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THE TORSIONAL VIBRATIONS OF THE AMMONIUM IONS IN AMMONIUM IODIDE AND AMMONIUM BROMIDE

Shinji ONODERA
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira-2-chome, Sendai 980

The far-infrared spectra of NH_4I and NH_4Br have been measured at temperatures of -223 to -53 °C. The torsional vibrations of the NH_4^+ ions in the phase III crystalline salts were observed at 301 cm^{-1} for NH_4I at -223 °C and at 348 cm^{-1} for NH_4Br at -166 °C.

It is known that ammonium iodide occurs in three crystalline phases and ammonium bromide in four phases. In the phase III at low temperature ($<$ -41.6 °C for NH_4I and -38.1∼-165 °C for NH_4Br), both salts have a tetragonal structure, which is a slightly distorted body-centered (CsCl type) cubic lattice. The torsional vibration of the ammonium ion was first inferred to be at 280 cm^{-1} for ammonium iodide and at 319 cm^{-1} for ammonium bromide from the analysis of the infrared combination bands.[1,2] It was also estimated from the heat capacity measurements[3,4] that the torsional frequencies should be 279 cm^{-1} for ammonium iodide and 340 cm^{-1} for ammonium bromide. The direct observation of the torsional frequency has been made by means of a neutron inelastic scattering technique (293 cm^{-1} for NH_4I and 335 cm^{-1} for NH_4Br)[5] and the laser Raman spectroscopy (287 cm^{-1} for NH_4I and 331 cm^{-1} for NH_4Br).[6] However, the examination of the far-infrared spectra of the salts by Durig and Antion[6] could not find out the absorption due to the torsion in the infrared active modes for the ammonium ion.

In order to ascertain the torsional frequencies for the ammonium ion, we have measured the far-infrared spectra of ammonium iodide and ammonium bromide at low temperatures by using a liquid helium cryostat.[7] The observations of the torsional frequencies will be reported in this paper.

Commercial ammonium iodide and ammonium bromide were purified by recrystallization from water, followed by the sublimation under a vacuum at 300°C. Each salt was mulled with a paraffin wax on a polyethylene sheet and subjected to the measurement of the far-infrared spectrum. To detect the weak absorptions of the salts, the specimens were prepared as thick as possible, and an attention was also paied to avoid the supercooling of the specimens. The temperature of the sample was varied with a heater in the liquid helium cryostat and detected with a Au:Co-Cu thermocouple. A Hitachi FIS-1 far-infrared spectrophotometer was used to record the spectra.

Fig. 1 shows the spectra of ammonium iodide (phase III) at various temperatures. As clearly seen in the figure, the spectrum of the salt varies with temperature. The relatively weak absorption at 301 cm^{-1} (-223°C) shifted to lower frequency and weakened with a rise in temperature, accompanying the decrease of the background transmission. The increase of the background absorption would be ascribed to the thermal motions of the crystalline lattice, which eclipse the low frequency vibrations at high temperatures. The frequency shift with temperature may be caused by the expansion of the lattice. The observed frequency 298.5 cm^{-1} at -153°C is quite reasonable, because the average value of the infrared and Raman5) frequencies is in agreement with the frequency obtained by the neutron scattering measurement,5) which is independent of selection rules.

The far-infrared spectra of ammonium bromide at various temperatures are shown in Fig. 2. Since the transition of the phase IV ammonium bromide to the phase III occurs at -165°C, the spectrum of Fig. 2a is referred to the phase IV (CsCl

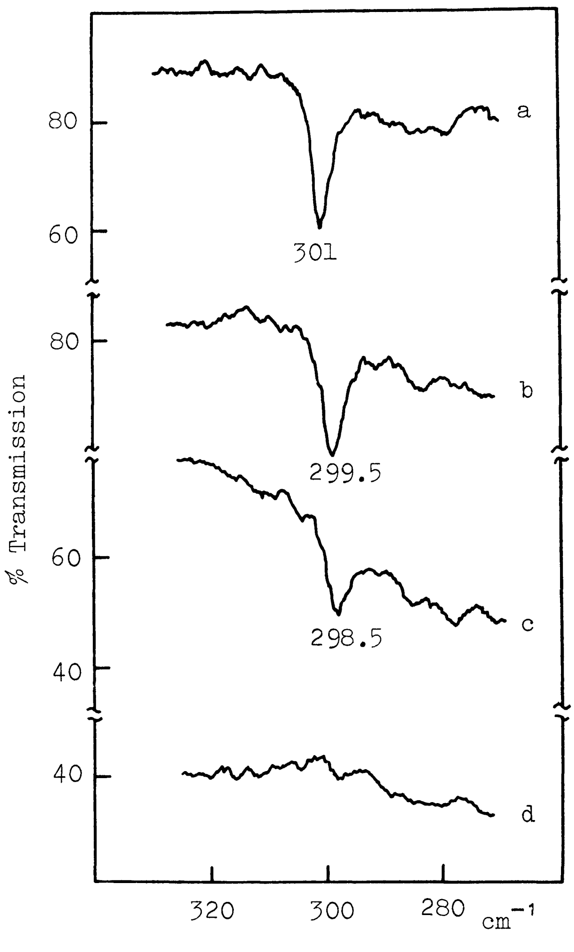

Fig. 1. Far-infrared spectra of ammonium iodide at various temperatures.
a : -223°C, b : -188°C, c : -153°C, d : -53°C.

