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The Librational Motion of the ND_4^+ ion in ND_4I

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Synopsis

The far-infrared spectra of ND_4I mulled with paraffin wax were recorded from 47 K to 200 K. The band at 238 cm^{-1} observed at temperatures lower than 149 K was assigned to the librational motion of the tetradeuterioammonium ion. The bands observed at 470 and 420 cm^{-1} in phase III were assigned to the overtone and combination band, respectively. The data for ND_4Br were also discussed.

I. Introduction

Many investigators have studied the phase transitions of ammonium halides by means of various experimental techniques and their results elucidated that the halides occur phase transitions summarized in Table 1 referring to the reports by some authors.[1,2,3]

Table 1. Phase transformations for ammonium halides[a)]

	Phase I(α)	Phase II(β)	Phase III(γ)	Phase IV(δ)
Lattice type NH_4^+ ions	NaCl (Disordered)	CsCl (Disordered)	(Tetragonal) (Antiparallel ordering)	CsCl (Parallel ordering)
Structure	$O_h^5(Fm3m)$	$O_h^1(Pm3m)$	$D_{4h}^7(Pm/nmm)$	$T_d^1(P\bar{4}3m)$
NH_4Cl	α ← 457.7K → β ← 242.9K → δ			
ND_4Cl	α ← 348.4K → β ← 249.6K → δ			
NH_4Br	α ← 411.2K → β ← 235K → γ ⇄ δ (78K →, ← 105K)			
ND_4Br	α ← 405K → β ← 215K → γ ⇄ δ (158K →, ← 165K)			
NH_4OI	α ← 255.8K → β ← 231.8K → γ			
ND_4I	α ← 254K → β ← 224K → γ			

a) See references 1 and 2.

(1) C.H. Perry and R.P. Lowndes, J. Chem. Phys., **51** (1969), 3648.
(2) V. Hovi, K. Paavola, and E. Nurmi, Ann. Acad. Sci. Fennicae (Finland), Ser. A, VI, **328** (1969), 1.
(3) Y. Ebisuzaki, J. Chem. Phys., **61** (1974), 3170.

The librational motion of the ammonium ion was first inferred to be at 280 cm^{-1} for NH_4I and at 319 cm^{-1} for NH_4Br from the infrared combination bands.[4,5] It was also estimated from the heat capacity measurements[6,7] that the librations should be 279 cm^{-1} for NH_4I and 340 cm^{-1} for NH_4Br. The direct observation has been made by means of a neutron inelastic scattering technique (293 cm^{-1} for NH_4I and 335 cm^{-1} NH_4Br)[8] and the laser Raman spectroscopy.[9] The laser Raman study by Durig and Antion[9] of NH_4I and NH_4Br, together with the tetradeuterio derivatives, found the librational frequencies at 278 and 331 cm^{-1} for NH_4I and NH_4Br, respectively, but they could not find out the infrared active modes in their far-infrared spectra. On the other hand, Schumaker and Garland[10] assigned the ND_4^+ ion libration for ND_4Br to be at 252 cm^{-1} on the basis of the analysis of infrared combination bands and overtones of the libration. No librational frequency has been reproted for ND_4I.

In our previous far-infrared study,[11] the librations of the NH_4^+ ions were found at 301 and 348 cm^{-1} for NH_4I and NH_4Br, respectively, in the phase III crystalline salts. This paper reports the far-infrared spectra of ND_4I and ND_4Br with the discussion on the librations of the ND_4^+ ion.

II. Experimental

ND_4I and ND_4Br were prepared by repeated exchange reactions of NH_4I and NH_4Br with D_2O. No NH vibrations were observed in the infrared spectra of the deuterium salts. The powder samples were mulled with paraffin wax and extended on a 0.5 mm thick polyethylene sheet in a dry box. To find out the weak absorption bands, the specimens were prepared as thick as possible. A Hitachi FIS far-infrared spectrophotometer (500–60 cm^{-1}) was used to record the spectra. A liquid helium cryostat used in this study is shown in Fig. 1. The temperature of the specimen in the cryostat could not be cooled down below 45 K because of the low thermal conductivity of the polyethylene window.

