VI. OPTICAL AND INFRARED SPECTROSCOPY[*]

Academic and Research Staff

Prof. C. H. Perry

Graduate Students

Jeanne H. Fertel　　　　　　　　J. F. Parrish
D. J. Muehlner　　　　　　　　　E. F. Young

Undergraduate Students

T. F. McNelly
J. F. Reintjes, Jr.
J. D. Wrigley, Jr.

A. WORK COMPLETED

The theses with titles and authors listed below were submitted to the Department of
Physics, M. I. T. , May 1966, in partial fulfillment of the requirements for the degree
of Bachelor of Science.

T. F. McNelly, "Reflectivity and Raman Studies of $KTaO_3$ and $(K, Na)TaO_3$."

J. F. Reintjes, Jr. , "Temperature Dependence of the Reflectivity and Raman Spectra
in Ammonium Chloride and Ammonium Bromide."

C. H. Perry

B. INFRARED REFLECTIVITY AND OPTICAL CONSTANTS OF TEKTITES

The room-temperature reflectance of three Tektites having carrying compositions has
been studied from 2. 5-500 μ (4000-20 cm^{-1}), with the use of a variety of instruments.[1,2]
The optical constants were obtained from a Kramers-Kronig analysis of the reflectivity
data.[3] A classical dispersion formula was used to fit the measured reflectivity curve,[4]
and approximate values for the frequencies (ω), oscillator strengths (s^2), and damping
constants (γ) were obtained for the two strongest vibrations. The results are the following

$$\omega_1 = 457 \pm 1 \ cm^{-1} \qquad\qquad \omega_2 = 1060 \pm 5 \ cm^{-1}$$

$$s_1^2 = 1.85 \pm .01 \times 10^5 \ (cm^{-1})^2 \qquad s_2^2 = 5.63 \pm .01 \times 10^5 \ (cm^{-1})^2$$

$$\gamma_1 = 55 \pm 5 \ cm^{-1} \qquad\qquad \gamma_2 = 80 \pm 5 \ cm^{-1}$$

The Tektites that were investigated had been completely analyzed for the major con-
stituents,[5] which are listed in Table VI-1. The reflectivity curves for a Moldavite (T5309)
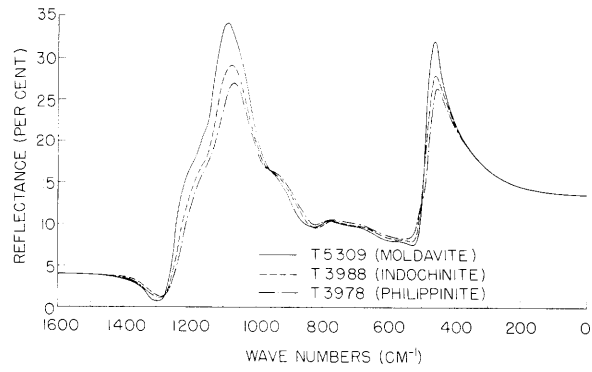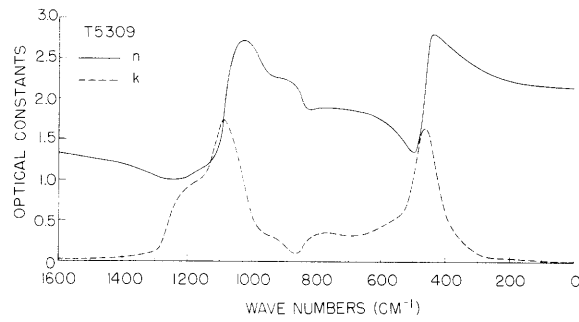

Fig. VI-1. Reflectivity curves for three Tektite samples.

Fig. VI-2. Optical constants of Tektites (Moldavite T5309).

