

VI. OPTICAL AND INFRARED SPECTROSCOPY*

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A. WORK COMPLETED

The theses listed here were submitted to the Department of Physics, M. I. T., May 1967, in partial fulfillment of the requirements for the degrees indicated.

E. M. Immerman, "Analysis of KCl-KBr Mixed Crystals Using Infrared Spectroscopy," S. B. Thesis.

J. Z. Mase, "Infrared and Raman Spectra of Several Ionic and Molecular Crystals," S. B. Thesis.

J. F. Parrish, "Lattice Vibrational Spectra of $\text{Cd/S}_x\text{:Se}_{1-x}$ Mixed Crystals," S. M. Thesis.

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B. FURTHER INFRARED AND RAMAN MEASUREMENTS OF THE AMMONIUM HALIDES

1. Introduction

The reflection spectra of the ammonium halides have been previously reported by Reintjes and Perry.^{1,2} Kramers-Kronig analyses and classical oscillator fits to the reflectivity have provided the transverse and the longitudinal optical frequencies. The Raman spectra of NH_4Cl crystal and powder, ND_4Cl powder, and NH_4Br powder were also measured by Reintjes.^{1,2} The investigation of the transverse optical phonon frequency by thin-film measurements has been completed on NH_4Cl , ND_4Cl , NH_4Br , and ND_4Br , at 300°K and 100°K . The Raman spectrum of NH_4Br single crystal has been measured as a function of temperature and was found to be substantially in agreement with that reported by Krishnan,³ but differs from the powder data.¹ The transmission

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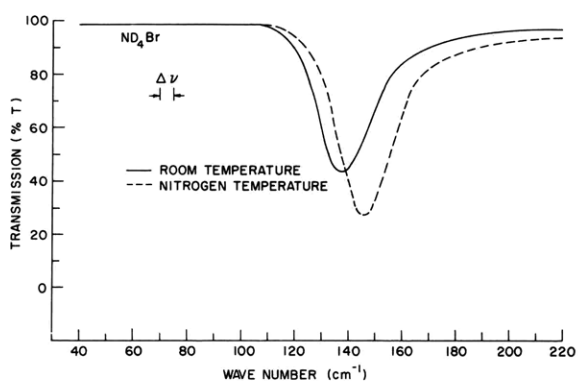
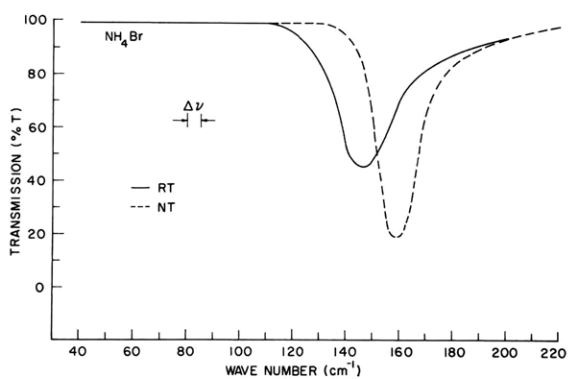
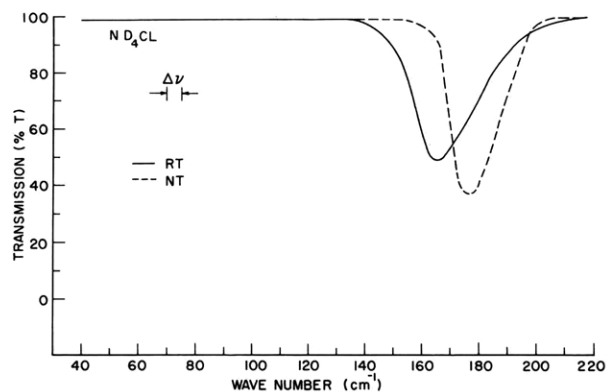
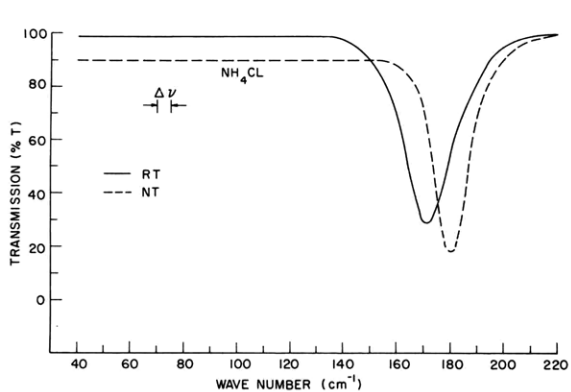


Fig. VI-1. Transmission spectra of thin film of NH_4Cl , ND_4Cl , NH_4Br , and ND_4Br , at room temperature (RT) and liquid nitrogen temperature (NT) from 40-220 cm^{-1} .

of the single crystals NH_4Br has also been measured from $10\text{-}105\text{ cm}^{-1}$ to check the infrared activity of bands seen in the Raman spectrum and to investigate the possibilities of impurity-induced absorption.

