

Volume dependence of the Raman frequencies in ammonia solid I

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The volume dependence of the Raman frequencies in ammonia solid I has been measured. The Grüneisen parameters obtained at 195 K are 2.7 and 2.4 for two translational modes and 0.8 for a librational mode. In the range between 195 and 172.8 K, these values are independent of temperature within experimental uncertainties. The unusually low value of the Grüneisen parameter of the librational mode is attributed to electrostatic multipole interactions between molecules.

Figure 1 shows the ammonia phase diagram for temperatures between 170 and 232 K and molar volumes between 20.0 and 22.5 cm³/mol, which includes two solid phases. The transition lines and the isobars were drawn from the data of Mills *et al.*^{1,2} except for the sublimation line which was drawn using the data of McKelvey and Taylor.³

Solid I is known to have a $P2_13$ structure,^{4,5} and all zone-center lattice modes, four translations ($A + E + 2F$) and five rotations ($A + E + 3F$), are Raman active. Several Raman and infrared studies of solid I have been reported, the most complete being by Binbrek and Anderson.⁶ These authors, by comparing the spectra of NH₃ and ND₃, assigned the observed lattice frequencies to translational or librational modes (hindered rotations). We present here measurements of the volume dependence of lattice frequencies in solid I.

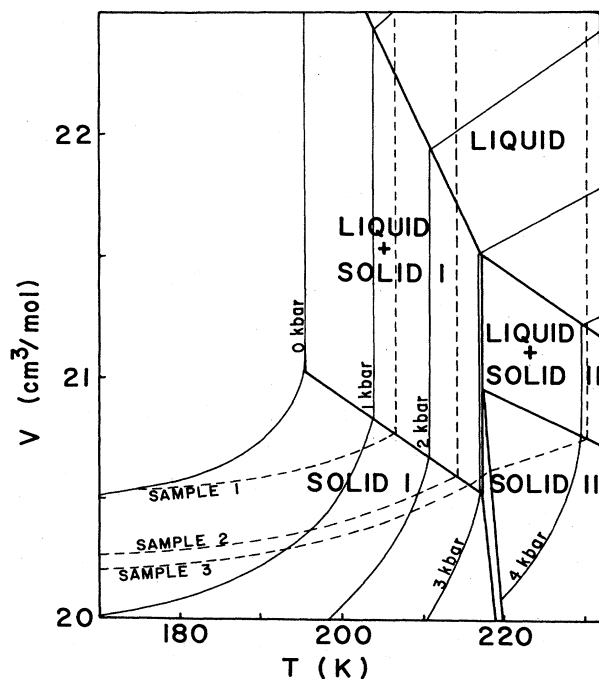


FIG. 1. Ammonia phase diagram reproduced from Refs. 1–3.

Using liquid ammonia as the pressure-transmitting fluid, solid samples were grown within an optical cell by keeping the temperature constant and slowly increasing the pressure. The samples, annealed overnight, were optically clear. Three samples were grown at different temperatures, the last being in a different phase, solid II, before it was cooled across the solid I–solid II transition. The nearly isochoric paths followed by the samples upon cooling, shown in Fig. 1 by the dashed lines, were calculated using elasticity theory⁷ and the known elastic and thermal properties of maraging steel⁸ and sapphire,⁹ the cell materials. Sample 3 followed a rather unusual path in that it made a transition from solid II into the region where solid I coexists with the liquid and finally became all solid I at a calculated temperature of 215.7 K. The fact that this change was observed to happen at 215.6 K gives us confidence on our volume calculation. Sample 1, on the other hand, reached zero pressure at a calculated temperature of 172.5 K. In fact, that sample cracked and became opaque near 150 K, probably under tensile stress as it pulled away from the cell walls.

Raman spectra were obtained with the 514.5-nm line from an argon-ion laser, a Spex double monochromator, and photon-counting techniques. Figure 2 shows the spectrum of the lattice region of sample 3 at 187.6 K. Binbrek and Anderson⁶ assigned the lines near 103 and 134 cm⁻¹ to translational modes and the line near 282

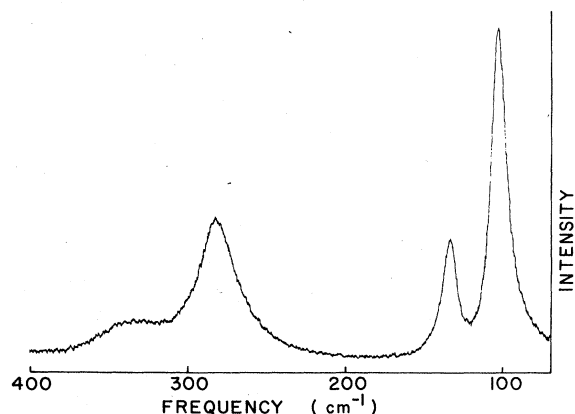


FIG. 2. Raman spectrum of solid I in the lattice region for sample 3 at 187.6 K. Instrumental resolution is 2.7 cm⁻¹.

TABLE I. Measured lattice frequencies.

T (K)	Lattice frequency (cm^{-1})			Molar volume (cm^3/mol)
	Translations		Libration	
195.0	98.5	128.4	276.4	20.62
	102.1	132.5	279.4	20.35
	102.7	133.2	280.0	20.29
187.6	99.1	129.0	278.2	20.58
	102.6	133.2	281.2	20.31
	103.4	133.9	281.8	20.24
180.0	99.6	129.6	279.9	20.55
	103.2	133.8	283.1	20.28
	103.8	134.3	283.4	20.22
172.8	100.2	130.2	281.6	20.52
	103.7	134.2	284.3	20.26
	104.2	135.1	284.9	20.20

cm^{-1} to a librational mode. Several weaker lines which they observed cannot be resolved at the temperatures of the present study. Table I contains the measured frequencies and the calculated molar volume of each sample at four temperatures between 195.0 and 172.8 K.