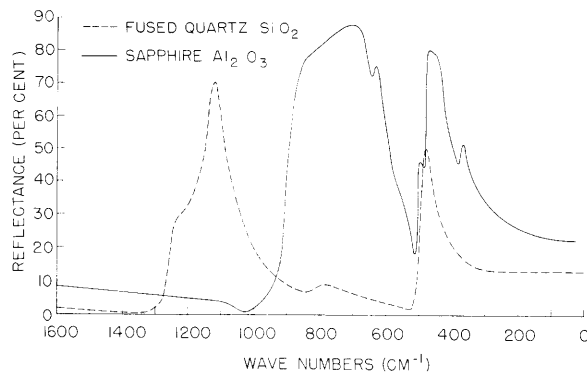Fig. VI-3. Reflectivity curves for fused quartz (SiO_2) and Sapphire (Al_2O_3).

Table VI-1. Major constituents of the Tektites investigated.

	Moldavite T5309	Indochinite T3988	Philippinite T3987
SiO_2	79. 6	73. 3	70. 1
Al_2O_3	10. 7	12. 4	14. 7
CaO	2. 8	2. 0	3. 3
K_2O	3. 5	2. 5	2. 6
FeO	1. 5	4. 2	4. 2
MgO	1. 9	2. 3	2. 4

an Indochinite (T5309) and a Philippinite (T3978) are shown in Fig. VI-1. The Moldavite had the largest percentage of SiO_2, and this appears to be the major contribution to the reflectivity curve, although all three samples show essentially similar features.

The optical constants n and k for the moldavite sample only are shown in Fig. VI-2, as the values are essentially the same for all three materials. The reflectivity curve (Fig. VI-1) shows slight shoulders in the region of 1200 cm^{-1}, 925 cm^{-1}, 750 cm^{-1}, and 400 cm^{-1}, as well as the major peaks in the reflectivity at ~1080 cm^{-1} and 460 cm^{-1}.

Figure VI-3 shows the reflectivity curves for fused quartz and sapphire. The Tektite reflectivity measurements are similar in most respects to a composite curve of these materials when the relative compositions of the two major constituents are taken into account by weighting their individual dielectric dispersion curves. A thin slice, approximately 50 μ thick, of the T5309 sample was used for transmission measurements and the curve is shown in Fig. VI-4. Owing to the large absorption coefficient, no measurable transmission could be obtained in the region of the lattice bands, but two broad bands were observed at 1600 cm^{-1} and 1850 cm^{-1} and a shoulder at 1950 cm^{-1}.
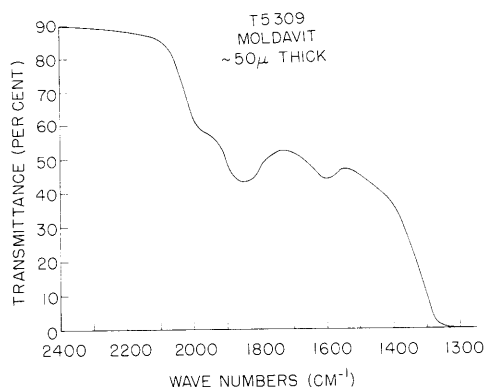

Fig. VI-4. Transmittance of 50-μ thick slice of the Moldavite sample (T5309).

The interpretation of these bands is not understood, as they could be due to second-order effects or absorption caused by the minor constituents in the materials. It is possible that studies of thin slices of the other two materials could help in the identification of these bands, but no measurable shift in the band centers or sharpening of the bands was observed on cooling the sample to liquid-nitrogen temperature.

Although the results of these studies do not specifically lead to the mode of origin for Tektites, the reflectivity curves are consistent with the major constituents and do show a measurable difference in intensity, which depends on the geographic location. The curves may be of significant importance in the identification of the major constituents of the lunar surface, for example, when studied by infrared techniques.

We would like to thank Professor W. H. Pinson, Jr., Department of Geology and Geophysics, M.I.T., for the samples.

<div align="right">C. H. Perry, J. D. Wrigley, Jr.</div>

References

1. C. H. Perry, "Techniques of Far Infrared Study," Quarterly Progress Report No. 70, Research Laboratory of Electronics, M.I.T., July 15, 1963, p. 19.
2. C. H. Perry, Japan. J. Appl. Phys., Suppl. I, p. 564, 1965.
3. C. H. Perry, B. N. Khanna, and G. Rupprecht, Phys. Rev. 135, A408 (1964).
4. W. G. Spitzer and D. A. Kleinman, Phys. Rev. 121, 1324 (1961).
5. C. C. Schnetler and W. H. Pinson, Jr., Geochim. Cosmochim. Acta 28, 793 (1964).

