Effective and Debye temperatures of solid N_2, N_2O, N_2O_2, and N_2O_4

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Some current and previous data of nuclear-resonance photon-scattering measurements are analyzed to deduce the effective temperatures T_e of the N-containing molecular solids N_2, N_2O, N_2O_2, and N_2O_4. The value of T_e is related to a weighted average over the vibrational spectrum of the molecular lattice at 0 K and also to the Debye temperature. For N_2 the results have been found to be in good agreement with those reported by other investigators using different techniques.

I. INTRODUCTION

The nuclear-resonance photon-scattering (NRPS) technique has been used to study the effective temperature T_e of the N atom in N_2, N_2O, N_2O_2, and N_2O_4. This was done by measuring the resonance-scattering cross section from the 6324-keV level of ^{15}N in the temperature range 300–10 K using highly enriched isotopic samples. The value of T_e measured in the present work is related to the total zero-point kinetic energy of the molecular lattice including that of the internal vibrations of the molecules. A Debye temperature Θ_0 characterizing the "external" vibrations of the molecular lattice is defined here (see Sec. II A below), which is practically independent of T; it is different from the commonly used "caloric" Debye temperature Θ_D related to specific heats which depend strongly on T.

In the present work, we used the random photoexcitation method[1] in which one of the γ lines of the photon beam [arising from the $Cr(n,\gamma)$ reaction] overlaps, by chance, the 6324-keV nuclear level in ^{15}N. It turns out that, in this process, the scattering cross section σ_s is strongly dependent on the Doppler broadening of the nuclear level and, hence, can be viewed as a measure of the weighted average over all vibrational and librational frequencies in which the N atom participates. Contributions to this come partly from the external kinetic vibrations of the molecular lattice and partly from the internal kinetic degrees of freedom of each molecule. At low temperatures, the thermal motion is practically frozen and the main contributor to the external and internal kinetic energies are the zero-point motions. Since the internal vibrational frequencies are well known from infrared measurements, the effect of the external vibrational frequencies of the lattice on the Doppler broadening of the nuclear level can be determined. This, in turn, is related to the Debye temperature Θ_0 of the solid molecular lattice. More details concerning this method may be found elsewhere.[1,2]

In the case of N_2, N_2O, and N_2O_2, the determination of Θ_0 is done by analyzing previous scattering cross-section data,[3-5] while for N_2O_4 the data are reported here. In addition, for N_2O we report cross-section results taken at a markedly different γ-ray source temperature.

II. THEORETICAL REMARKS

A. Effective temperatures

As mentioned above, the resonance-scattering cross section σ_s depends mainly on the total kinetic energy of the N atom and may be expressed in terms of an effective temperature T_e of the N atom in the sample. Here we distinguish between samples in gaseous and solid phases. As an illustration we evaluate T_e for these two cases; the Debye temperature Θ_0 enters only in the solid phase.

1. Pure NO_2 gas

The value of T_e of the N atom for NO_2 gas assumed to be in a monomer form can be written as

$$T_e = S_T T + S_R T + \sum_{j=1}^{0} S_j k \alpha_j / 2 , \qquad (1)$$

where the first two terms on the right-hand side correspond to the translational and rotational motions which together constitutes the external modes of the NO_2 molecule as a whole. The internal modes of vibrations are contained in the third term where the factor $\frac{1}{2}$ arises form 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. The factors S_T, S_R, and S_j are the energy fractions shared by the N atom in the translational, rotational, and internal j-vibrational mode of the molecule. It should be added that NO_2 is a bent symmetric molecule with a N—O bond distance of 1.197 Å, an O—N—O bond angle of 134.25°, and has three normal modes: $\nu_1 = 1306$ cm^{-1}, $\nu_2 = 740.2$ cm^{-1}, $\nu_3 = 1580.3$ cm^{-1}, taken from literature on infrared spectroscopy.[6-8] The vibrational energy $\alpha_j k$ is given by

$$\alpha_j = (h\nu_j/k)\{[\exp(h\nu_j/kT)-1]^{-1}+\tfrac{1}{2}\} . \qquad (2)$$

$S_T \approx \frac{15}{47}$ is the mass ratio of the ^{15}N atom to that of the $^{15}NO_2$ molecule. More accurately, $S_T=0.3192$ is obtained by substituting the accurate atomic masses of ^{15}N and $^{15}NO_2$. Similarly, $S_R=0.2391$ is obtained by considering the moments of inertia around the three principal axes of the molecule. The values of S_j may be obtained from the relative amplitudes of vibration A_{ij} of the atoms in the molecule by using the relation

