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Raman Frequency Shifts for Ammonia Solid I Near the Melting Point

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We have performed in this study the calculation of the Raman frequencies for two translational modes and one librational mode in the ammonia solid I near the melting point. We have obtained the Raman frequencies as a function of temperature for some fixed pressure by means of the Grüneisen relation using the volume data from the literature. Our calculated Raman frequencies can be compared with experimental data available in the literature.

1. Introduction

There have been extensive studies on NH_3 using Raman and infrared techniques in the literature. Experiments by Binbrek and Anderson,[1] an infrared study by Bromberg et al.,[2] and a Raman study on liquid NH_3 by Lundeen and Koehler[3] have been referenced in the work of Hanson and Jordan.[4] At high pressures Hanson and Jordan[4] have studied NH_3 using the Raman spectroscopic technique, and they have obtained the $T-P$ phase diagram of ammonia including solid III (phase III).

The crystal structure of solid I (phase I) has been studied experimentally using X-ray diffraction techniques[5] and neutron scattering.[6] According to these experimental techniques, solid I has a simple cubic structure with four molecules per unit cell. On the other hand, more recent X-ray measurements indicate that solid II (phase II) is not cubic (hexagonal closed-packed) and that the structure of solid III (phase III) is face-centered cubic.[7]

More recently, the volume dependence of the Raman frequencies in ammonia solid I has been studied experimentally by Nye and Medina.[8] They have measured the Raman frequencies of two translational modes and of one librational mode in the ammonia solid I at various temperatures at atmospheric pressure. They have obtained the volume dependence of the Raman frequencies for those modes studied by means of the mode Grüneisen parameter in ammonia solid I. Considering those lattice modes, modes at 103 and 134 cm^{-1} have been assigned to two translational modes and the one at 282 cm^{-1} to a librational mode by Binbrek and Anderson,[1] as also indicated in the work of Nye and Medina.[8]

Very recently, we have calculated the Raman frequencies as a function of pressure for some fixed temperatures for those two translational modes and for one librational mode in ammonia solid I.[9]

In this study we calculate the Raman frequencies of two translational modes ($\sim$100 and $\sim$130 cm^{-1}) and of one librational mode ($\sim$280 cm^{-1}) in ammonia solid I, which have been obtained experimentally.[8] The approximations used in deriving the equations are valid for all the Raman allowed modes of the ammonia system. Among all the zone-center lattice modes, four translations (A + E + 2F) and five rotations (A + E + 3F), which are Raman active, as indicated in the work of Nye and Medina,[8] in this study we concentrate our calculations on the two translational modes at 103 and 134 cm^{-1} and one librational mode at 282 cm^{-1}. We calculate the Raman frequencies as a function of temperature at some fixed pressures for which we have used our volume values calculated in our recent work,[10] together with the volume data obtained by Nye and Medina.[8] By means of the Grüneisen relation, we then calculate the Raman frequencies of those modes studied as a function of temperature for some fixed pressures in ammonia solid I near the melting point.

In section 2 we give the theoretical background. In section 3 the Raman frequencies calculated are presented. Sections 4 and 5 give our discussion and conclusions, respectively.

2. Theory

In our recent study[10] we have investigated the critical behavior of the isothermal compressibility, thermal expansivity, and specific heat of solid ammonia near the melting point. Starting from the critical behavior of the isothermal compressibility

$$\kappa_T = k(P - P_m)^{-\gamma} \tag{2.1}$$

which is given along the pressure line near the melting pressure P_m, with the critical exponent γ and the amplitude k, we can obtain the pressure dependence of the solid volume V_s in the ammonia.[11] This is given by

$$V_s = V_c \exp[-k(1-\gamma)^{-1} (P - P_m)^{1-\gamma}] \tag{2.2}$$

Here V_c is the critical volume for the solid ammonia. Near the melting point (T_m,P_m) in the $P-T$ plane of the solid ammonia, we can write as a first approximation[10]

$$[P - P_m(T)]/[T - T_m(P)] = dP_m/dT \tag{2.3}$$

By using eq 2.3 in eq 2.2 where the melting pressure is $P_m = P_m(T)$ and the melting temperature is $T_m = T_m(P)$, we get

$$V_s = V_c \exp[-k(1-\gamma)^{-1} (dP_m/dT)^{1-\gamma}(T - T_m(P))^{1-\gamma}] \tag{2.4}$$

This gives the volume V_s as a function of temperature near the melting point in ammonia.