2. Experimental Results

The transmission of thin films of NH_4Cl , ND_4Cl , NH_4Br , ND_4Br , at 300°K and 100°K are shown in Fig. VI-1. The measurements were made on the Michelson interferometer in the range $40\text{-}220\text{ cm}^{-1}$.

Reagent grade granular NH_4Cl and NH_4Br were used to prepare the thin film. The deuterated compounds of ND_4Cl and ND_4Br were made by repeated exchange.

The thin films were evaporated either on 0.04-mm polyethylene or 0.5-mm wedged crystal quartz in an Edwards Model 6E4 vacuum coating unit. Various film thickness were observed at both temperatures, and the transmission minimum was essentially independent of film thickness or substrate. The quartz substrate had the advantage that at low temperatures equilibrium was reached more rapidly.

In addition to the evaporated films, the ammonium halide powders contained in a polyethylene matrix were investigated, but only broad absorption bands were found with this technique and the procedure was abandoned in favor of evaporated films.

The transmission of a single crystal of NH_4Br was measured between $15\text{-}105\text{ cm}^{-1}$ at $\sim 77^\circ\text{K}$ and $\sim 4^\circ\text{K}$. The results are shown in Fig. VI-2. The reflectivity of the

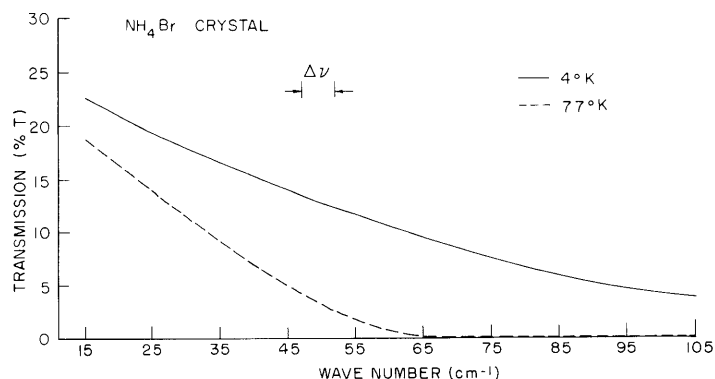


Fig. VI-2. Transmission spectra for a single crystal of NH_4Br (4 mm thick) at 77°K and 4°K from $15\text{-}105\text{ cm}^{-1}$.

NH_4Br crystal was also run at 4°K to insure that it was below the "78°K phase transition." No observable difference in the reflection spectrum previously reported by Reintjes and Perry² was observed, except for a very slight increase in reflectivity

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at the reststrahlen peak.

The Raman spectra were recorded on the Cary 81 spectrophotometer in the Spectroscopy Laboratory, M. I. T. The measurements of Reintjes^{1,2} for the powders were repeated at various temperatures and extended to 4°K for the NH₄Br powder. No significant differences were observed, except for a frequency shift of the bands and

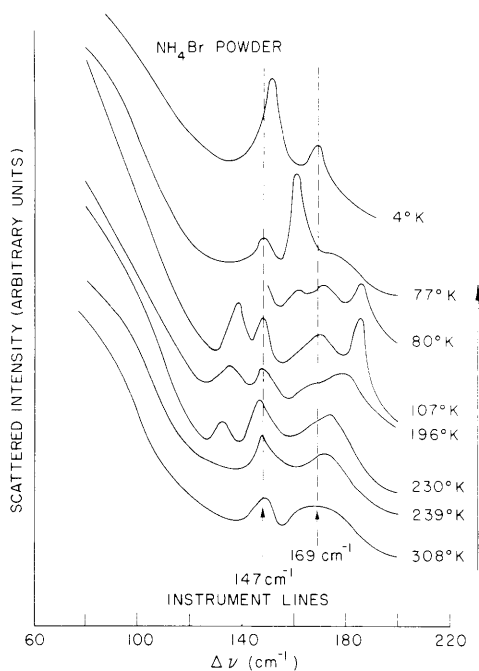


Fig. VI-3. Raman spectra of NH₄Br powder at various temperatures.