III. Results and discussion

1. Librational frequency for ND_4I

The spectra of ND_4I at various temperatures are shown in Fig. 2. The librational frequency for the ND_4^+ ion is expected in this region and the band

(4) L.F.H. Bovey, J. Opt. Soc. Am., **41** (1951), 836.
(5) E.L. Wagner and D.F. Hornig, J. Chem. Phys., **18** (1950), 296.
(6) C.C. Stephenson, L.A. Landers, and A.G. Cole, J. Chem. Phys., **20** (1952), 1044.
(7) M. Sorai, H. Suga, and S. Seki, Bull. Chem. Soc. Jpn., **38** (1965), 1125.
(8) G. Venkataraman, K.U. Deniz, P.K. Iyengar, A.P. Roy, and P.R. Vijayaraghavan, J. Phys. Chem. Solids, **27** (1966), 1103.
(9) J.R. Durig and D.J. Antion, J. Chem. Phys., **51** (1969), 3639.
(10) N.E. Schumaker and C.W. Garland, ibid., **53** (1970), 392.
(11) S. Onodera, Chem. Lett., (1973), 17.

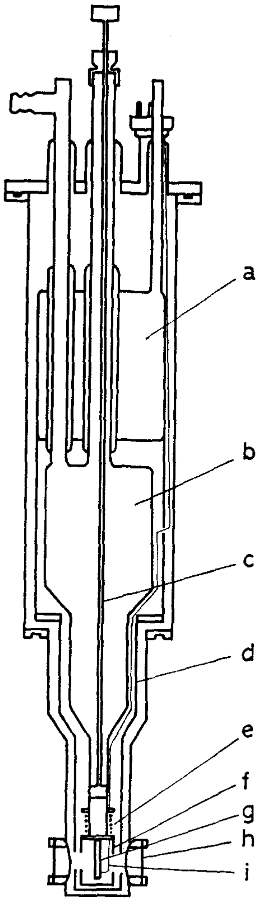

Fig. 1

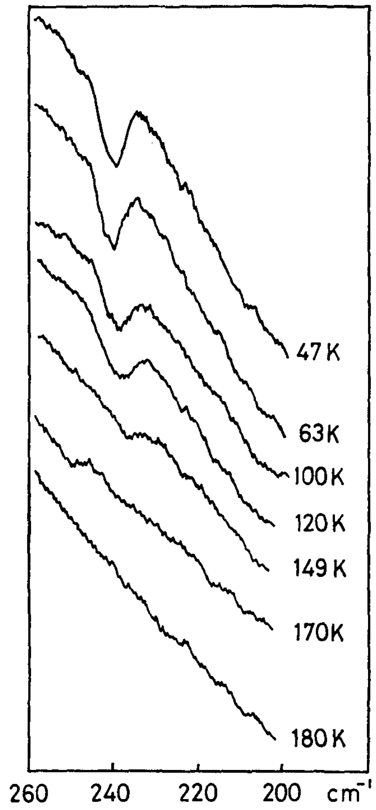

Fig. 2

Fig. 1. A temperature variable liquid helium cryostat.
a: Liq. N_2 reservoir b: Liq. He reservior c: Piston controlling a helium level
d: Liq. N_2 radiation shield e: Heater f: Liq. He radiation shield
g: Specimen holder h: Polyethylene window i: Thermocouple

Fig. 2. Far-infrared spectra of ND_4I at various temperatures in the region 260–200 cm^{-1}.

appeared at 149 K became stronger with cooling down the temperature. This absorption at 238 cm^{-1} would be attributable to the libration of the ion in consideration of the followings.

In the phase III, ND_4I and ND_4Br have a tetragonal structure which is a slight distortion of CsCl type structure. The space group is D_{4h}–$P4/nmm$ with two molecules per unit cell.(12) The tetrahedral ammonium ions are situated on the sites which have D_{2d} symmetry. The irreducible representations for the acoustical translations (AT), otpical translations (OT), and optical librations (OL) are

$$\Gamma(\mathrm{AT}) = A_{1u}+E_u ,$$

$$\Gamma(\mathrm{OT}) = A_{1g}+B_{1g}+2E_g+A_{2u}+E_u ,$$

$$\Gamma(\mathrm{OL}) = A_{2g}+E_g+B_{2u}+E_u .$$

(12) J.A.A. Ketelaar, Nature, **134** (1934), 250.