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

where $E_{ij}=4\pi\nu_j^2 M_1 A_{ij}^2$ and $E_{Tj}=4\pi\nu_j^2\sum_{i=1}^{3} M_i A_{ij}^2$ are the kinetic energies of vibrations of N and NO_2 in the j normal mode of frequency ν_j. Further, M_i, and A_{ij} are the mass and relative amplitude of vibration of the N atom. M_i, and A_{ij} ($i=2,3$) are the corresponding quantities of the two O atoms. The amplitudes A_{ij} were calculated using computational methods of infrared spectroscopy.[6]

Substituting the values of S_T, S_R, S_j, we may obtain an approximate expression for T_e for the case where NO_2 is assumed to be a monomeric gas, and valid for relatively low T where $kT \ll h\nu_j$:

$$T_e=0.5583T+384.9 , \qquad (4)$$

which implies that the zero-point kinetic energy of the ^{15}N atom in the NO_2 molecule (contributed by the three normal modes of vibration) is equal to 384.9 K. The above illustrates the calculation of T_e for the relatively simple case of the NO_2 molecule in a gaseous phase.

2. Pure N_2O_4 gas

In the vapor phase at $T > 294$ K, NO_2 occurs as a mixture of monomeric NO_2 and dimeric N_2O_4. The internal vibrational frequencies of the dimer are different from those of the monomer; it is thus expected that the value of T_e for the dimer is also different. To calculate T_e of the N atom for the dimer, we note that (1) N_2O_4 is a planar molecule which has 12 internal normal modes compared to only 3 modes in the NO_2 molecule, (2) the structural parameters are N-O and N-N distances of 1.180 and 1.1750 Å respectively; O-N-O angle 133.7°. The corresponding expression of T_e for the N atom is similar to Eq. (1) namely,

$$T_e=S_T T+S_R T+\sum_{j=1}^{12} S_j k\alpha_j/2 , \qquad (5)$$

where the fraction $S=S_T+S_R=0.205$ is a sum over the translational and the rotational fractions shared by the N

TABLE I. Calculated fractions S_T, S_R, and S_j of the vibrational, librational, and internal vibrational motions of the molecules in the solid lattice. The normal frequencies ν_j (given in units of K) are enclosed in parentheses and were taken from infrared literature. The calculated fractions are normalized so that $\sum S_i=1$ ($i=R,T, j=1,\ldots$).

	$^{15}N_2$	$^{15}N^{14}NO$	$^{15}N_2O_2$	$^{15}N_2O_4$	$^{15}NH_3$
S_T	0.5000	0.3333	0.2419	0.1596	0.8323
S_R	0.3333	0.3320	0.2207	0.0454	0.0240
S_1	0.1667	0.0570	0.0863	0.1116	0.0208
$h\nu_1/k$	(3288)	(3167.2)	(2633)	(2448.1)	(4942.2)
S_2		0.1651	0.0863	0.1076	0.0208
$h\nu_2/k$		(1826.9)	(2487)	(2407.9)	(4942.2)
S_2		0.0563	0.1401	0.0917	0.0073
$h\nu_3/k$		(842)	(368.3)	(1946.6)	(4795.6)
S_4		0.0563	0.0996	0.0462	0.0231
$h\nu_4/k$		(842)	(282)	(1794.7)	(2335.6)
S_5			0.0240	0.05896	0.0231
$h\nu_5/k$			(238.8)	(1288.1)	(2335.6)
S_6			0.1012	0.06727	0.04861
$h\nu_6/k$			(136.7)	(1046.3)	(1360.2)
S_7				0.1388	
$h\nu_7/k$				(939.2)	
S_8				0.11347	
$h\nu_8/k$				(639.4)	
S_9				0.0160	
$h\nu_9/k$				(568.8)	
S_{10}				0.0374	
$h\nu_{10}/k$				(392)	
S_{11}				0.0059	
$h\nu_{11}/k$				(368.7)	
S_{12}				0.00002	
$h\nu_{12}/k$				(138.4)	

atom in the N_2O_4 molecule. S_T, S_R, and S_j may be calculated by considering the planar shape and the interatomic distances of the dimer. Table I lists the values of the calculated coefficients appearing in Eq. (5) not only for the N_2O_4 molecule but also for the other N-containing molecules studied previously using the NRPS technique.[3-5,9] It is important to note that S_T, S_R, and S_j do not change when passing from the vapor to the liquid and the solid phases. This is because the vibrational frequencies seem to be unaffected by such a phase transformation.[10] It is helpful to remember a simple "sum rule" obeyed by the values of S_i ($i = T$, R; $j = 1, \ldots$):

$$\sum_i S_i = 1 \ , \tag{6}$$

where the left-hand side is a sum over all energy fractions carried by the N atom in the external and internal modes of motion of each molecule, and should sum up to unity; this is found to be the case for all gases appearing in Table I.