C. LOW-FREQUENCY VIBRATIONS IN AMMONIUM-CHLORIDE AND AMMONIUM-BROMIDE CRYSTALS

1. Introduction

Ammonium chloride has a well-known order-disorder transition[1] at 242.8°K, and the Cs Cl structure both above and below the transition, with the ammonium ion in the center of a cube of eight chloride ions.[2] The deuterated compound ND_4Cl has the same structure, with a similar transition at 249.5°K.

Ammonium bromide has an order-disorder transition[1] at 235°K, which is accompanied by a structure change from cubic to tetragonal, with two molecules per unit cell, and has a further transition back to body-centered cubic at 78°K. This structure is an ordered one similar to the low-temperature phase of ammonium chloride. A thermal hysteresis of approximately 30° in specific-heat measurements has been observed in the lower transition temperature by Professor C. C. Stevenson, Department of

Physical Chemistry, M. I. T.

Hettich[3] found that ammonium chloride becomes piezoelectric below the transition, and Kamiyoshi[4] observed discontinuities in the static dielectric constants of both ammonium chloride and ammonium bromide. Menzies and Mills,[5] in 1935, reported the appearance of a low-frequency line in the Raman spectrum of the chloride below the transition, and Krishnan[6] has reported several low-frequency Raman lines in the bromide below its transition at 235°K. The far infrared reflection spectrum of NH_4Cl at room temperature was measured by Hojendahl,[7] in 1938, and the reflection spectrum of NH_4Br was reported by Rubens and Wartenburg,[8] in 1914.

Since all previous investigations had been performed more than thirty years ago, we decided to repeat both the infrared and Raman studies with the considerably improved instrumentation now available. The measurements were extended over a wider temperature range, more careful studies were made in the region of the transitions, and the results of both investigations were correlated and interpreted in terms of the low-frequency lattice vibrations.

2. Experimental Results

The reflectivity curves of NH_4Cl at room temperature and liquid-nitrogen temperature are shown in Fig. VI-5 and the reflectivity curves of NH_4Br at room temperature, dry-ice temperature and liquid-nitrogen temperature are shown in Fig. VI-6.

The reststrahlen frequency of NH_4Cl occurs at 193 cm^{-1} at room temperature and shifts to 210 cm^{-1} at liquid-nitrogen temperature. There is a sideband on the high-frequency side of the reflection peak which moves to higher frequencies as the temperature is lowered.

The reststrahlen frequency of NH_4Br occurs at 162 cm^{-1} at room temperature, 172 cm^{-1} at CO_2 temperature, and 175 cm^{-1} at liquid-nitrogen temperature.

The real and imaginary parts of the dielectric constant were obtained with a Kramers-Kronig analysis, and values of ϵ_o, ϵ_∞, ω_t and ω_ℓ are shown in Table VI-2.

The Lyddane-Sachs-Teller relation $\left(\dfrac{\omega_\ell^2}{\omega_t^2} = \dfrac{\epsilon_o}{\epsilon_\infty} \right)$ was satisfied by the frequency of

NH_4Br at room temperature and of NH_4Cl at room temperature and liquid-nitrogen temperature.

The effective charges of the ions in the lattice were calculated, and the results are shown in Table VI-3.

The Raman spectra of NH_4Cl, ND_4Cl and NH_4Br are shown in Fig. VI-7.