The vibrations of A_{2u} and E_u species are infrared active and the all of the gerade species except A_{2g} are Raman active.[9] The phase II of ND_4I corresponds to the space group O_h–$Pm3m$,[12] a body-centered cubic lattice containing one molecule in a unit cell. Both ammonium and halide ions occupy sites with O_h symmetry. The irreducible representations for the case are

$$\Gamma(\mathrm{AT}) = F_{1u} ,$$
$$\Gamma(\mathrm{OT}) = F_{1u} ,$$
$$\Gamma(\mathrm{OL}) = F_{1g} .$$

The selection rules for the optical transitions in crystals belonging to the O_h space group require the F_{1u} mode to be infrared and Raman active, but the F_{1g} mode to be neither infrared nor Raman active.

Since the librational motion of the ND_4^+ ion is infrared inactive in the phase II and active in the phase III, it would be expected that the band appears at around the transition temperature (224 K) with a gradual drop in temperature. The result is not accord very well with the expectation, as the band does not appear even at 170 K. However, such a case has been shown in our previous study[11] for the librations of the NH_4^+ ions in NH_4I and NH_4Br, in which the librational motion could not be observed at high temperature in the phase III range. This phenomenon is explained by that the band was masked with an intense and broad absorption due to the thermal motion of the lattice (OT; E_u). In conclusion, the band at 238 em^{-1} may be assigned to the libration of ND_4^+ ion. The analysis of overtone and combination band, shown later, reasonably supports the conclusion.

The ratio of the librational frequencies for ND_4I (238 cm^{-1}) and NH_4I (301 cm^{-1}) is 0.79. This value is larger than those for other halides (0.720 for the chloride and 0.724 for the bromide), in which the ions are ordered in CsCl type lattice. If the libration is a harmonic vibration and the potential barrier of the libration is same for both ND_4I and NH_4I, the absorption is expected to appear at 213 cm^{-1}. The potential barrier (V_0) for an electrostatic force for the CsCl type lattice is interpreted with the following equation;[13]

$$V_0 = 46.8(e/4)^2 \cdot r^4/d^5 ,$$

where r is the distance between nitrogen and halogen atoms and d is the lattice dimension. According to the estimation of the lattice dimensions for ND_4I and NH_4I in the temperature range 190 to –170°C by Hovi et al.,[2] the difference between those of ND_4I and NH_4I is extremely small in the phase III, but the ratio of the c and a axes for ND_4I increases with a lowering of temperature, as compared with that for NH_4I. Therefore, the higher frequency observed for ND_4I would be explained by the distortion of lattice observed in the axis ratio at low temperature.

(13) H.S. Gutowsky, G.E. Pake, and R. Bersohn, J. Chem. Phys., **22** (1954), 643.

2. On the libration for ND_4Br

The measurements of the far-infrared spectrum of ND_4Br did not show any absorptions in the frequency range expected for the libration, while the libration was expected at 252 cm^{-1} at 21 K (phase IV) from the analysis of combination bands by Shumaker and Garland.[10] ND_4Br in the phase IV belongs to the space group T_d^1–$P\bar{4}3m$, a body-centered cubic lattice containing one molecule per unit cell. In the irreducible representations, $\Gamma(AT)=F_2$, $\Gamma(OT)=F_2$, and $\Gamma(OL)=F_1$, the OT mode is infrared and Raman active and the OL mode is neither infrared nor Raman active. Thus, the libration can not be observed in the phase IV.

In spite of the infrared active mode for the phase III, the libration for ND_4Br was not observed. This may be caused by that the band was masked with a broad absorption due to the thermal motion of the lattice (OT; 145 cm^{-1}). The masking in this salt will be more effective than that in NH_4Br in which the libration (348 cm^{-1}) is far from the OT frequency.

3. Overtones and combination bands

Schumaker and Garland[10] found the first and second overtones of the libration for ND_4Br at 490 and 720 cm^{-1}, respectively, at 21 K. The combination band of the librational and translational mode (OL+OT) was also reported by them at 394 cm^{-1} as an extremely weak band. The selection rule for the overtones and combinations[14] are loose in a solid and then many transitions are allowed at wave vector $\mathbf{k}\neq0$. The first overtone of OL mode for ND_4Br was clearly observed in the present measurement, but the combination band was not identified because of the weakness.

