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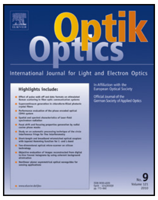

Original research article

Calculation of the Raman and IR frequencies from the volume data at high pressures in N_2

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ABSTRACT

Raman and IR frequencies of N_2 in the molecular state are calculated as a function of pressure up to 160 GPa by using the volume data from the literature through the mode Grüneisen parameter. By determining the Grüneisen parameters for the lattice modes and vibrons which decrease mostly with increasing pressure from the observed frequency (Raman, IR) and volume data, the Raman and IR frequencies of those modes are calculated at various pressure at room and low temperatures. We find that the Raman and IR frequencies increase as the pressure increases in N_2 as observed experimentally. This method of calculating the Raman and IR frequencies from the volume data can be applied to the some other molecular crystals.

1. Introduction

Nitrogen is an ideal molecule to study because its intramolecular triple bond remains stable up to relatively high pressures and temperatures [1]. It transforms to a monatomic single bonded polymeric network with the cubic gauche (cg-N) structure under pressures of about 50–75 GPa on the basis of theoretical calculations [2–6] as also pointed out previously [7]. The cg-N represents a new class of single-bonded nitrogen materials with the unique properties such as energy capacity [8]. The experimental measurements show that nitrogen forms a polymeric solid under pressure [9]. Atomic single bonded nitrogen with the cg-N structure has been synthesized at high pressure of ≈110 GPa and high temperature of ≈200 K [8]. Evidence has been found of the existence of polymeric nitrogen with a cubic gauche structure which grows in single crystals if the pressure-temperature conditions are close to the boundary of molecular nitrogen cg-N [10]. So, it undergoes the non-molecular (NM) transition (destabilization of its triple bond) in the pressure range accessible to the experimental techniques forming polymorphs with three weaker ring N—N bonds [11,12], as studied above.

Raman spectroscopy is a powerful experimental technique to characterize pressure –induced phases of nitrogen. Regarding the low-pressure phases of α, β, and γ in nitrogen, a number of Raman spectroscopic studies have been reported in the literature [13–18]. We have also calculated Raman frequencies for those low-pressure phases in nitrogen in our previous studies [19–24]. At higher pressures, the Raman spectroscopic studies have investigated the effect of the pressure on the mechanism of phase transitions between the phases including δ (δ_{loc}), ε, ζ, η, κ, ι, θ and cg-N as given in various T-P phase diagrams of nitrogen. Some of those Raman studies that have been reported in the literature, include experimental [8,11,18,25–27] and theoretical [2,9,28–33] works.

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Table 1
Values of the coefficients according to Eq. (4) fitted to the observed volume data [34] for solid nitrogen.

$V(\text{Å}^3)$	b_0 (Å^3)	b_1 $(\text{Å}^3/\text{GPa})$	$b_2 \times 10^{-4}$ $(\text{Å}^3/\text{GPa}^2)$
Solid N_2	11.75	−0.076	2.58

Table 2
Values of the coefficients according to Eq. (3) fitted to the observed Raman and IR frequencies [11] for the lattice modes indicated within the pressure interval for solid nitrogen.

$\upsilon(\text{cm}^{-1})$	a_0 (cm^{-1})	a_1 $(\text{cm}^{-1}/\text{GPa})$	$-a_2 \times 10^{-2}$ $(\text{cm}^{-1}/\text{GPa}^2)$	$a_3 \times 10^{-4}$ $(\text{cm}^{-1}/\text{GPa}^3)$	Pressure interval P(GPa)
υ_{I}	309.9	4.61	0.88	–	$42.9 < P < 139.8$
υ_{II}	308.5	4.91	1.23	–	$80.4 < P < 160.1$
υ_{III}	195.5	4.82	1.05	–	$24.7 < P < 111.0$
υ_{IV}	204.5	4.72	2.80	0.86	$42.9 < P < 110.5$
υ_{V}	70.2	4.28	1.15	–	$60.7 < P < 124.1$
υ_{VI}	20.3	4.71	4.45	1.62	$23.4 < P < 110.5$

In this study, we calculate the Raman and IR frequencies of the lattice modes and the internal modes (υ_1 and υ_2) as a function of pressure up to 150 GPa (at room temperature) for the high pressure phases of, ε, ζ, κ and cg-N solid nitrogen. Using the observed data for volume [34] and Raman and IR frequencies [11], the pressure dependence of the isothermal mode Grüneisen parameter γ_T of the lattice and internal modes is determined. By using the γ_T values, the Raman and IR frequencies of those modes are predicted at various pressures for the phases considered in the solid nitrogen.

Below, in Section 2 we give our calculations and results. In Sections 3 and 4, discussion of our results and conclusions are given, respectively.

2. Calculations and results

Volume dependence of the Raman frequency which measures the anharmonicity, can be defined as the mode Grüneisen parameter γ

$$\gamma = -\frac{d\ln\upsilon}{d\ln V} \tag{1}$$

Depending on the crystal volume and the Raman frequency at various pressures (at constant temperature) isothermal mode Grüneisen parameter $\gamma_T(P)$ can be defined as

$$\gamma_T(P) = -\frac{V(P)\,(\partial\upsilon/\partial P)_T}{\upsilon(P)\,(\partial V/\partial P)_T} \tag{2}$$

The pressure dependence of the Raman frequency υ and the crystal volume can be assumed as

$$\upsilon_T(P) = a_0 + a_1 P + a_2 P^2 \tag{3}$$

and

$$V_T(P) = b_0 + b_1 P + b_2 P^2 \tag{4}$$

respectively, where a_0, a_1, a_2 and b_0, b_1, b_2 are constants.

By analyzing the experimental data for the frequencies of various Raman modes and the crystal volume as a function of pressure according to Eqs. (3) and (4), respectively, the coefficients can be determined and the pressure dependence of the isothermal mode Grüneisen parameter $\gamma_T(P)$ can be obtained (Eq. (2)). This can be used to predict the Raman frequencies by solving Eq. (2) with the additional pressure-dependent term A(P) according to

$$\upsilon_T(P) = A(P) + \upsilon_0 \exp\left[-\gamma_T(P)\ln\left(\frac{V_T(P)}{V_0}\right)\right] \tag{5}$$

where υ_0 and V_0 are the values of the Raman frequency and volume at ambient conditions ($T = 300$ K, $P = 0$). The pressure-dependent term can also be assumed as

$$A(P) = a + bP + cP^2 \tag{6}$$

with constants a–c, which can be used to fit to the experimental data for the Raman frequencies.

We first analyzed the pressure dependence of the crystal volume V (Eq. (4)) using the observed volume data [34] and determined the coefficients b_0, b_1 and b_2, as given in Table 1. We then analyzed the Raman and IR frequencies of the lattice modes and vibrons (Eq. (3)) using the experimental Raman and IR data [11] and also determined the coefficients in the pressure intervals indicated in Tables 2 and 3, respectively. For the lattice modes of υ_{IV} and υ_{VI} we used the cubic