A measure of the volume dependence of a lattice frequency is its mode Gruneisen parameter, given by $\gamma = -(\partial \ln \omega / \partial \ln V)$, where ω is the frequency and V the molar volume. These parameters are critically dependent on the form of the intermolecular potential, especially the

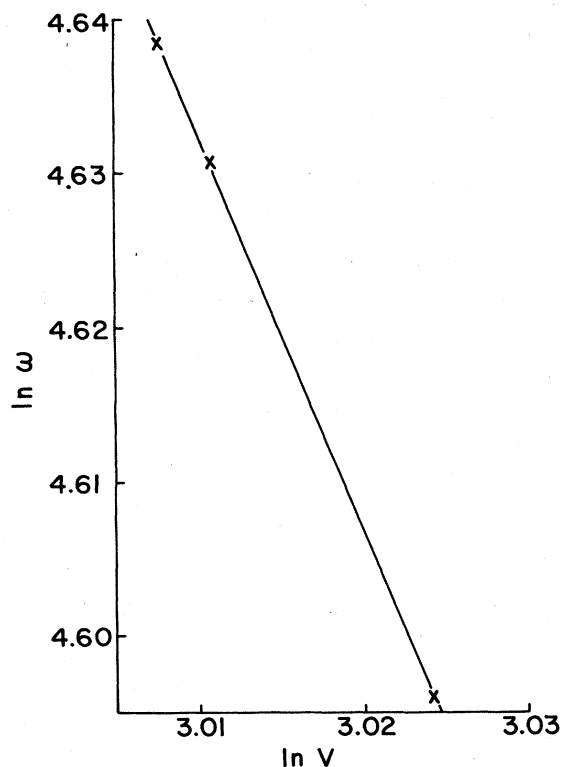


FIG. 3. Plot of $\ln \omega$ vs $\ln V$ for the translational mode near 100 cm^{-1} at a temperature of 187.6 K.

TABLE II. Gruneisen parameters of the lattice modes.

T (K)	Translation ($\sim 100 \text{ cm}^{-1}$)	Translation ($\sim 130 \text{ cm}^{-1}$)	Libration ($\sim 280 \text{ cm}^{-1}$)
195.0	2.7 ± 0.1	2.4 ± 0.1	0.8 ± 0.1
187.6	2.6 ± 0.1	2.3 ± 0.1	0.8 ± 0.1
180.0	2.6 ± 0.1	2.3 ± 0.1	0.8 ± 0.1
172.8	2.6 ± 0.1	2.4 ± 0.1	0.7 ± 0.1

short-range repulsive part. Typically, the Gruneisen parameters of translational modes are higher than those of librational modes. For example, in another molecular solid, α -nitrogen, Gruneisen parameters of 2.8 and 3.4 were obtained for the two infrared-active translational modes,¹⁰ while those of the three Raman-active librational modes ranged between 1.6 and 2.0.¹¹

Figure 3 shows $\ln \omega$ vs $\ln V$ for one of the translational modes at 187.6 K. The experimental points fall nearly on a straight line. The negative of the slope of this line is the mode Gruneisen parameter. Table II contains the Gruneisen parameters obtained from least-squares fits to the data of Table I. Although there seems to be a slight upward trend with temperature, the Gruneisen parameters are essentially constant within the experimental uncertainties.

The Gruneisen parameters obtained in the present study support the assignments of Binbrek and Anderson⁶ in terms of translational or librational modes. As expected, the translational modes have higher Gruneisen parameters. Although the Gruneisen parameter of the librational mode is rather low, it is not entirely unexpected. The so-called Gruneisen coefficient, which is an average of all the mode Gruneisen parameters, is related to the coefficient of thermal expansion, the volume, the isothermal compressibility, and the heat capacity at constant volume. Using experimental values of those quantities, Manzhelii and Tolkachev¹² calculated the temperature dependence of the Gruneisen coefficient of solid I and extracted from it a Gruneisen coefficient characteristic of hindered molecular rotations equal to 0.7. The agreement between this and the value presently obtained for one of the librational modes suggests that all librational modes in solid I have rather low Gruneisen parameters.

In a theoretical study of the lattice dynamics of solid ammonia, Neto *et al.*^{13,14} assumed atom-atom interactions plus electrostatic multipole interactions between molecules. They concluded that the octupolar interactions are essential for the description of the A and E modes involving rotation about the molecular symmetry axis. A purely octupolar interaction potential, which has an r^{-7} dependence on the intermolecular separation, would yield a mode Gruneisen parameter of $\frac{7}{6}$ (1.2) in the quasiharmonic approximation. The present results indicate that lower multiple interactions are also important.

In another lattice-dynamical calculation, Righini and Klein¹⁵ used a long-range dispersive interaction, short-range atom-atom interactions, and point charges for the electrostatic interaction. Their calculated frequencies at 77 K, which include anharmonic contributions of 2–6% for the librational modes, are all within 5% of the experi-

mental values obtained by Binbrek and Anderson.⁶ However, in a more extensive theoretical study, Klein *et al.*¹⁶ concluded that none of the existing atom-atom models is satisfactory. A similar conclusion in the case of solid nitrogen led to more realistic intermolecular potentials, such as that of Raich and Gillis.¹⁷ The type of measurements reported here provide a more direct comparison to existing models and a critical test for the intermolecular poten-

tials used. In addition, a study of the temperature dependence of the Raman frequencies and linewidths presently underway will provide a direct measurement of the anharmonic self-energies in solid ammonia.

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