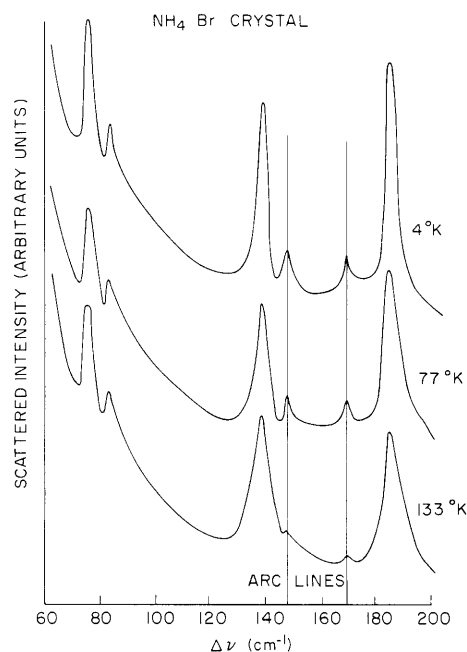


Fig. VI-4. Raman spectra of NH₄Br single crystal at various temperatures.

some intensity changes. The results for NH₄Br are shown in Fig. VI-3. Measurements of NH₄Br crystals were, however, significantly different from the powder measurements, and the spectra recorded at 133°K, 77°K, and 4°K are shown in Fig. VI-4.

2. Discussion

a. Thin Films of Ammonium Halides

The transmission spectra of thin films of NH₄Cl, ND₄Cl, NH₄Br, and ND₄Br are shown in Fig. VI-1. The effective resolution is 5 cm⁻¹, as indicated by $\Delta\nu$.

NH₄Cl. In the spectrum of NH₄Cl evaporated on quartz, the single absorption at 172 ± 1 cm⁻¹ (RT) shifted to 181 ± 1 cm⁻¹ (NT) and became sharper and more intense, as did the reflectivity measured by Reintjes.¹ The frequencies are only in fair

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agreement with the ω_t of 175 cm^{-1} (RT) and 188 cm^{-1} (NT) and a Raman line at 188 cm^{-1} (NT).¹ In slightly better agreement are classical oscillator frequencies of 173 (RT) and 184 cm^{-1} (NT). The neutron scattering spectra of Woods et al.⁵ show a peak at 185 cm^{-1} at 90°K . No error estimate is given; from the spectrum it seems to be on the same order as Palevsky's,⁶ making it $\approx \pm 5 \text{ cm}^{-1}$. More favorably, Krishnan⁷ has reported a very intense Raman line of frequency 183 cm^{-1} at 85°K .

ND₄Cl. The spectrum of ND₄Cl evaporated on polyethylene likewise exhibited a single absorption. The band at $166 \pm 2 \text{ cm}^{-1}$ (RT) moved to $177 \pm 1 \text{ cm}^{-1}$ (NT), deepened, and became sharper. The nitrogen temperature measurement agrees with Reintjes^{1,2} Raman measurement of 177 cm^{-1} at 77°K .

NH₄Br. The spectrum of NH₄Br evaporated on polyethylene or quartz showed only one absorption at both 300°K (RT) and 77°K (NT). At room temperature, the maximum absorption occurs at $147 \pm 1 \text{ cm}^{-1}$. This value compares well with the transverse optical frequency of 146.8 cm^{-1} obtained by Reintjes^{1,2} from a Kramers-Kronig analysis of the crystal reflectivity. A classical oscillator fit of the reflectivity has provided a frequency of 144 cm^{-1} for ω_1 , the primary oscillator.⁸ Also in agreement is a value of $148 \pm 6 \text{ cm}^{-1}$ measured by Palevsky⁶ at 293°K , using the inelastic scattering of neutrons.