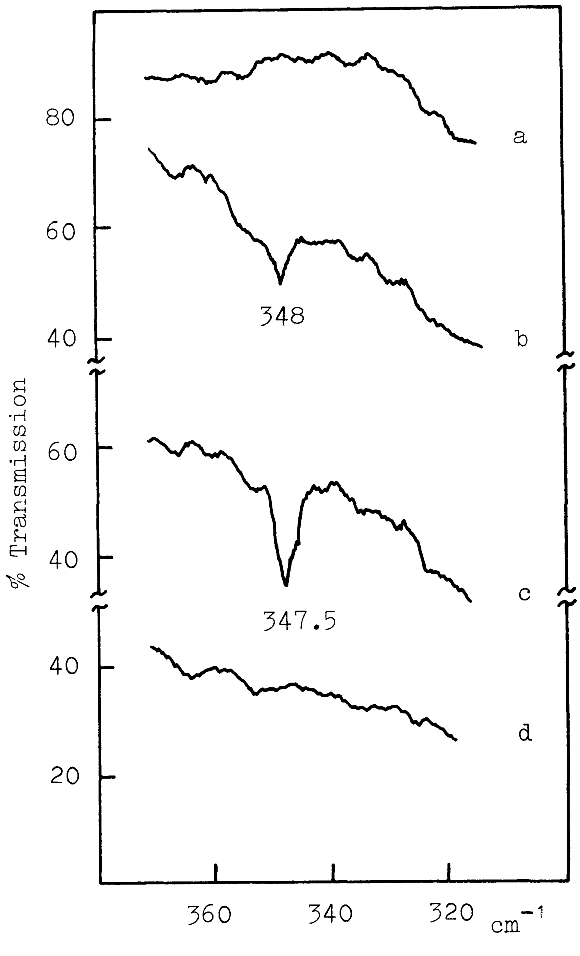

Fig. 2. Far-infrared spectra of ammonium bromide at various temperatures.
a : -233°C, b : -166°C, c : -152°C, d : -58°C.

type), in which the torsional vibration of the ammonium ion would be inactive in the infrared. Thus, the appearance of the absorption at 348 cm^{-1} (Fig. 2b) at around the transition temperature suggests that this band originated from the torsion of the ammonium ion in the phase III. The intensity of the absorption band at -166 °C is weaker than that at -152 °C. This implies that the transition achieved gradually within a temperature interval of about 10 °C or that the specimen did not warm up uniformly. The frequency shift and the decrease of the background transmission with a rise in temperature are interpreted similarly to the spectrum of ammonium iodide. The average value of the infrared and Raman$^{6)}$ frequencies is close to the frequency observed for ammonium bromide at -150 °C by a neutron scattering technique.$^{8)}$ The observed frequencies and the reference values are summarized in Table 1.

Table 1. Torsional Frequencies (cm^{-1}) for the Ammonium Ions in Ammonium Iodide and Ammonium Bromide

	Far-infrared (Present study) ($\underline{E_u}$)	Raman^a ($\underline{E_g}$)	Neutron scattering	Combination band in i.r.	Heat capacity
NH_4I	301 ± 0.5 (-223 °C)	287 (-160 °C)	293 ± 1.5^b (-173 °C)	280^d (-150 °C)	279^f
NH_4Br	348 ± 0.5 (-166 °C)	331 (-135 °C)	340^c (-150 °C)	319^e (-190 °C)	340 ± 7^g

a: Ref. 6, b: Ref. 5, c: Ref. 8, d: Ref. 1, e: Ref. 2, f: Ref. 3, g: Ref. 4.

In the phase III crystals of ammonium iodide and ammonium bromide, the ammonium ions are situated on $\underline{D_{2d}}$ sites and the halide ions occupy $\underline{C_{4v}}$ sites. Such a crystal permits of the twelve external fundamental vibrations represented as two acoustical translations, six optical translations, and four optical librations.$^{6)}$ Among these, one libration ($\underline{E_u}$) and two optical translations ($\underline{A_{2u}}$ and $\underline{E_u}$), which are all inactive in Raman, are permitted in the infrared spectrum. The observed frequencies, 301 cm^{-1} for ammonium iodide and 348 cm^{-1} for ammonium bromide, are readily assigned to the $\underline{E_u}$ librational vibration.

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