the cation translational frequency at 100 K in MVO_3 vs. $m^{-1/2}$ (m = mass of the cation).

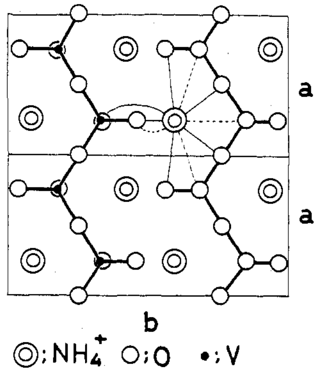

Figure 4. Arrangment of ion and atoms in the crystal of NH_4VO_3. This figure was depicted by using the data in ref 1. Lines show the distances between the NH_4^+ ion and the oxygen atoms.

Cation Translation. Among the absorption bands in each spectrum of Figures 1 and 2, one can find two bands which shift largely depending on the cation.[8] One is strong and the other is medium in intensity. The strong one of KVO_3 is split into two peaks. The observed frequencies are summarized in Table I and the dependency on the cation is depicted in Figure 3 as a linear relationship to $m^{-1/2}$ (m = mass of the cation). The frequency 242 cm^{-1} observed for NH_4VO_3 at room temperature agrees with the frequency 234 cm^{-1} of the NH_4^+ translation observed by a neutron scattering technique at room temperature.[3] Therefore, the frequencies listed in Table I can be assigned to the cation translational modes, which correspond to any of five infrared-active modes ($2\ B_{1u} + B_{2u} + 2\ B_{3u}$) predicted by a factor group analysis.

According to the X-ray analyses of NH_4VO_3 and KVO_3 crystals, a cation is surrounded irregularly by ten oxygen atoms and the distances between the cation and oxygen atoms in NH_4VO_3 cover a range of 2.85–3.40 Å. The positions of hydrogen atoms have not been determined. While such a

Table II. Librational Frequencies (cm^{-1}) for the NH_4^+ Ion in NH_4VO_3 and the ND_4^+ Ion in ND_4VO_3

temp, K	ν		$\nu(ND_4^+)/\nu(NH_4^+)$
	NH_4^+	ND_4^+	
296	362	267	0.74
50	375	283	0.75

situation is quite complicated, as shown in Figure 4, the translational motion of the cation surrounded by oxygen atoms can be considered approximately as that in the CsCl-type lattice. Considering only the short-range force for the vibrational translation of a cation to the neighboring oxygen atom, the frequency is approximately written by

$$\nu_t = \frac{1}{2\pi c}\sqrt{\frac{2K}{\mu}} \qquad (1)$$

$$\frac{1}{\mu} = \frac{1}{m_M} + \frac{1}{m_O}$$

where K is the force constant between the cation and oxygen atom, m_M the mass of the cation, and m_O the mass of oxygen. ν_t can be approximated by the observed frequency (ν_{obsd}) and $1/\mu$ is proportional to $1/m_M$. Accordingly, the close slopes of two dependencies, A and B, in Figure 3 strongly suggest that these salts all have similar force constants for the cation translational modes.

Librational Motions of Ammonium Ion. Besides the translational motions, NH_4VO_3 and ND_4VO_3 would show librational motions of their ammonium ions in the far-infrared region. According to the measurements of neutron scattering of NH_4VO_3, the NH_4^+ ion shows two librational bands at 371 and 308 cm^{-1}.[3] The study on the NMR relaxation time for this crystal suggested the assignments for the band at 371 cm^{-1} to the twofold librational mode (C_2 libration) and at 308 cm^{-1} to the threefold one (C_3 libration).[4]

As seen in Figure 2 the weak absorption at 362 cm^{-1} of NH_4VO_3 at room temperature shifted to 375 cm^{-1} at 50 K, accompanying an increase in intensity. The band at 267 cm^{-1} of ND_4VO_3 at room temperature shifted toward a same direction to 283 cm^{-1} at 50 K. These frequencies are shown in Table II together with the ratios of isotopic shifts. The two ratios at 296 and 50 K are close, supporting the assignments of these bands to the NH_4^+ librations. The frequency 375 cm^{-1} at 50 K coincides well with the C_2 libration (371 cm^{-1}) obtained by the NMR study,[4] but the absorption corresponding to the C_3 libration has not been found in the present measurement.

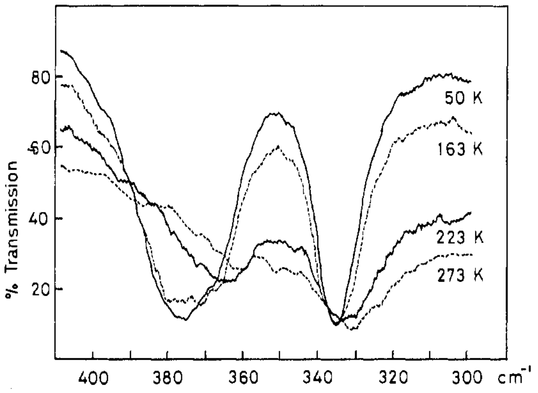

Figure 5. Far-infrared spectra of NH_4VO_3 at various temperatures.

Figure 5 shows the spectra of NH_4VO_3 measured with a thick specimen at various temperatures. The absorption band at around 330 cm^{-1} is due to the VO_2 bending vibration. The librational broad band at 365 cm^{-1} observed at 273 K became narrower and shifted toward the higher frequency side with a lowering in temperature, finally showing the strong band at 375 cm^{-1}. Since the NH_4^+ ion at room temperature is located in a state of equilibrium at such a position as seen in Figure 4 and rotates restrictedly around the two- or threefold axis, the temperature dependence of the librational band is probably ascribed to the idea that the ion moves gradually with lowering temperature toward a site where the twofold libration predominates. This movement is also surmised from the study in the second moment of proton NMR for NH_4VO_3,[9] which pointed out that the motion of the ion is not random at 20 K, oscillating about the C_2 axis, and a rise in temperature causes various types of oscillation. Thus, the observed absorption at 362 cm^{-1} may be understood as an average of the NH_4^+ librations about both C_2 and C_3 axes.

Potential Barrier Height of NH_4^+ Libration. If the NH_4^+ ion is in a CsCl-type lattice, the potential barrier (V_0) of the restricted rotation would be given by an expression[10]

$$V_0 = \frac{1}{16}\,\frac{(\hbar\nu_l + 5\hbar/2I)^2}{\hbar/2I} \qquad (2)$$

where I is the moment of inertia and ν_l the librational frequency. Adopting the N-H bond length (1.035 Å) of NH_4Br and the frequency 375 cm^{-1} at 50 K, V_0 is estimated to be 5.0 kcal/mol. This value agrees well with the value (5.1 ± 0.1 kcal/mol) estimated by the NMR measurements as the activation energy of the twofold NH_4^+ libration.[4] This agreement for the NH_4^+ ion supports the foregoing assumption that a cation in MVO_3 under study is bathed in the CsCl-type potential at 50 K. However, the lower frequency 362 cm^{-1} at room temperature may not be attributable to such a potential of pure C_2 libration.

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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