When the sample cooled to 77°K , the absorption shifted to a higher frequency, and became deeper and sharper. Its frequency of $160 \pm 2 \text{ cm}^{-1}$ agrees with Reintjes^{1,8} values of 159 cm^{-1} for ω_t and 155 cm^{-1} for ω_1 . The half-height width of the absorption narrowed approximately 38 per cent on cooling from 300°K to 77°K , while that of Reintjes' reflectivity narrowed 36 per cent. Mikke and Kroh⁹ report a frequency of $\sim 165 \text{ cm}^{-1}$ for a so-called optical peak from their neutron scattering measurements at 120°K . The curve was less well defined, however, than Palevsky's⁶ room temperature measurement, so the error for the 165 cm^{-1} frequency must be larger than the $\pm 6 \text{ cm}^{-1}$ of Palevsky. Wagner and Hornig¹⁰ infer a limiting lattice frequency of approximately 160 cm^{-1} for phase IV (below 78°K) NH₄Br from combination bands in their near infrared spectra of thin films. The observed value of $160 \pm 2 \text{ cm}^{-1}$ thus agrees well with the reported values, and is identified with the transverse optical lattice frequency, ω_{t0} .

To insure that the NH₄Br was indeed in the ordered cubic phase (below 78°K), a measurement was made with liquid helium in the cryostat. The frequency observed was $159 \pm 2 \text{ cm}^{-1}$, which is within the experimental error of the measurements at 77°K .

ND₄Br. The spectra of the deuterated ammonium bromide films are of the same type as those of NH₄Br. The single absorption at $138 \pm 1 \text{ cm}^{-1}$ (RT) shifted to $147 \pm 2 \text{ cm}^{-1}$, and became sharper and more intense on cooling to nitrogen temperature. These frequencies are also identified with ω_{t0} , the transverse optical frequency.

For the run made at 77°K , ω_{t0} of ND₄Br is $\sim 13 \text{ cm}^{-1}$ less than that of NH₄Br at the same temperature. This frequency shift is completely accounted for by the increase in mass of the ammonium ion. Using $\omega \sim 1/\sqrt{M}$, and the values of ω_{t0} at 77°K , we obtain

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$$\frac{\text{ND}_4\text{Br}}{\text{NH}_4\text{Br}} = 0.919 \text{ and } \left[\frac{M_{\text{NH}_4\text{Br}}}{M_{\text{ND}_4\text{Br}}} \right]^{1/2} = 0.923.$$

b. NH_4Br Reflectivity

No appreciable change was observed in the reflectivity as the crystal was cooled from 77°K to 4°K, thereby confirming that the nitrogen temperature measurements of Reintjes^{1,2} were indeed those of the crystal below the 78°K transition.

c. NH_4Br Crystal Transmission

At ~77°K, the large NH_4Br crystal was essentially black to the far infrared. At ~4°K, the crystal opened up, but showed only general absorption, nothing sharp. It was hoped that infrared evidence would be found for two low-frequency Raman lines reported by Krishnan³ and observed in our measurements. Impurity resonance modes may also be expected to absorb in this region, but nothing was found. The spectra are shown in Fig. VI-2.

d. Raman Spectra

The Raman spectra of ND_4Br powder are shown in Fig. VI-5. No lines were present at room temperature; only the arc lines at 147 and 169 cm^{-1} were observed. The transition temperature from phase III (tetragonal) to phase IV (CsCl) was determined to be between 150°K and 160°K, which compares favorably with the previously reported value.¹¹ A line appears just below the transition temperature near the arc line, and becomes sharper, more intense, and shifts to higher frequencies as the temperature is lowered. For comparison, the infrared and Raman frequencies are listed in Table VI-2. The Raman line is assigned as the transverse optical lattice vibration frequency, and its value of 149 cm^{-1} agrees well with the infrared frequency of 147 cm^{-1} at 77°K obtained from the transmission of the thin film.

NH_4Br . The Raman spectra of the large NH_4Br crystal are shown in Fig. VI-4. The spectra at the 3 temperatures are quite similar and show the same lines, with a sharpening of the lines as the temperature was lowered. The two strong lines at 138 and 185 cm^{-1} agree with Krishnan's³ Raman frequencies of 136 and 182 cm^{-1} observed at 85°K.

Because of the tetragonal structure in this phase, these lines may be the split fundamental, ω_{to} , but only a single band at 151 cm^{-1} was found in the reflectivity at 200°K.⁹ Since unpolarized light was used in the reflectivity measurement, this may explain why a single peak was observed at a frequency between the two Raman lines. If these lines are identified as a split ω_{to} , there should be a change back to a single line as the sample is cooled below the 78°K transition to the cubic phase. This is, in fact,

what was observed by Reintjes^{1,2} as a sample of NH_4Br powder was cooled to 77°K ; a single line at 162 cm^{-1} was observed and identified as the cubic phase ω_{to} . There is

good agreement between this value and the infrared frequency of 160 cm^{-1} measured with the thin film at 77°K .