For the N_2O_4 dimer in a gaseous phase and for low T, where $kT \ll h\nu_j$, Eq. (5) takes the approximate form

$$T_e = 0.205T + 585.1 \ . \tag{7}$$

It is important to note that the zero-point kinetic energy is now 585.1 K and illustrates the huge increase in the zero-point kinetic energy of the internal vibration of the ^{15}N atom when the NO_2 molecule passes from monomer to dimer form.

3. Pure solid N_2O_4

For the analysis of the experimental data, we are interested in an expression for T_e of a molecular solid of NO_2 which occurs in a pure dimer form, N_2O_4. Here we have to account for the fact that, when passing from a vapor phase to a solid phase, the translational and rotational degrees of freedom turn into a distribution of frequencies of external vibrational and librational motions of the whole molecule in the solid lattice. If these modes of motion are represented by a frequency distribution function $g(\nu)$, we may use Eq. (5) to write the expression of T_e of the N atom in the solid molecular lattice by replacing the first two terms on the right-hand side by a single term as follows:

$$T_e = S \int_0^\infty \frac{h\nu}{k} g(\nu) \left[\frac{1}{\exp(h\nu/kT)-1} + \frac{1}{2} \right] d\nu$$

$$+ \sum_{j=1}^{12} S_j \alpha_j / 3 \ . \tag{8}$$

The factor multiplying S in the first term of the right-hand side of Eq. (5) is an expression for T_e deduced by Lamb[11] under the harmonic approximation. For a Debye-type phonon spectrum, $g(\nu) = 3\nu^2/\nu_0^3$ (with ν_0 the cutoff frequency related to the Debye temperature Θ_0 of the molecular lattice), T_e takes the form

$$T_e = S(3T^2/\Theta_0^3) \int_0^{\Theta_0/T} x^3 \left[\frac{1}{\exp(x)-1} + \frac{1}{2} \right]$$

$$+ \sum_{j=1}^{12} S_j \alpha_j / 3 \tag{9}$$

with $x = h\nu/kT$. The limiting value of T_e at $T = 0$ K is

$$T_0 = S\frac{3}{8}\Theta_0 + \sum_{j=1}^{12} S_j h\nu_j / 6k \ . \tag{10}$$

The first term on the right-hand side is related to the zero-point kinetic energy of the external modes of motion of the molecular lattice while the second term is related to that of the internal modes of motion of the N_2O_4 molecule (where ν_j are assumed to be unaffected by passing from the gas phase to a solid phase as was found by experiment[10]). Equation (10) may be viewed as a different definition of the Debye temperature which is related to the phonon spectrum $g(\nu)$. It should be noted that S_j, ν_j, and S can be calculated while T_e versus T is measured, therefore Θ_0 may be determined as a function of T as seen from Eq. (8). This Θ_0 was found to be practically independent of T and, hence, is markedly different from the "caloric" Debye temperature Θ_D, which is strongly dependent on T.

B. Scattering cross sections

The important measured quantity is the scattering cross section σ_s, which is related to the effective temperature T_e. The calculation of σ_s versus T_e involves a knowledge of the parameters of the resonance process such as the total and ground-state radiative widths Γ and
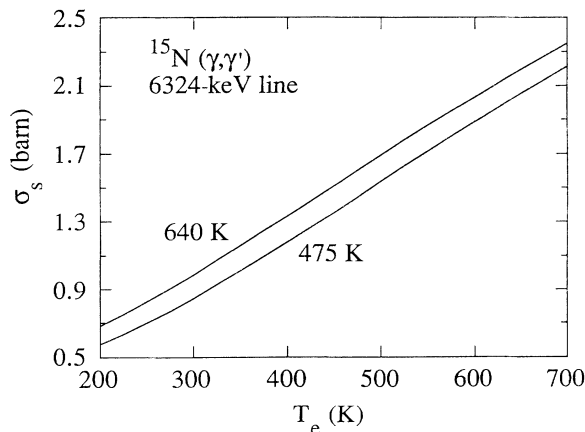

