

Nuclear-resonance photon-scattering study of the vibrational spectrum of NH₃

R. Moreh

*Nuclear Research Center-Negev, Beer-Sheva, Israel
and Ben-Gurion University of the Negev, Beer-Sheva, Israel*

O. Shahal

*Nuclear Research Center-Negev, Beer-Sheva, Israel
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The nuclear-resonance photon-scattering cross section σ_s from ¹⁵N in the form of gaseous, liquid, and solid NH₃ was studied as a function of temperature in the range 15–600 K. The value of σ_s was found to be in excellent agreement with that calculated using an effective temperature of the N atom in which the internal vibrations of NH₃ and the external vibrations of the lattice were taken into account. The Debye temperature of NH₃, as determined from the motion of the N atom only, was found to be $\Theta = 241 \pm 8$ K.

The nuclear-resonance photon-scattering (NRPS) technique has been used to study the lattice vibrational energies of solid ammonia, and its internal molecular vibrational modes. This is done by measuring the scattering of photons from the 6324 keV level in ¹⁵N in the form of gaseous, liquid, and solid NH₃.

In this technique¹ one monitors the Doppler broadening of the 6324-keV level of ¹⁵N arising from the instantaneous velocity of the N atom. For solid NH₃, contributions to this velocity come in part from the zero-point kinetic energies of the internal vibrational motion of the NH₃ molecule and also from the external vibrations of the lattice. This method relies on the fact that the 6324-keV nuclear level of ¹⁵N is photoexcited by a chance overlap with one of the γ lines of the Cr(*n*, γ) reaction. It turns out that in this nuclear resonance process, the scattering cross section σ_s is proportional to the Doppler broadening and hence can be viewed as a measure of the integral over all vibrations in which the ¹⁵N atom participates. A measure of σ_s as a function of temperature may provide a test of the phonon spectrum obtained by other methods and can yield the Debye temperature of NH₃. More detail concerning this method was given in Ref. 1; similar studies using the present technique for metals and chemical compounds were published elsewhere.^{2,3}

The value of σ_s is entirely dependent on the kinetic energy of the N atom in solid ammonia; it may be expressed in terms of an effective temperature T_e of the N atom in solid NH₃. It is important to emphasize that the present technique measures the mean kinetic energy of the N atom including that of its zero-point motion and thus it is unique in two respects: first, it monitors the mean kinetic energy of a single isotope in the lattice. Second, at low T , it yields a measure of the zero-point motion of the scattering atom and hence is very sensitive to the high-frequency modes of the system.

We first evaluate T_e for NH₃ assumed to be in a gaseous phase. In this case, the contributions to the kinetic energy of the N atom should come from the translational, rotational, and internal vibrations of NH₃ and should sum up to 3 kinetic degrees of freedom; thus T_e may be written

as

$$3kT_e/2 = S_T(3kT/2) + S_R(kT) + \sum_{j=1}^6 S_j k\alpha_j/2, \quad (1)$$

where S_T , S_R , and S_j are the energy fractions shared by the N atom in the translational, rotational, and the internal j -vibrational mode of the NH₃ molecule ($j=1, \dots, 6$). The factor $\frac{1}{2}$ in the last term of Eq. (1) arises from the fact that only the kinetic part of the vibrational energy $\alpha_j k$ contributes to the Doppler broadening of the nuclear level and hence to T_e , where α_j are given by

$$\alpha_j = (hv_j/k) \{ \exp(hv_j/kT) - 1 \}^{-1} + \frac{1}{2}. \quad (2)$$

$S_T \approx \frac{15}{18}$ is obtained from the mass ratio of the ¹⁵N atom to that of the ¹⁵NH₃ molecule. More accurately, $S_T = 0.8323$ obtained by substituting the accurate atomic masses of the ¹⁵N atom and the ¹⁵NH₃ molecule. Similarly, $S_R = 0.036$ is obtained by considering the moments of inertia around the three principal axes of the molecule which has a pyramidal shape,⁴ where the H atoms form an equilateral triangle with the N atom at the top; the parameters are