We can now obtain the volume dependence of the Raman frequencies by defining the mode Grüneisen parameter

$$\gamma_p = -\frac{V}{\nu}\left(\frac{\partial \nu}{\partial V}\right)_p \tag{2.5}$$

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Here γ_p is the isobaric mode Grüneisen parameter. Equation 2.5 can be written as

$$\gamma_p = -\frac{1}{\alpha_p}\frac{1}{\nu}\left(\frac{\partial \nu}{\partial T}\right)_p \tag{2.6}$$

where the thermal expansivity is $\alpha_p = (1/V)(\partial V/\partial T)_p$. We assume here that the isobaric mode Grüneisen parameter γ_p remains constant right through the melting region in ammonia. We can then solve eq 2.6 to obtain the temperature dependence of the Raman frequencies as

$$\nu_p(T) = \Delta_p + A(P) + \nu_1 \exp[-\gamma_p \ln(V_p(T)/V_1)] \tag{2.7}$$

where the pressure-dependent term is

$$A(P) = a_0 + a_1 P + a_2 P^2 \tag{2.8}$$

Here a_0, a_1, and a_2 are constants. In eq 2.7 ν_1 and V_1 are the values of the Raman frequency and the volume at atmospheric pressure ($T_1 = 195.48$ K). Δ_p is the order−disorder contribution to the frequency. We take $\Delta_p \neq 0$ for $T < T_c$ and $\Delta_p = 0$ for $T > T_c$, where T_c is the critical temperature. Equation 2.7 has also been given in our earlier studies.[12−14]

3. Calculations and Results

To calculate the Raman frequencies, we first obtained the solid volume V_s as a function of temperature according to eq 2.4. In this equation we used the empirical relation[11]

$$dP_m(I)/dT_m = 1.967 \times 10^{-8} T_m \tag{3.1}$$

for the ammonia solid I. For the critical volume V_c(I) we used the empirical relation

$$V_c(\mathrm{I}) = V_\mathrm{I} - d_\mathrm{I}(T - T_{\mathrm{g-l-I}}) \tag{3.2}$$

as given in the work of Pruzan et al.[11] In eq 3.2 we took the values of $V_\mathrm{I} = 21.61$ cm^3/mol, $d_\mathrm{I} = 0.0316$ cm^3/(mol·K), and $T_{\mathrm{g-l-I}} = 195.48$ K as the triple point. From eq 3.2 we got the temperature dependence of the critical volume as

$$V_c(\mathrm{I}) = 27.79 - 0.0316T \tag{3.3}$$

Now, using the values of the critical exponents $\gamma = 0.49$ and the amplitude $k = 0.0137$ for the ammonia solid I[11] in eq 2.4, we obtained the solid volume V_s as a function of temperature by means of eqs 3.1 and 3.3. The values of the melting temperature T_m which we used in eq 2.4 as a function of pressure were obtained from the empirical relation[7]

$$P_m(\mathrm{I}) = 5.886[(T_m/T_{\mathrm{g-l-I}})^{3.960} - 1] \tag{3.4}$$

where the temperature of the triple point is $T_{\mathrm{g-l-I}} = 195.48$ K. As an empirical relation, eq 3.4 was obtained from the Simon expressions which were fitted to the experimental data by Mills et al.[7] We also note that the slope $dP_m(\mathrm{I})/dT_m$ given by eq 3.1 was derived from eq 3.4. Table 1 gives our calculated values of V_c(I) (eq 3.2), the T_m values (eq 3.4), and the values of $dP_m(\mathrm{I})/dT_m$ (eq 3.1) for various pressures ranging from 0 kbar up to the pressure of the triple point ($P_m = 3.070$ kbar) along the phase line between ammonia solid I and liquid in the $P-T$ phase diagram due to Mills et al.[7] According to the values given in Table 1, we were then able to calculate the values of the solid volume V_s as a function of temperature using eq 2.4 for fixed pressures of 0 kbar up to the triple pressure of 3.070 kbar in ammonia solid I.