FIG. 1. Resonance scattering cross section σ_s of the 6324-keV γ line as a function of the effective temperature T_e of ^{15}N calculated for two γ-source temperature of $T_s = 475$ and 640 K. The parameters of the resonance process are $\Gamma = \Gamma_0 = 2.9$ eV with Γ and Γ_0 the total and ground-state radiative widths of the 6324-keV level in ^{15}N. $\delta = 29.5$ eV is the energy distance between the peak of the γ line of the $^{53}Cr(n,\gamma)$ reaction and the ^{15}N nuclear level. The Debye temperature of the Cr γ source was taken to be 510 K. Details of the calculation are given in Refs. 1 and 2.

Γ_0 of the resonance level ($\Gamma = \Gamma_0 = 2.9$ eV) and the energy separation δ between the incident γ line and the resonance level ($\delta = 29.5$ eV); the calculation is explained in detail elsewhere.[1,2] The result of calculating σ_s versus T is shown in Fig. 1 for two γ-source temperatures of 475 and 640 K. The value of σ_s may be seen to be strongly dependent on the γ-source temperature. Since σ_s also depends on the sample temperature, the γ-source temperature should be monitored carefully to avoid possible errors in interpreting the data. As an illustration, it may be noted that an uncertainty of ± 60 K in the determination of the γ-source temperature for the case of N_2O_2 could change the deduced value of Θ_0 by $\sim \mp 25$ K.

The strong effect of the zero-point energies on the scattering cross sections, and hence the validity of the above model, was tested by comparing the scattered intensities from two different samples $^{15}N_2O_4$ and $^{15}N^{14}NO$ (containing exactly the same amount of ^{15}N) and whose values of T_e are markedly different: At $T = 297$ K, the corresponding values are $T_e = 678$ and 485.5 K from which the ratio of the scattering intensities can be predicted using Fig. 1 yielding $R = 1.46$. At $T = 10$ K, the effective temperatures are predicted to be $T_e = 610$ and 343 K, respectively, leading to a scattering cross-section ratio of 2.08 (see below). These values are in excellent agreement with the experimental ratios, found to be

$$R = \sigma_s(^{15}N_2O_4)/\sigma_s(^{15}N^{14}NO) = \begin{cases} 1.46 \pm 0.06 & \text{at } T = 297 \text{ K} . \\ 2.12 \pm 0.09 & \text{at } T = 10 \text{ K} . \end{cases}$$

It should be emphasized that this huge deviation from $R = 1$ is due primarily to the effect of the zero-point motion of the internal modes of vibrations of the N atom in N_2O and N_2O_4 causing a large difference between the Doppler broadenings of the nuclear level in the two cases.

III. EXPERIMENTAL METHOD

Experimentally, the photon beam is generated from the (n, γ) reaction on three metallic chromium discs (7.5 cm diameter $\times 1.0$ cm thick) placed along a tangential beam tube and near the core of the IRR-2 reactor. The photon beam was collimated and neutron filtered using a 40-cm length of borated paraffin. The intensity of the 6324-keV γ line was around 10^4 photons/cm^{2}s on the target position. In the present work, we used 2.014 g of enriched NO_2 (99% ^{15}N) contained in a spherical stainless-steel container 20 mm i.d. and 2 mm thick which could sustain high pressures. In this small volume, most of the NO_2 at 297 K occurs in the form of a liquid dimer, N_2O_4, because of the high-pressure buildup.

A similar spherical cell was employed for the N_2O measurement, where a 993-mg isotopic target was used. Each of the above gases was admitted in a gaseous form through a valve fitted to the cell which was kept at liquid-nitrogen temperature. The target was then placed inside a Displex cryostat which varies the temperature between 297 and 12 K. The temperature of the cell was monitored at the top and the bottom of the sample holder. A 150-cm^3 hyperpure Ge detector was used for detecting the scattered radiation. For background measurements an empty, but otherwise identical, stainless-steel cell was employed. The temperature of the γ source was monitored using a thermocouple and was found to vary during the reactor operation within ± 15 K. This temperature measurement was important for obtaining a precise value of Θ_0 (see Sec. III B). In fact, at $T = 0$ K, where all thermal motion is frozen, a measurement of the scattering cross section may directly determine Θ_0. This is because, at $T = 0$ K, the Debye temperature is related to the effective temperature T_e by $\Theta_0 = \frac{3}{8} T_e$.