A low-frequency line appears in the NH_4Cl spectra when the sample is cooled below 241 °K. A similar line appears in the ND_4Cl spectra when the sample is cooled below 249.5°K. The shift in frequency of the line from the light to the heavy compound is
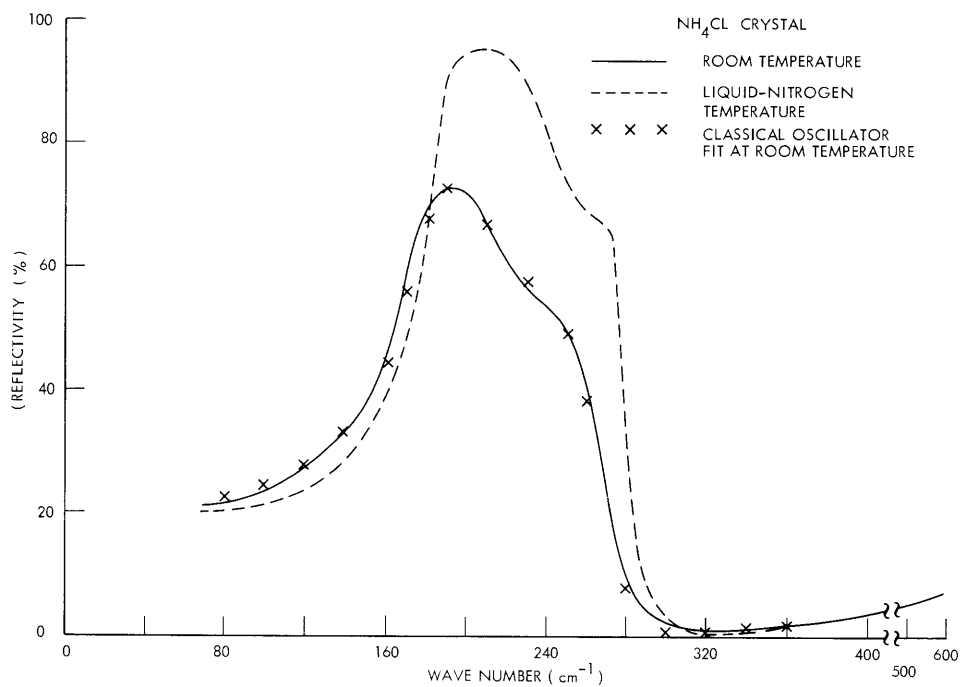
Fig. VI-5. Reflectivity curves of NH_4Cl at room temperature and liquid-nitrogen temperature.
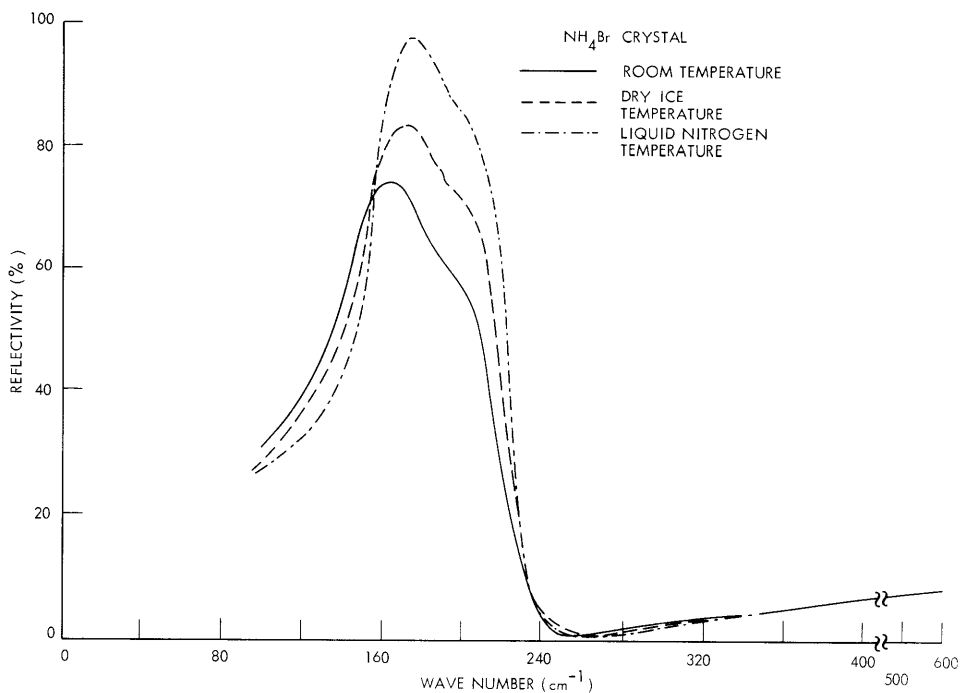

Fig. VI-6. Reflectivity curves of NH_4Br at room temperature, dry-ice temperature, and liquid-nitrogen temperature.