Fig. 3 shows the spectra of ND_4I in the phase III. Both a weak band at 470 cm^{-1} and an intense band at 420 cm^{-1} are observed in the spectra. The band at 470 cm^{-1} is readily assigned to the first overtone of the libration ($2\times234=476$ cm^{-1}). This band vanished at 149 K with a rise in temperature in a similar manner to the fundamental seen in Fig. 2. The librational frequencies and the overtones are listed in Table 2 with the reference values. The intense band at 47 K is composed of two peaks at 420 and 430 cm^{-1} (shoulder). On warming, this band became broad and the shoulder vanished at 120 K. At 170 K, the peak shifted to 410 cm^{-1}, followed by the disappearance at 202 K. Since the band is strong and the OT band intensity is extremely strong, the two peaks may be assigned to the combination bands at $\mathbf{k}=0$ related to the OL and OT modes. The OT modes have been observed as an infrared band at 140 cm^{-1} (E_u) and two Raman active bands at 43 (A_g) and 145 cm^{-1} (E_g). The direct production of the ternaly

(14) S. Nudelman and S.S. Mitra, *Optical Properties of Solids*, Plenum, New York, (1969), Chap. 4.

Table 2. Librational frequencies of the ammonium ions for the halides, in cm^{-1}

	NH_4I	ND_4I	NH_4Br	ND_4Br
E_u(IR)	301[a]	238	348[a]	(252)[b]
E_g(Raman)	287[c]	—	331[c]	—
2×OL	—	470	(672)[b]	(490)

The value in parenthesis is in the phase IV. a; ref. 11, b; ref. 10, and c; ref. 9.

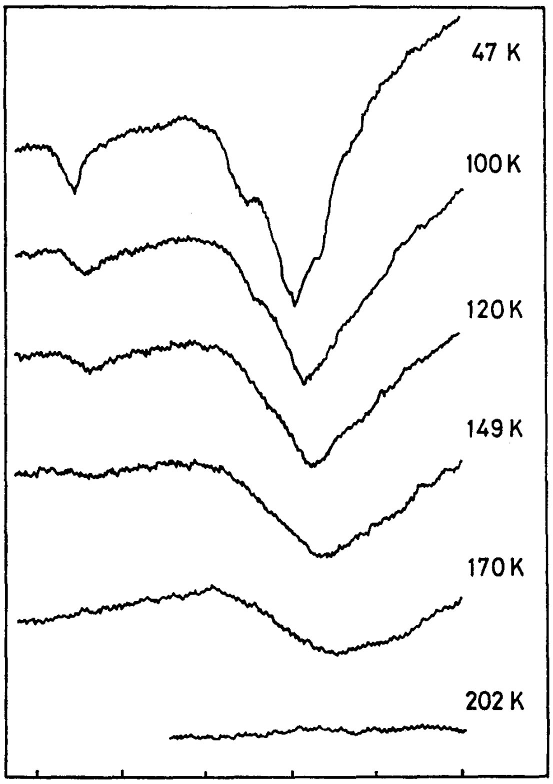

Fig. 3. Far-infrared spectra of ND_4I at various temperatures in the region 500–380 cm^{-1}.

combinations(15) is written as follows,

$$E_u(\mathrm{OL})\times E_u(\mathrm{OT})\times A_g(\mathrm{OT}) = A_{1u}+A_{2u}+B_{1u}+B_{2u}$$
$$= E_u(\mathrm{OL})\times E_g(\mathrm{OT})\times A_g(\mathrm{OT}).$$

The A_{2u} species is infrared active. The combination bands are then calculated to be

$$238(E_u)+140(E_u)+43(A_g) = 421\,\mathrm{cm}^{-1},$$

$$238(E_u)+145(E_g)+43(A_g) = 426\,\mathrm{cm}^{-1}.$$

The values agreed well with the observed frequencies, 420 and 430 cm^{-1}, at 47 K.

(15) E.B. Wilson, Jr., J.C. Decius, and P.C. Cross, *Molecular Vibration*, McGraw-Hill New York (1955), 331.