IV. RESULTS AND DISCUSSION

The results of σ_s versus T for N_2O_4 and N_2O are displayed in Fig. 2, which also shows previous data on N_2, N_2O_2, and N_2O taken from Refs. 3–5. The present data for N_2O_4 and N_2O were taken at a γ-source temperature of $T = 475$ and 503 K, respectively.

For deducing Θ_0, it was first necessary to calculate a curve of T_e and hence of σ_s as a function of T using Eq. (8) and Fig. 1. This was then compared to the data of Fig. 2 and Θ_0 was deduced by a best-fit procedure. The results are given in Table II, which also lists the value of Θ_0 for NH_3 obtained using the NRPS technique.[12]

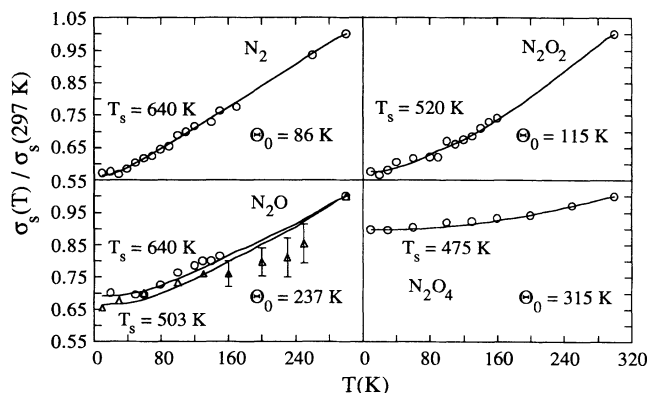The N_2O data taken above 160 K has a large statistical error associated with it. Thus, in deducing Θ_0 for this

FIG. 2. Scattered intensity ratios (relative to 297 K) from pure samples of $^{15}N_2$, ^{15}NO, $^{15}N^{14}NO$, and $^{15}N_2O_4$ each contained in a 2-cm diam spherical stainless-steel container. The actual temperature of the Cr γ source is indicated in each case where parentheses indicate uncertainty. The solid curves were calculated using Eq. (2) for deducing T_e in the gaseous phase and Eq. (4) for deducing T_e in the liquid and solid phases; Fig. 1 was then applied to get the corresponding cross section. The Debye temperatures Θ_0 were obtained by best fitting the solid curves to the experimental data. Typical errors are indicated.

TABLE II. Measured values of the isotopic Debye temperatures of some molecular solids (containing ^{15}N) as obtained by a best-fit procedure to the data of Fig. 2 and using Eq. (4). The calculated value of Θ_0 for the natural composition of the samples (containing ^{14}N) obtained by integrating over the phonon spectra are also listed.

Sample	NRPS Θ_0 (K) (^{15}N)	Phonons Θ_0 (K) (^{14}N)
^{15}N	86 ± 8	79 ± 2[a]
$^{15}N_2O_2$	$(115\pm^{20}_{30})$[b]	
$^{15}N^{14}NO$	237 ± 20	
$^{15}N_2O_4$	315 ± 30	
$^{15}NH_3$	241 ± 8	235[c]

[a]The error was estimated from Ref. 13 after correcting the density of states (see text).

[b]The relatively large error in this case is caused by the fact that the temperature of the γ source was not monitored in the course of measuring σ_s versus T (see text).

[c]This value was calculated using the density of states of Ref. 11 where the weighing factor of the rotational motion of the NH_3 molecule was the same as that of the NRPS technique (see Ref. 12).

case (Fig. 2 and Table II), only the data points at $T < 100$ K were best fitted with the calculated curves. This procedure was justified because Θ_0 is most sensitive to the low-temperature data.

The value $\Theta_0 = 115$ K deduced for N_2O_2 from the data of Ref. 4 should be treated with caution because the γ-source temperature was not monitored during the course of this measurement and was taken as 520 K; it is believed that it could have been between 480 and 580 K. Assuming a γ-source temperature of $T = 460$ K, the deduced value would have been $\Theta_0 = 135$ K, while, for $T = 580$ K, the deduced value is $\Theta_0 = 85$ K. Thus, the uncertainty in the γ-source temperature has contributed the major part of the error for this case.