TABLE 1: Calculated Values of Melting Temperatures T_m (Eq 3.4), Slope Values of $dP_m(I)/dT_m$ (Eq 3.1), Critical Volume $V_c(I)$ (Eq 3.2), and Critical Frequencies at Various Pressures for Ammonia Solid I along the Melting Curve

P (kbar)	V_c(I) (cm^3/mol)	T_m (K)	$dP_m(\mathrm{I})/dT_m$ (kbar/K)	ν_c (cm^{-1})		
0	21.71	192.5	0.114	84.25	111.87	265.19
0.06	21.60	196	0.120	85.24	113.21	265.61
0.56	21.47	200	0.127	86.41	115.03	266.80
1.93	21.15	210	0.147	89.17	120.45	270.26
2.70	21.00	215	0.158	90.38	123.54	272.45
3.02	20.93	217	0.162	90.99	125.03	273.55
3.07	20.92	217.34	0.163	91.06	125.26	273.71

TABLE 2: Values of $\Delta_p + a_0$, a_1, and a_2 Calculated through Eqs 2.7 and 2.8, Values[4] of the Isobaric Mode Grüneisen γ_p, and Extrapolated Values of ν_1 at $T_1 = 195.48$ K from the Measured Frequencies[4] for the Translational Modes (∼100 cm^{-1} and ∼130 cm^{-1}) and for the Librational Mode (∼280 cm^{-1}) in Ammonia Solid I

lattice freq (cm^{-1})	$\Delta_p + a_0$ (cm^{-1})	a_1 (cm^{-1}/kbar)	a_2 (cm^{-1}/(kbar)^2)	γ_p	ν_1 (cm^{-1})
∼100	−13.045	−1.01	0.0055	2.7	98.47
∼130	−15.11	−0.27	0.281	2.35	128.36
∼280	−10.10	−0.89	0.315	0.8	276.31

To calculate the Raman frequencies by means of eq 2.7, we first determined the coefficients a_0, a_1, and a_2 given in eq 2.8 and also the order−disorder contribution Δ_p. For this determination we used our calculated values of the Raman frequencies and the volume data by choosing the three pressures of $P = 0$ kbar, $P = 1.93$ kbar, and $P = 3.07$ kbar along the phase line between the ammonia solid I and the liquid. According to eq 2.4, when $T = T_m(P)$ along the pressure line, V_s(I) takes on its critical values V_c(I). Using the values of the critical volume V_c(I) and of the critical frequency ν_c(I) for two translational modes and one librational mode of the ammonia solid I, which are given in Table 1, we were able to determine the coefficients $\Delta_p + a_0$, a_1, and a_2 according to eq 2.7. The critical frequencies given in Table 1 for two translational modes and one librational mode were calculated by means of the pressure dependence of the Raman frequencies for some fixed temperatures in our recent study.[9] The critical frequencies were determined for fixed temperatures from 192.5 to 217.3 K corresponding to the fixed pressures in the range of 0−3.1 kbar using the values of the coefficients which we calculated according to the $\nu_T(P)$ relation.[9] By means of the critical frequencies given in Table 1, we then determined the coefficients of $\Delta_p + a_0$, a_1, and a_2 using the values of ν_1, V_1, γ_p, and $V_p(T)$ for the pressures of 0, 1.9 and 3.1 kbar, according to eq 2.7. The values of the coefficients $\Delta_p + a_0$, a_1, and a_2 for two translational modes (∼100 and ∼130 cm^{-1}) and for the librational mode (∼280 cm^{-1}) are given in Table 2.

For calculating the Raman frequencies as a function of temperature for two translational modes and one librational mode of the ammonia solid I, we used eq 2.7 where we took the isobaric mode Grüneisen parameter γ_p as the isothermal mode Grüneisen parameter γ_T. In this equation the value of the solid volume $V_1 = 21.61$ cm^3/mol was obtained by extrapolating the volume data given in the work of Nye and Medina[8] at $T_1 = 195.48$ K.

For the translational mode of ∼100 cm^{-1} the value of $\gamma_p = 2.6$[8] for the isobaric mode Grüneisen parameter and the extrapolated value of $\nu_1 = 98.47$ cm^{-1} at $T_1 = 195.48$ K were used in eq 2.7. Thus, by using in eq 2.7 the values of all the