Table VI-2. Dielectric constants and vibrational frequencies of NH_4Cl and NH_4Br.

	ϵ_o	ϵ_∞	ω_t	ω_ℓ	$\left(\dfrac{\epsilon_o}{\epsilon_\infty}\right)\omega_t$ (calc.)
NH_4Cl Room Temperature	7.25	2.94	175.0 cm^{-1}	272.8 cm^{-1}	275.0 cm^{-1}
NH_4Cl Nitrogen Temperature	6.70	2.94	188.0 cm^{-1}	281.5 cm^{-1}	284.0 cm^{-1}
NH_4Br Room Temperature	7.10	3.19	146.8 cm^{-1}	224.3 cm^{-1}	219.0 cm^{-1}
NH_4Br CO_2 Temperature	7.10	3.19	154.0 cm^{-1}	226.8 cm^{-1}	
NH_4Br Nitrogen Temperature	7.10	3.19	159.0 cm^{-1}	229.0 cm^{-1}	

Table VI-3. Effective charges for NH_4Cl and NH_4Br in cubic phase.

	O_{eff}
NH_4Cl Room Temperature	0.820
NH_4Cl Nitrogen Temperature	0.815
NH_4Br Room Temperature	0.753

Note: These values of O_{eff} are of the same magnitude as those obtained for the alkali halides.

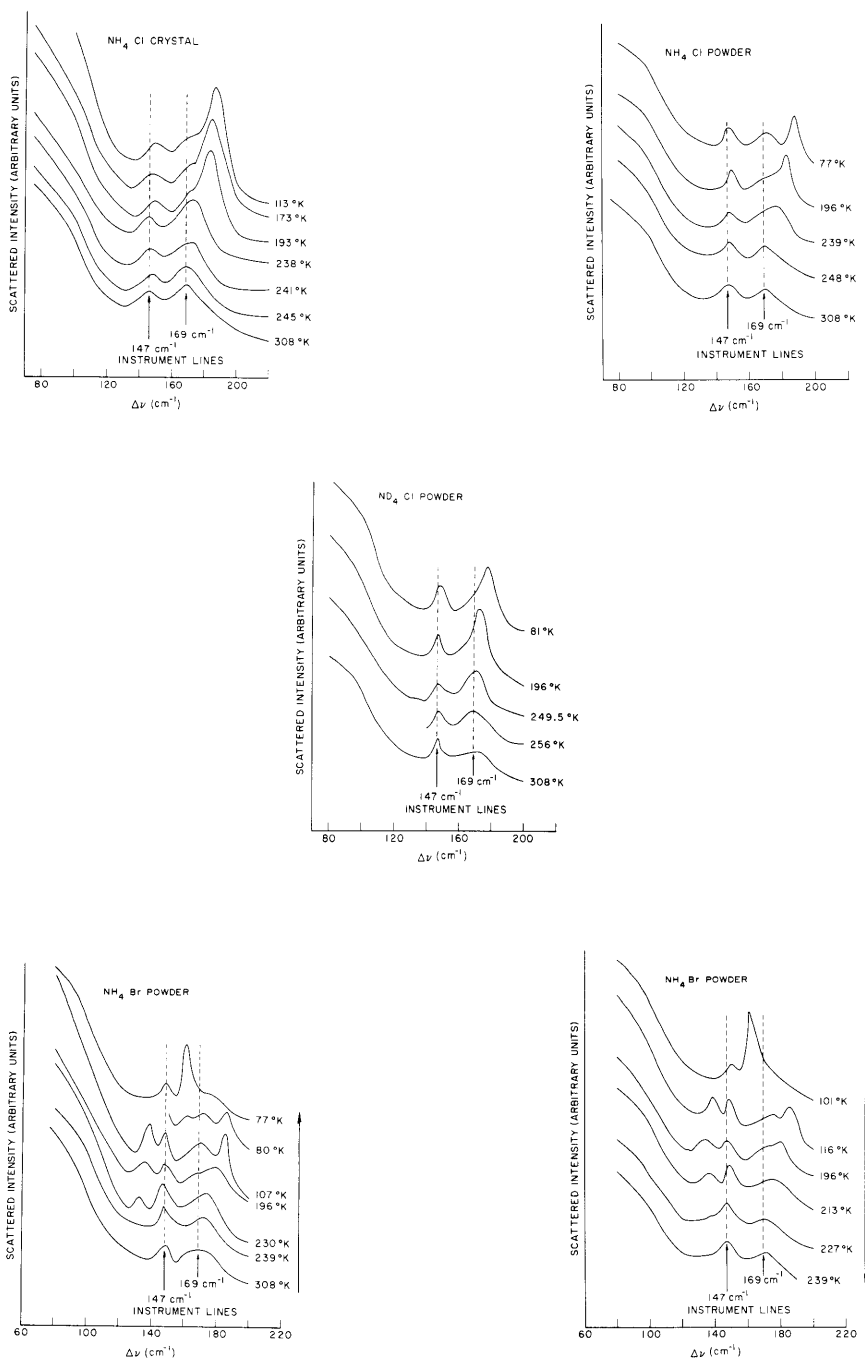Fig. VI-7. Raman spectra of NH_4Cl, ND_4Cl, and NH_4Br.