$$r(\text{N-H}) = 1.014 \text{ \AA}, \quad r(\text{H-H}) = 1.628 \text{ \AA}, \\ \angle \text{H-N-H} = 106^\circ 47', \quad \beta = 67^\circ 58',$$

where β is the angle which N-H makes with the H-H-H plane. The experimental normal frequencies of the ¹⁴NH₃ in the gaseous phase is given in Table I together with the spring constants (taken from Refs. 4 and 5), and the calculated frequencies of ¹⁵NH₃. The values of S_j were obtained from the relative amplitudes of vibration A_{ij} of the various atoms by using the relation

$$S_j = \frac{E_{1j}}{E_{Tj}} = \frac{M_1 A_{1j}^2}{\sum_{i=1}^6 M_i A_{ij}^2}, \quad (3)$$

where $E_{1j} = 4\pi v_j^2 M_1 A_{1j}^2$ and $E_{Tj} = 4\pi v_j^2 \sum_{i=1}^6 M_i A_{ij}^2$ are

the kinetic energies of vibrations of N and NH₃ in the j normal mode of frequency ν_j . Further, M_1 , A_{1j} are the mass and relative amplitude of vibration of the N atom. M_i, A_{ij} ($i=2,3,4$) are the corresponding quantities of the three H atoms. The amplitudes A_{ij} were calculated using computational methods of infrared spectroscopy.⁵

Equation (1) applies to gaseous ammonia and can be used for obtaining an approximate expression for T_e valid at low T (where $h\nu_j \gg kT$) and hence $\alpha_j \approx h\nu_j/2k$. For such cases, we obtain

$$T_e \approx 0.8563T + 206.7, \quad (4)$$

which implies that the zero-point kinetic energy of the ¹⁵N atom in a NH₃ molecule (contributed by the six normal modes of vibration) is equal to 206.7 K. Here we assumed that NH₃ stays as a gas down to 0 K. It is of interest to compare this value of T_e with that of pure nitrogen gas (¹⁵N₂) given by¹

$$T_e \approx 0.8333T + 274. \quad (5)$$

At $T=293$ K, this yields $T_e=518.2$ K which is higher than that of pure NH₃ at the same temperature by 13%. The relative scattering cross section was measured and found to be higher by about 12% because of the nearly linear dependence of σ_s on T (see below).

Figure 1 shows the calculated values of σ_s against T_e for the 6324-keV level in ¹⁵N; details of this calculation are given in Ref. 1. At lower T and higher pressures, ammonia turns into a liquid and to a solid phase; the translational and rotational degrees of freedom turn into a distribution of frequencies of translational and rotational motions of the whole molecule in the solid. Denoting the corresponding distributions by $g_t(\nu)$ and $g_r(\nu)$, we may write the expression of T_e by modifying Eq. (1):

$$T_e = S_t \int_0^a \alpha_i g_i(\nu) d\nu + S_r \int_0^a \alpha_r g_r(\nu) d\nu + \sum_{j=1}^6 S_j \alpha_j / 3, \quad (6)$$

where $S_t = S_T$ and $S_r = 2S_R/3 = 0.024$ [see Eq. (1)]; α_t and α_r are defined in a similar manner to that of Eq. (2). The frequency distributions $g_t(\nu)$ and $g_r(\nu)$ are normalized so that

$$\int_0^a g_t(\nu) d\nu = \int_0^a g_r(\nu) d\nu = 1. \quad (7)$$

In Eq. (6), it was assumed that the vibrational frequencies in the liquid and solid phases are the same as those of