A few remarks concerning the calculated curves appearing in Fig. 2 are in order: (1) At 297 K, the N_2, NO, and N_2O samples were in a gaseous phase at elevated pressures and turned to a liquid phase at around 78, 122, and 186 K, and then to a solid phase at around 63, 110, and 183 K, respectively. The values of T_e of the N atom in the liquid and solid phases are higher than that of the gaseous phase at the same T. The difference which is contributed by the vibrations of the lattice may show up as a kink in the calculated curve of σ_s versus T at the boiling point of the molecular lattice. This effect is, however, small and usually is not visible in Fig. 2. (2) In the liquid and solid phases, NO occurs in a dimer N_2O_2 form and, hence, the deduced value of Θ_0 refers to this form only. (3) The present values of Θ_0 refer to that of the molecular solids at 10 K which is the lowest temperature achieved in the present work. Thus, for solid N_2 (which, at normal pressure occurs in two phases: a cubic α phase existing below 35.6 K and a hexagonal β phase existing between 35.6 K and the melting point at 63.2 K), the present value of Θ_0 refers to that of the α phase. (4) The

N_2O_4 sample occurs in a liquid form at 297 K because of the elevated pressure and turns to a solid at around 262 K.

It is important to emphasize again that the present value of Θ_0 is related to a weighted average of the phonon spectrum as defined in Eqs. (8) and (9) and hence may be viewed as providing a test of the vibrational spectrum of the molecular solid lattice. In fact, such a test has already been made in Ref. 12 for the case of NH_3 and an excellent agreement was found between our value of Θ_0 and that deduced from the vibrational spectrum of solid NH_3 (see Table II). This shows that the NRPS technique can be used reliably for testing the phonon spectra and for deducing the Debye temperatures of molecular solids.

For solid N_2, such a comparison is not straightforward because the only reported density of states[13] was based on an erroneous Raman assignment caused by the fact that only two Raman lines, the E_g line at 31 cm^{-1} and a T_g line at 36 cm^{-1}, were known in the early work as pointed out in Ref. 14. The missing T_g third line was later found at 60 cm^{-1}. In the present work we incorporated this line to correct the phonon density of states reported in Ref. 13. Another correction was introduced in which the frequency of the highest T_u line (calculated to be at 72 cm^{-1} in Ref. 13) was adjusted to coincide with 70 cm^{-1} observed by inelastic-neutron-scattering[15] and infrared measurements. We used this information to modify the phonon density of states of Ref. 13 for solid N_2 in the cubic α phase from which we deduced the value of Θ_0 (Table II). The result is seen to be in good agreement with that measured by us using the NRPS technique. This should also be compared with $\Theta_0 = 78$ K deduced from the temperature dependence of the shape of the molecular absorption bands of N_2 in the solid phase.[16] This is also close to the values of the caloric Debye temperature Θ_D obtained by specific-heat measurements[17-19] ranging between 73 and 83.5 K. As mentioned above, Θ_0 and Θ_D are defined differently and are expected to have different values.

It is of interest to examine the results of σ_s versus T for the case of N_2O carried out at two different γ-source temperatures: 640 and 503 K, which are displayed in Fig. 2. Note the large difference between the two sets of data. The most interesting result is that the deduced values of Θ_0 for N_2O are almost identical irrespective of the γ-source temperature. This constitutes a nice test for the validity of the present procedure for deducing the Debye temperatures in molecular lattices.

Another remark concerning the above comparison is in order. The present measurement was carried out for isotopic $^{15}N_2$ while other measurements such as specific heat and neutron inelastic measurements were carried using natural nitrogen (containing 99.64% $^{14}N_2$). A proper comparison should correct for the isotopic effect by a factor of $1/M^{1/2}$, namely, $(\frac{15}{14})^{1/2} = 1.035$. However, the ratio of Θ_D for the two isotopic species $^{14}N_2$ and $^{15}N_2$ at 16 K reported[18] to be $\frac{73}{72} = 1.014$, is smaller than this value; the reason for this discrepancy is not clear yet. It should be remarked that the NRPS technique was also employed to measure the Debye temperatures of metallic elements,

such as Ti, Ni, Zn, Cr, and Pb; the results were found to be consistently higher by about 10% than the values which were deduced from the phonon spectra.[20] Thus, the 10% higher value of Θ_0 measured here in the case of N_2 is compatible with those earlier measurements carried out by the NRPS technique.

In conclusion, we have measured the scattering cross section from the 6324-keV level in ^{15}N and used it to obtain the effective temperature of the ^{15}N atom in few molecular solids using the NRPS technique. The result has been used to deduce a Debye temperature of the sam-ples and may provide a test of the phonon spectra of the molecular solid lattices. It is of interest to note that the values of Θ_0 obtained for all samples are higher than the melting points for all samples.

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