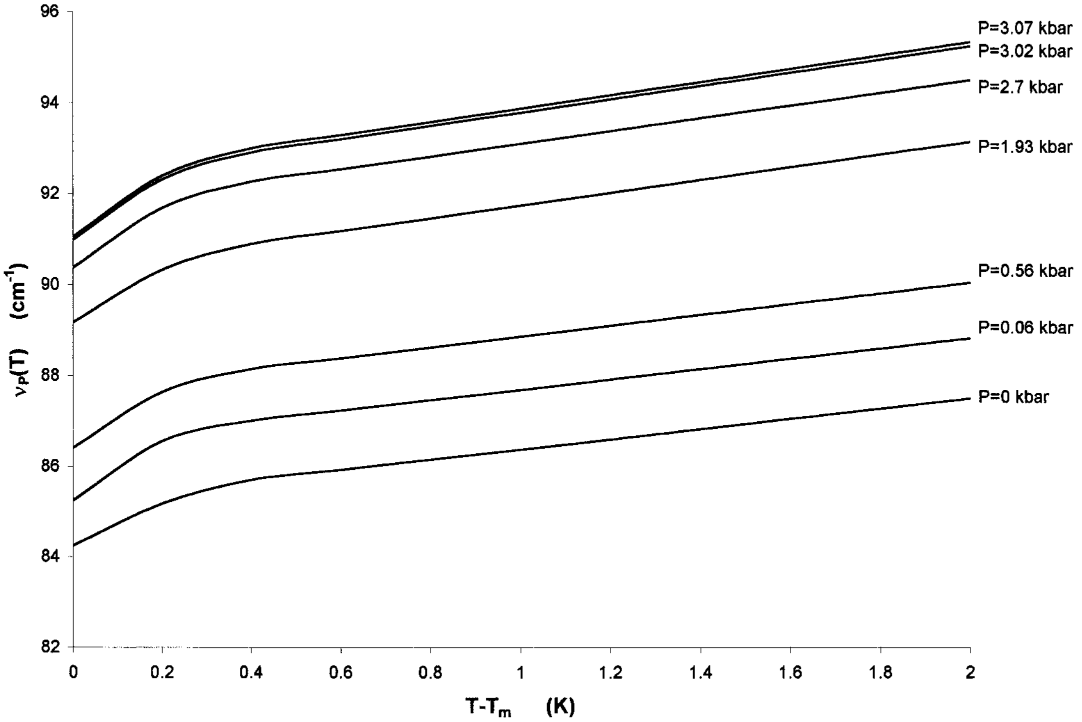

Figure 1. Calculated Raman frequencies as a function of reduced temperature $T - T_m$, where T_m is the melting temperature, for the translational mode (~100 cm^{-1}) of ammonia solid I for some fixed pressures from 0 kbar up to 3.07 kbar (triple pressure).

coefficients which we calculated for the translational mode of ~100 cm^{-1} and also our values for the $V_p(T)$ calculated through eq 2.4, we were able to calculate the Raman frequencies for this mode as a function of temperature for some fixed pressures in the ammonia solid I. The fixed pressures we chose varied from 0 kbar up to the pressure of the triple point (3.07 kbar), as given in Table 1. Figure 1 shows our calculated Raman frequencies for the translational mode of ~100 cm^{-1} as a function of temperature for those fixed pressures considered in the ammonia solid I.

For the translational mode of ~130 cm^{-1} we had the value of $\gamma_p = 2.35$ for the isobaric mode Grüneisen parameter and we obtained the value of $\nu_1 = 128.36$ cm^{-1} from the extrapolation of the measured frequencies[8] at $T_1 = 195.48$ K. We inserted the values of the coefficients $\Delta_p + a_0$, a_1, and a_2 given in Table 2 and the values of γ_p and ν_1 for the translational mode of ~130 cm^{-1} into eq 2.7. In this equation by using our values of the solid volume V_s(I) calculated from eq 2.4, we then calculated the Raman frequencies for this phonon mode in the ammonia solid I.

Figure 2 gives our calculated Raman frequencies for the translational mode of ~130 cm^{-1} as a function of temperature for the fixed pressures indicated in the Table 2 for the ammonia solid I.

Finally, for the librational mode of ~280 cm^{-1} we took the value of $\gamma_p = 0.8$ [8] for the isobaric mode Grüneisen parameter. From the extrapolation of the frequencies measured[8] between 172.8 and 195 K we had the values of $\nu_1 = 276.31$ cm^{-1} at $T_1 = 195.48$ K. Using in eq 2.7 the values of the coefficients $\Delta_p + a_0$, a_1, and a_2 given in Table 2 and also the other values given above, we calculated the Raman frequencies for the librational mode of ~280 cm^{-1} by means of our values of the solid volume V_s(I) obtained through eq 2.4. We calculated the Raman frequencies of this phonon mode as a function of temperature for the fixed pressures ranging from 0 to 3.07 kbar (pressure of the triple point between solid I-solid II and liquid phases), as indicated in Table 1. Figure 3 gives our calculated Raman frequencies for the librational mode of ~280 cm^{-1} as a function of temperature for those fixed pressures given in Table 2 for the ammonia solid I.