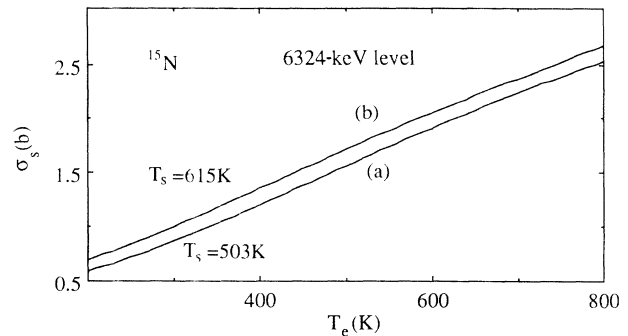


FIG. 1. Nuclear resonance scattering cross section σ_s of the 6324-keV γ line as a function of the effective temperature T_e of ¹⁵N calculated for two γ -source temperatures of chromium: (a) $T_s=503$ K and (b) $T_s=615$ K. Details of the calculation are given in Refs. 1 and 6.

gaseous ¹⁵NH₃. The validity of this assumption may be justified by noting that the frequency distribution spectrum of solid ammonia,⁷ deduced from neutron inelastic scattering at 106 K, was found to consist of two separate portions: translational and rotational with almost no overlap. In addition, these two distributions possess much lower frequencies than those of the internal vibrational model of the molecule.

It is helpful to remember a simple "sum rule" obeyed by the values of S_i ($i=t,r,j=1,\dots,6$):

$$\sum S_i = 3, \quad (8)$$

where the right-hand side is the number of kinetic degrees of freedom of the N atom in NH₃. Equation (8) may be used as a quick check on the correctness of the calculated values of S_i (Table I). The theoretical value of σ_s vs T has been calculated as explained in Ref. 1 by using the value of T_e of Eqs. (1) and (6); the following parameters of the resonance scattering process were used for the calculation:^{1,6} $\Gamma = \Gamma_0 = 2.9$ eV; $\delta = 29.5$ eV is the energy distance between the peak energy of the incident γ line and that of the resonance level; $J = \frac{3}{2}$ and $J_0 = \frac{1}{2}$ are the spins of the resonance and ground states of ¹⁵N, respectively. The results is displayed in Fig. 1 for two temperatures of the γ source: (a) $T_s=503$ K, (b) $T_s=615$ K, which were the operating temperatures during the measurements.

Experimentally, the photon beam was generated from the (n,γ) reaction on three chromium disks placed near

TABLE I. Normal frequencies ν_j ($j=1,2,\dots,6$) in units of cm^{-1} of ¹⁴NH₃ and ¹⁵NH₃ molecules (taken from Ref. 4) and the calculated fractions S_j , S_t , S_r of the kinetic energies of the N atom in ¹⁵NH₃. The corresponding normal modes together with the spring constants k (in units of 10^5 dyn/cm) are also listed.

		¹⁴ NH ₃		¹⁵ NH ₃	
		ν_j	ν_j	k	S_j
ν_1	N-H sym stretch	3336.2	3333.5	5.861	0.02187
$\nu_2 = \nu_3$	H-N-H bend	3443.4	3435.4	0.223	0.06246
ν_4	H-H stretch	950.2	945.5	0.317	0.14584
$\nu_5 = \nu_6$	H-H-H bend	1627.8	1623.5	0.635	0.06923
					$S_t = 0.8323$
					$S_r = 0.0240$

the reactor core. The intensity of the 6324-keV γ line arising from the $^{53}\text{Cr}(n, \gamma)$ reaction is $\approx 10^4$ photons/cm 2 s on the scatterer. More details concerning the experimental system was published elsewhere.⁶

To test Eq. (1), a target consisting of 2.194 g of enriched gaseous NH_3 target (99% ^{15}N) was used. The gas was contained in a 7.8-cm-diam, 63-cm-long glass cylinder fitted by three thermocouples to measure the temperature of the gas and any gradients which may occur when the gas is heated; an electric heater was mounted directly on the glass cylinder for this purpose. The background was measured by freezing the ammonia gas on the walls of the glass cylinder using a cooled external jacket, so that no NH_3 molecules remained along the path of the γ beam. The scattered radiation from the target was measured using the 12.7×12.7 cm 2 NaI detector. The results of the temperature-variation measurement is displayed in Fig. 2(a), which also shows the predicted cross sections obtained using the results of Fig. 1. An excellent agreement between the measured and the calculated cross sections is revealed. It is important to emphasize that this nice agreement was obtained with no free parameters and all input data were taken either from published nuclear measurements of the ^{15}N level parameters¹ or from infrared data.⁵ This verifies the validity of the procedure used in Eq. (1) for evaluating the effective temperature of the ^{15}N atom in NH_3 .