accounted for by the increase in mass of the ammonium ion.

The spectra of NH_4Br have two low-frequency lines for temperatures below 230°K, and one low-frequency line at 77°K. A 30° hysteresis was observed in the temperature of the lower transition, with the single line remaining until the temperature was raised to 116°K, in agreement with the specific-heat data of Professor Stevenson.

Table VI-4. Raman and infrared frequencies of NH_4Cl and NH_4Br.

	RT		~196°		77°	
	IR	R	IR	R	IR	R
NH_4Cl	175	—		184	188	188
NH_4Br	146.8	—	154	134,180	159	162

The Raman and infrared frequencies are compared in Table VI-4. The good agreement between the transverse optical frequencies and the Raman frequencies at 77°K indicates that the Raman lines are due to lattice vibrations. The presence of these lines in the Raman spectrum indicates a diviation from ideal cubic symmetry in the low-temperature ordered phase.

The presence of two lines in the Raman spectrum at 196°K agrees with measurements of a tetragonal structure at this temperature. The appearance of only one line in the reflection curve may be due to the insensitivity of this method of measurement.

The investigation of the temperature dependence of the eigen vibrations by infrared transmission measurements of thin films of these materials is now in progress.

We would like to thank Professor C. W. Garland, Deparment of Chemistry, M. I. T., (and Materials Center for Science and Engineering) for supplying most of the crystals used in this work, and Mr. Joseph Lastovka for supplying a large NH_4Cl crystal used for the reflectivity measurements.

J. F. Reintjes, Jr., C. H. Perry

References

1. E. L. Wigner and D. F. Hornig, J. Chem. Phys. 18, 296 (1950).
2. A. Smits and C. MacGillivray, Z. Physik. Chem. (Frankfurt) A166, 97 (1933).
3. A. Hettick and A. Schleede, Z. Physik 50, 249 (1928).
4. K. Kamiyoshi, Sci. Res. Inst., Tohoku U. A8, 252 (1956).
5. A. C. Menzies and H. R. Mills, Proc. Roy. Soc. (London) 148A, 407 (1935).
6. R. S. Krishnan, Proc. Indian Acad. Sci. A27, 321 (1948).
7. K. Hojendahl, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 16, 2 (1938).
8. H. Rubens and H. V. Wartenburg, Sitzber. preuss. Akad. Wiss. 169 (1914).