When the NH_4Br crystal was cooled to 130°K , to 77°K , and then to 4°K , no change was observed in the Raman spectrum, except for an increase in the intensity of the bands. There is a possible explanation for this unexpected result. Reintjes^{1,2} noticed a lingering of the tetragonal phase for approximately 20 minutes after cooling NH_4Br powder to 77°K . Perhaps, what was observed at nitrogen and helium temperatures was the Raman spectrum of the supercooled tetragonal phase. At such low temperatures the energy available for the phase change is undoubtedly small, which explains the slow transition. Further evidence of the tetragonal structure is found in Fig. VI-3, the Raman spectra of NH_4Br powder. In the spectrum at

107°K the powder is indeed in the tetragonal phase, and the frequencies are listed as 138 and 185 cm^{-1} by Reintjes.^{1,2} These frequencies agree perfectly with the ones observed in the crystal at 133°K and 4°K .

More difficult to explain are the low-frequency Raman lines at 72 and 79 cm^{-1} . Krishnan's³ spectrum at 85°K shows an intense line at 69 cm^{-1} and a weaker one at 77 cm^{-1} . He identifies these as part of the lattice spectrum, but gives no further assignment. Three things are strange about these lines. First, they were not observed in the spectra of the powder (Fig. VI-3), although they may be hidden in the relatively broad Rayleigh line. Second, they are not infrared active, as is shown by the infrared transmission of the single crystal of NH_4Br (Fig. VI-2). Finally, they were not observed in the neutron spectrum,⁶ which is not limited by the usual infrared and Raman selection rules. Two explanations of the lines are possible. There might be an impurity in the crystal that was not in the powder sample. Krishnan³ states that his crystal was a pale yellow; the one used here was a pale yellow-green. Stephenson¹³ has advised that the color arises from a copper impurity. Since both were similarly colored, the two

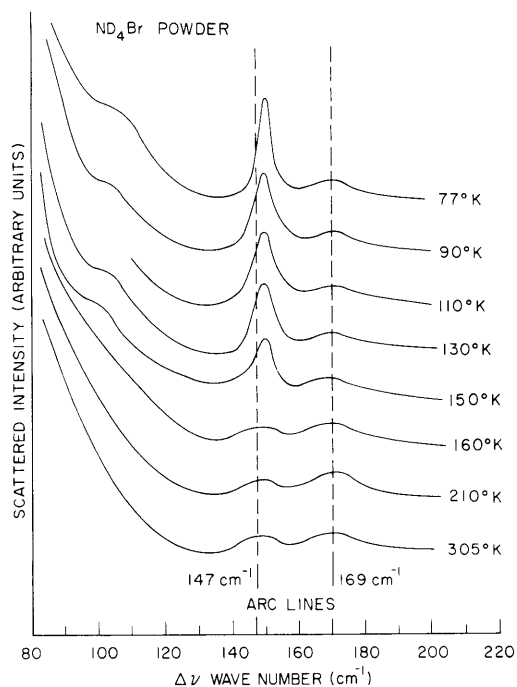


Fig. VI-5. Raman spectra of ND_4Br powder at various temperatures.

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low-frequency lines may be attributed to a copper impurity. The other explanation is that they are the frequencies of some lattice fundamental other than the transverse optical mode, possibly librations. The splitting into two lines is again due to the persistence of the tetragonal structure below the 78°K transition. Infrared inactivity explains why they were not observed in the transmission spectrum. It is likely that the broad Rayleigh line obscured them in the Raman spectra of the powder. A spectrum of the crystal definitely in the low-temperature ordered phase would probably decide the question. The tetragonal splitting would be removed, and impurity lines would probably stay unchanged. Any change would thus support the lattice vibration hypothesis.