4. Discussion

We calculated in this study the Raman frequencies as a function of temperature for some fixed pressures in the ammonia solid I. The Raman frequencies were calculated for the translational modes of ~100 and ~130 cm^{-1} and also for the librational mode of ~280 cm^{-1}, as plotted in Figures 1, 2, and 3, respectively. The pressure region for these Raman frequencies was chosen from 0 kbar up to the triple pressure of 3.07 kbar. As we see from Figures 1−3, the Raman frequencies increase at various temperatures systematically, as the pressure increases from 0 to 3.07 kbar. This critical behavior is expected for the Raman frequencies of the modes studied here, since the solid volume V_s decreases as the pressure increases in the melting region for the ammonia solid I. We also see in Table 1 the decreasing behavior of the volume V_c(I) and the increasing behavior of the critical frequencies for the Raman modes of ~100, ~130, and ~280 cm^{-1}, as the pressure increases.

We calculated the Raman frequencies as a function of temperature under the assumption that the isobaric mode Grüneisen parameter γ_p remained constant across the phase transition from the ammonia solid I to the liquid. We used the average values of the isobaric mode Grüneisen parameter $\gamma_p = 2.6$ and $\gamma_p = 2.35$ for the translational modes of ~100 and ~130 cm^{-1}, respectively, and $\gamma_p = 0.8$ for the librational mode of ~280 cm^{-1}, since they did not vary significantly for the temperatures between 172.8 and 195 K at zero pressure in the ammonia solid I.[8] In fact, from the Raman frequency measurements it was estimated that the uncertainties in the values of the mode Grüneisen parameter were ±0.1.[8] As a consequence of this, our calculated Raman frequencies vary within the uncertainties of ±0.5 cm^{-1} for the translational modes of ~100 and ~130 cm^{-1} and also for the librational mode of ~280 cm^{-1}.

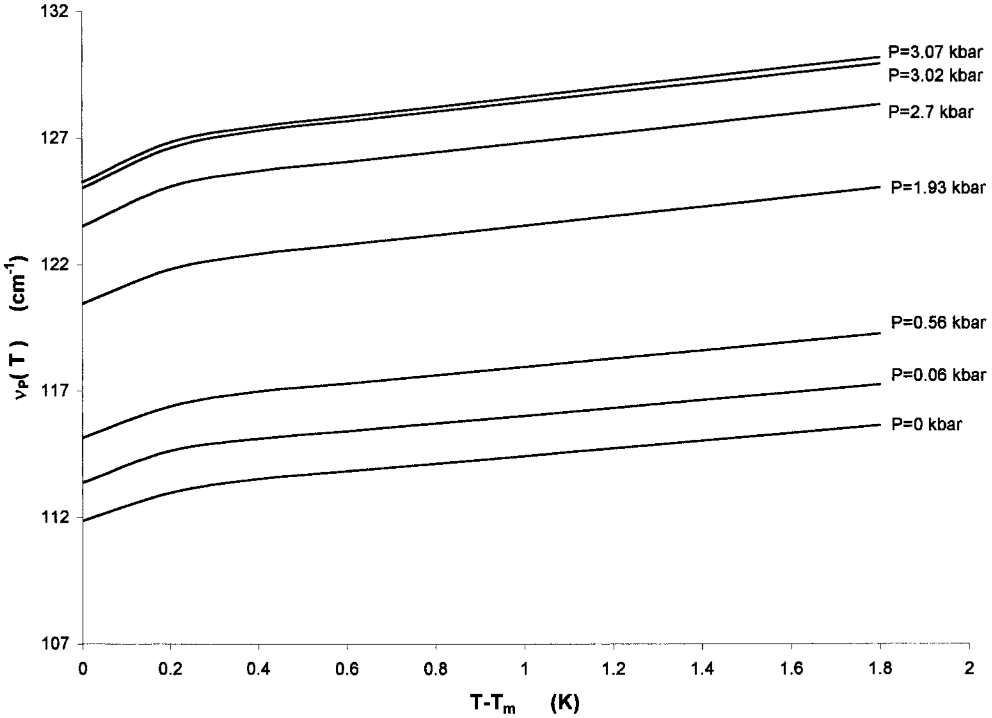

Figure 2. Calculated Raman frequencies as a function of reduced temperature $T - T_m$, where T_m is the melting temperature, for the translational mode (~130 cm^{-1}) of ammonia solid I for some fixed pressures from 0 kbar up to 3.07 kbar (triple pressure).