For calibration purposes and as another test of the present model, the cross section σ_s from a pure $^{15}\text{NH}_3$ sample at $T=293$ K was compared to that of a similar

sample containing pure nitrogen gas ($^{15}\text{N}_2$). In this measurement both the $^{15}\text{NH}_3$ and the $^{15}\text{N}_2$ gaseous samples were inserted in similar glass containers. The cross-section ratio was found to be

$$R = \sigma_s(^{15}\text{N}_2)/\sigma_s(^{15}\text{NH}_3) = 1.12 \mp 0.03,$$

which is in excellent agreement with that expected from the ratio of the effective temperatures given in Eqs. (4) and (5).

To test the lattice dynamics of ammonia, we used 1.714 g of enriched NH_3 (99% ^{15}N) contained in a spherical stainless-steel container with a 20-mm inner diameter and 2 mm thick, which could sustain high pressures. In this small volume and the corresponding high-pressure build-up, ammonia occurs in the liquid phase at 300 K and turns into the solid phase at $T < 195$ K. The gas was admitted through a valve fitted to the cell while keeping the cell at liquid nitrogen temperature. This target was placed inside a Displex cryostat which varied the temperature in the range 300–12 K. The temperature of the sample was monitored at the top and the bottom of the sample holder. A 150-cm 3 high-purity Ge detector was used for monitoring the scattered radiation. For background measurements an identical stainless-steel cell with no ammonia was employed. A typical scattered spectrum from the target is shown in Fig. 3 and is obtained after subtracting the "background" spectrum. The results for the low- T measurement is displayed in Fig. 2(b) which also reveals the predicted cross section obtained using the lower curve corresponding to the lower γ -source temperature of Fig. 1. It may be seen that an excellent agreement is obtained between the measured and calculated cross sections. This indicates that the NRPS technique may be used for testing the phonon spectrum of the NH_3 solid lattice. In fact, Fig. 2(b) may also be used for deducing a particular Debye temperature Θ related to the motion of the ^{15}N atom in the lattice. The effective temperature T_e for this case can be deduced from Eq. (6) by replacing the first two terms of the right-hand side by a single term as follows:

$$T_e = S(3T^4/\Theta^3) \int_0^{\Theta/T} x^3 \left(\frac{1}{\exp(x) - 1} + \frac{1}{2} \right) dx + \sum_{j=1}^6 S_j a_j / 3, \quad (9)$$

where the fraction $S = S_t + S_r = 0.8563$ is a sum on the translational and the rotational motions. The factor multiplying S in the first term of the right-hand side of Eq. (9) is an expression for T_e deduced by Lamb⁸ under the harmonic approximation and by assuming a pure Debye solid. The value of Θ obtained is

$$\Theta = 241 \pm 8 \text{ K}.$$

It was deduced by best fitting the measured data of Fig. 2(b) to the cross sections obtained from the effective temperatures of Eq. (8) and using Fig. 1(a); it should be added that the resulting curve is almost indistinguishable from the solid curve displayed in Fig. 2(b) and calculated using Eq. (9). This value is to be compared with $\Theta_t = 230$ K reported by Goyal *et al.*⁷ and deduced from the translational part of the phonon spectrum of ammonia. It should