The one remaining feature of the NH₄Br Raman spectrum to be explained is the line at 148 cm⁻¹ observed at 4°K with the powder, as shown in Fig. VI-3. All other measurements in Fig. VI-3 were made by Reintjes,^{1,2} and have been explained by him. Again, there are two possibilities for the 4°K spectrum. The sample could have been in a supercooled tetragonal phase, with the 138 cm⁻¹ line of the tetragonal phase shifted to 148 cm⁻¹. The absence of the 185 cm⁻¹ tetragonal line makes this a remote possibility, however. The other explanation is that the powder actually was in the low-temperature cubic phase and the intense 162 cm⁻¹ line at 77°K shifted to ~170 cm⁻¹ at 4°K. The 148 cm⁻¹ line had previously been buried in the arc line at 147 cm⁻¹, and did not become intense enough to be observed until helium temperature. Neither explanation is very satisfactory, however, in view of the lack of change in both the reflectivity

Table VI-1. Infrared and Raman frequencies of NH₄Cl and ND₄Cl in cm⁻¹.

	Thin Film Transmission	Reflectivity Kramers-Kronig	Reflectivity Dispersion	Raman	Others
NH ₄ Cl (300°K)	172 ± 1	175 ¹	ω ₁ = 173 ⁸ ω ₂ = 225 ⁸		
NH ₄ Cl (77°K)	181 ± 1	188 ¹	ω ₁ = 184 ⁸ ω ₂ = 246 ⁸	188 ^{1,2} crystal 188 ^{1,2} powder	185 ± 6 ⁵ neutron 183 ⁷ Raman
ND ₄ Cl (300°K)	166 ± 2				
ND ₄ Cl (77°K)	177 ± 1			177 ^{1,2}	

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Table VI-2. Infrared and Raman frequencies of NH_4Br and ND_4Br in cm^{-1} .

	Thin Film Transmission	Reflectivity Kramers-Kronig	Reflectivity Dispersion	Raman	Others
NH_4Br (300°K)	147 ± 1	146.8^1	$\omega_1 = 144^8$ $\omega_2 = 184^8$		148 ± 6^6 neutron
NH_4Br (200°K)		154^1	$\omega_1 = 151^8$ $\omega_2 = 182^8$	$135^{1,2}$ 180 powder	
NH_4Br (~110°K)				$138^{1,2}$ 185 powder 72 79 138 crystal 185	165 ± 6^9 neutron
NH_4Br (77°K)	160 ± 2	159^1	$\omega_1 = 155^8$ $\omega_2 = 192^8$	$162^{1,2}$ powder 72 79 138 crystal 185	160 inferred ¹⁰ 69 77 136 Raman ³ 182
NH_4Br (4°K)	159 ± 2			148 powder 72 79 138 crystal 185	
ND_4Br (300°K)	138 ± 1				
ND_4Br (77°K)	147 ± 2			149	

and thin-film transmission from nitrogen to helium temperature. The spectra of both the crystal and powder should be rechecked at 4°K, with care to insure that the samples have changed phase at 78°K before the final cooling to 4°K.

All of the observed and reported infrared and Raman frequencies of the ammonium halides have been listed for comparison in Tables VI-1 and VI-2. Table VI-3 shows further work by Reintjes and Perry,⁸ with a classical oscillator model used to fit the reflectivity spectrum at various temperatures, and shows the frequencies, oscillator

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Table VI-3. Parameters used in the classical oscillator model to fit the infrared reflectivity of NH_4Cl and NH_4Br single crystals at various temperatures. (All in cm^{-1} .)

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{s_1^2}{\omega^2 - \omega_1^2 - i\omega\gamma_1} + \frac{s_2^2}{\omega^2 - \omega_2^2 - i\omega\gamma_2}$$

	NH_4Cl		NH_4Br		
	300°K	85°K	300°K	200°K	85°K
s_1	339.0	341.0	295.0	285.0	280.0
ω_1	173.0	184.0	144.0	151.0	155.0
γ_1	18.0	4.0	17.0	9.0	2.5
s_2	87.0	52.0	52.0	55.0	48.0
ω_2	225.0	246.0	184.0	182.0	192.0
γ_2	45.0	32.0	30.0	28.0	38.0

strengths, and damping constants that were obtained.

The good agreement between the transverse optical frequencies and the Raman frequencies at 77°K indicates that the Raman lines are due to these lattice vibrations. That these lines are found in the Raman spectrum, at all, may indicate a deviation from ideal cubic symmetry in the low-temperature ordered phase.^{1,2}

In no samples were the longitudinal frequencies, as calculated from the reflectivity, observed in the Raman spectra. Perhaps, the splitting of lines in NH_4Br in the tetragonal phase could be observed in the infrared if polarized radiation were used, and the crystal orientation varied.

J. Z. Mase, C. H. Perry

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