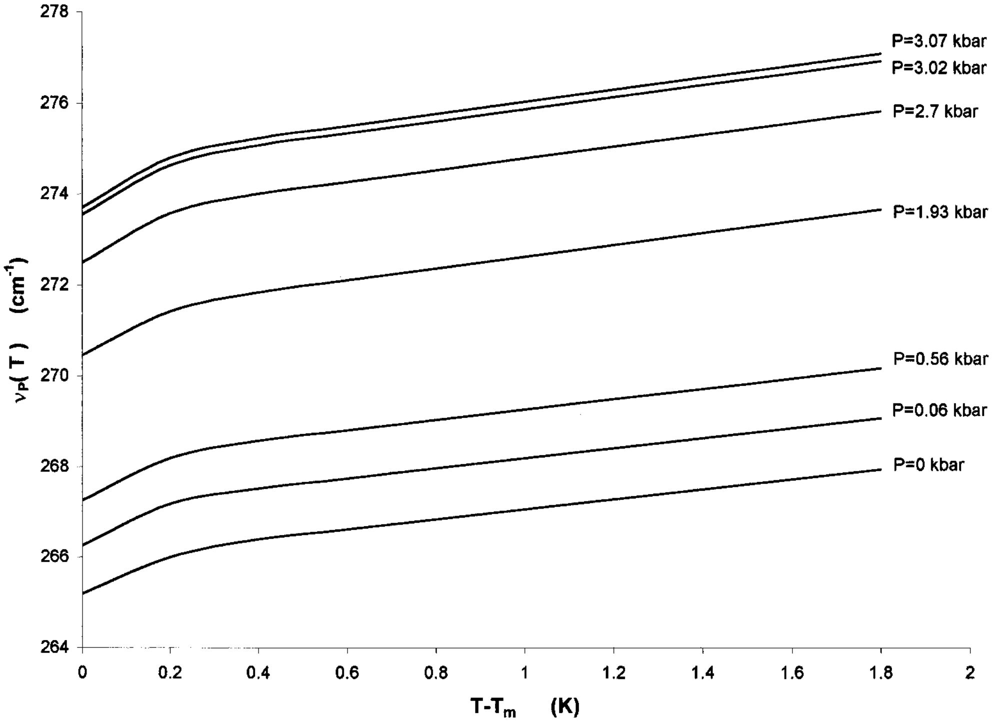

Figure 3. Calculated Raman frequencies as a function of reduced temperature $T - T_m$, where T_m is the melting temperature, for the librational mode (~280 cm^{-1}) of ammonia solid I for some fixed pressures from 0 kbar up to 3.07 kbar (triple pressure).

We determined the parameters $\Delta_p + a_0$, a_1, and a_2 according to eq 2.7. Since eq 2.7 contained Δ_p and a_0 as constant terms, we were not able to determine Δ_p and a_0 separately. Instead we determined $\Delta_p + a_0$ for the low-frequency modes, as given in Table 2. As we presented in Table 2, all a_1 terms were negative and all a_2 terms were positive, whereas all $\Delta_p + a_0$ terms were negative for the low-frequency modes. As we see from Figures 1−3, the Raman frequency shifts increase as the pressure increases, so that the pressure contribution to the Raman shifts is always positive for the low-frequency modes in the ammonia solid I.

For calculating the Raman frequencies for those phonon modes, we determined the coefficients $\Delta_p + a_0$, a_1, and a_2 by choosing three pressures, namely, 0, 1.93, and 3.07 kbar. Although we had some other pressures between 0 and 3.07 kbar, as given in Table 1, we assumed here that those values of the coefficients were also valid for the other pressures for which we calculated the Raman frequencies in the ammonia solid I.

This varied our calculated Raman frequencies within the uncertainties of ∼0.2−0.3 cm^{-1} for the phonon modes studied in the ammonia solid I.