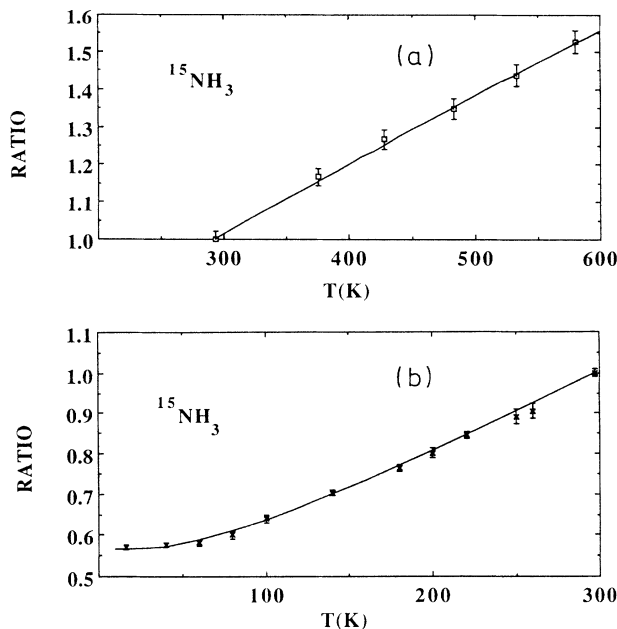


FIG. 2. (a) Scattered intensity ratio against T , relative to 293 K, from a pure gaseous NH_3 sample. The solid line is calculated using Eq. (1) for deducing T_e and applying Fig. 1(b) to get the corresponding cross section. (b) Same as (a) but for a liquid NH_3 sample which turns into the solid phase for $T < 195$ K. The solid line is calculated using Eq. (9) for deducing T_e and applying Fig. 1(a) to get the corresponding cross section. Typical errors are indicated.

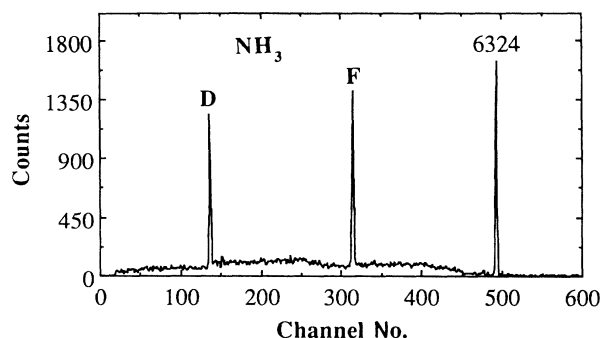


FIG. 3. Typical scattered radiation spectrum (after background subtraction) from a 1.714 g of $^{15}\text{NH}_3$ contained in a 2-cm-diam stainless-steel container as measured using a 150 cm^3 HPGe detector. *F* and *D* indicate single- and double-escape peaks while the other line is the photopeak of the 6324-keV γ line. The running time is 60 h.

be remarked that another value of the Debye temperature, namely Θ , ≈ 420 K, is reported in Ref. 7 and is attributed to the rotational part of the phonon spectrum of ammonia. Thus our measured value of Θ should be compared with a weighted contribution of both the translational and rotational parts,

$$\Theta' = (0.8323\Theta_t + 0.024\Theta_r) / 0.8563 = 235 \text{ K},$$

which is much closer and is within the uncertainty of our measured value. The above value of Θ' should also be

corrected due to the fact that our sample consisted of isotopic $^{15}\text{NH}_3$ while the phonon spectrum of Ref. 7 relates to $^{14}\text{NH}_3$. By applying a very simple $(1/M)^{1/2}$ correction to the phonon spectrum of Ref. 7, the effect on the value of T_e and on the resulting value of Θ was less than 1% and brought our measured value still closer to that deduced from Ref. 7. This excellent agreement shows that the NRPS technique can be used reliably for testing the phonon spectra and for deducing the Debye temperatures of molecular crystals.

Finally, it is of interest to note that while the present technique is very sensitive to the high-frequency modes of the phonon spectra through the zero-point energies, and can yield a relatively accurate value of the Debye temperature, it is much less sensitive to a phase transition such as that from a liquid to a solid phase. This is true especially if such a transition occurs at a relatively high temperature (≈ 195 K) such as that occurring in NH_3 . At such a temperature the thermal motion is large and overwhelms the relatively small effects in the kinetic energy of the N atom occurring in such a phase transition. This is not necessarily true for other phase transitions such as orientational transitions which can be easily detected using the NRPS technique as was illustrated in the case of the adsorption of NO on graphite.⁹

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