As seen in Figures 1−3, there is an inflection point when $T - T_m$ is about 0.3 K. This is an indication that the transition from the ammonia solid I to the liquid phase is of a second order, as has also been shown by the volumetric measurements.[15] Due to the divergence behavior of the isothermal compressibility near $T = T_m$ with the critical exponent value of $\gamma \approx 0.5$ for the ammonia solid I, it has been pointed out[15] that the phase transformation between the ammonia solid I and the liquid state can be considered as a second-order process. We show in this study that similar critical behavior is obtained from the Raman frequency shifts for the low-frequency modes in the ammonia solid I system, as given in Figures 1−3. Since the variation of the Raman frequencies with the temperature $(1/\nu)/\partial\nu/\partial T)_p$ at constant pressures is expected to show the divergence behavior as the thermal expansivity $(1/V)(\partial V/\partial T)_p$ near $T = T_m$ (see eq 2.6 for a constant γ_p), careful measurements for the Raman frequency shifts are required near the melting temperature T_m. Considering our calculations for the low-frequency modes of the ammonia solid I in this study, the Raman frequencies should be measured carefully as a function of temperature, in particular, within the temperature region of $T - T_m \approx 0.3$ K at constant pressures between 0 and ∼3 kbar, as shown in Figures 1−3. Thus the experimental conditions must be carefully chosen for validation of our calculations given here.

Similarly, the variation of the Raman frequencies with the pressure $(1/\nu)(\partial\nu/\partial P)_T$ at constant temperatures shows the divergence behavior as the isothermal compressibility $(1/V)(\partial V/\partial P)_T$ near $T = T_m$, as pointed out in our recent study.[9] Thus, for the low-frequency modes the Raman frequencies which we calculated as a function of pressure at constant temperatures near the melting pressure P_m in the ammonia solid I should also be measured carefully, in particular, close to $P - P_m = 0.2$ kbar in order to validate our calculations.[9]

5. Conclusions

We studied here two translational and one librational Raman modes in the ammonia solid I near the melting point. The Raman frequencies of those phonon modes were calculated as a function of temperature for some fixed pressures between the phases of the ammonia solid I and of the liquid state. Our calculated frequencies increase at various temperatures as the pressure increases, as expected for the Raman modes studied here. We require here that the Raman frequencies be measured as a function of temperature for the ammonia solid I near the melting point. This then examines the validity of our method of calculating the Raman frequencies in the ammonia solid I near the melting point.

References and Notes

(1) Binbrek, O. S.; Anderson, A. *Chem. Phys. Lett.* **1972**, *15*, 421.

(2) Bromberg, A.; Kimel, S.; Ron, A. *Chem. Phys. Lett.* **1977**, *46*, 262.

(3) Lundeen, J. W.; Koehler, W. H. *J. Chem. Phys.* **1975**, *79*, 2957.

(4) Hanson, R. C.; Jordan, M. *J. Phys. Chem.* **1980**, *84*, 1173.

(5) Olovsson, I.; Templeton, D. H. *Acta Crystallogr.* **1959**, *12*, 832.

(6) Reed, J. W.; Harris, P. M. *J. Chem. Phys.* **1961**, *35*, 1730.

(7) Mills, R. L.; Liebenberg, D. H.; Pruzan, Ph. *J. Phys. Chem.* **1982**, *86*, 5219.

(8) Nye, C. I.; Medina, F. D. *Phys. Rev. B* **1985**, *32*, 2510.

(9) Yurtseven, H. Pressure dependence of the Raman frequencies of ammonia solid I near the melting point. Submitted for publication in *Int. J. Mod. Phys.* **1998**.

(10) Yurtseven, H. Critical behaviour of ammonia near the melting point. Submitted for publication in *Int. J. Mod. Phys.* **1998**.

(11) Pruzan, Ph.; Liebenberg, D. H.; Mills, R. L. *Phys. Rev. Lett.* **1982**, *48*, 1200.

(12) Yurtseven, H.; Sherman, W. F. *Phase Trans.* **1995**, *54*, 1.

(13) Yurtseven, H.; Güleç, M.; Sherman, W. F. *Phase Trans.* **1996**, *56*, 137.

(14) Yurtseven, H.; Demir, T. *J. Mol. Struct.* **1996**, *382*, 57.

(15) Pruzan, Ph.; Liebenberg, D. H.; Mills, R. L. *J. Phys. Chem. Solids* **1986**, *47*, 949.