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Pressure dependence of vibrational frequencies in α solid nitrogen

A El-Sadek, A A Helmy and S El-Eraky

Department of Engineering Physics, Faculty of Engineering, Cairo University, Giza, Egypt

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Abstract. Properties of solid nitrogen under pressure have been studied in terms of a harmonic intramolecular potential and a parametrized site–site Lennard-Jones [6–12]-type potential to describe the interaction between non-bonded atoms using the lattice sum. A computer simulation study as an alternative to the experiment has been used to obtain the pressurized nitrogen. The sublimation energy, the equation of state, the minimum potential energies of the crystal in the molar volume range 16–28 cm³ and the corresponding bond lengths were reproduced satisfactorily for α -nitrogen. The pressure dependence of the frequency change and bulk modulus were also estimated and compared with the experimental data.

List of symbols

B_m	Bulk modulus
g	Cubic constant for an isolated molecule
g'	Cubic constant for the molecule in the solid
k	Harmonic constant for an isolated molecule
k'	Harmonic constant for the molecule in the solid
k_B	Boltzmann's constant
M	Molecular weight
N	Total number of molecules in the system
N_0	Avogadro's number
p	Pressure
r	Instantaneous separation between atoms
r_0	Equilibrium separation between atoms in an isolated molecule
r_c	Intramolecular atomic separation in the solid
R_{ij}	Interatomic distance between the i th and the j th atom
T	Temperature
U	Total potential energy per molecule in the solid
U_{aa}	Atom–atom potential
U_{inter}	Intermolecular crystal potential
U_{intra}	Intramolecular potential
V	Volume
γ	Grüneisen's parameter

ϵ	Lennard-Jones potential constant
μ	Molecular reduced mass
ν	Frequency
ρ	Density
σ	Lennard-Jones potential constant

1. Introduction

Pressure causes substantial changes in the molar volume or density. This affects the solid in two important ways: the first is the change in intermolecular forces, and the second is the change in single molecular rotational states.

The pressure dependence for intramolecular vibration has been calculated for CO₂ by Hanson and Bachman [1]. They assumed that the external pressure causes small changes in bond lengths with subsequent effect on the force constant. Using the intramolecular force constants of Suzuki [2], they found that for $p = 100$ kbar and area of 4.995 \AA^2 the change in the bond length is -0.0083 \AA or -0.15 in the dimensionless stretching coordinate q . This model can be applied to any simple structure such as CO₂. Solid CO₂ has an FCC structure belonging to the space group $Pa\bar{3}$ with four molecules per unit cell. The CO₂ molecule has three fundamental normal vibrational modes: the symmetric stretching, the bending and anti-symmetric stretching modes. For solid nitrogen there is only one normal mode of vibration: the symmetric stretching mode. The α -phase of nitrogen belongs to $Pa\bar{3}$ as does CO₂ and we can apply this model for calculating the pressure dependence of the vibrational frequency. In concert with the development of the diamond cell technology [3], there has been a great advance in the utilization of Raman scattering and infrared absorption to study the pressure dependence of the intramolecular vibrational modes in molecular crystal. Raman scattering experiments [4] on the stretching mode in solid nitrogen at room temperature have been performed up to 374 kbar. There is a splitting of this mode in the region $54 \text{ kbar} \leq p \leq 118 \text{ kbar}$, because the crystal structure has two inequivalent sites [5]. Measurements of broadening and splitting from the ruby gauge indicate that solid nitrogen is reasonably plastic up to 130 kbar and $d\nu/dp$ is a decreasing positive quantity in the region $39 \text{ kbar} \leq p \leq 374 \text{ kbar}$ [6]. The purpose of this work is to show the pressure dependence of the intramolecular vibrational modes in the intermolecular and intramolecular potentials.

2. Method

The pressure dependence of the intramolecular mode frequencies in N₂ depends in detail on the intermolecular and intramolecular interactions. We utilize a microscopic model, in which the intermolecular part of the crystal potential energy is of the atom-atom form [7].

$$U_{\text{inter}} = \sum_{ij} U_{aa}(R_{ij}) \quad (1)$$

where the sum extends over all pairwise interactions between atoms of different molecules and R_{ij} is the interatomic distance. The intramolecular potential can be described

as an expansion in powers of the atomic displacements from equilibrium:

$$U_{\text{intra}} = \frac{1}{2}k(r - r_0)^2 + g(r - r_0)^3 + \dots \quad (2)$$

The constants k and g are determined by fitting to spectroscopic data, r_0 is the equilibrium separation between atoms in an isolated diatomic molecule and r is its instantaneous value. Keeping only terms up to cubic in equation (2), the total potential energy per molecule in the solid is

$$U = \frac{1}{2}k(r - r_0)^2 + g(r - r_0)^3 + (1/N)U_{\text{inter}} \quad (3)$$

where N is the total number of molecules in the system. Similarly U can be expressed as an expansion about the equilibrium intramolecular atomic separation r_c in the solid:

$$U = \frac{1}{2}k'(r - r_c)^2 + g'(r - r_c)^3 + \dots \quad (4)$$

where k' and g' are the quadratic and cubic force constants, respectively. Taking second derivatives of equations (3) and (4) with respect to r and equating them at $r = r_c$, we get

$$k' = k + 6g(r_c - r_0) + (1/N)(\partial^2 U_{\text{inter}}/\partial r^2)|_{r=r_c} \quad (5)$$

for the quadratic intramolecular force constant in a solid. Utilizing the binomial expression the normal mode frequency change in the solid is

$$\delta\nu(p) = \nu(p) - \nu_0 = A[r_c(p) - r_0] + B[\partial^2 U_{\text{inter}}/\partial r^2]|_{r_c(p)} \quad (6)$$

with

$$A = 3g/4\pi^2\mu\nu_0 \quad B = (8\pi\mu\nu_0N)^{-1}$$

where μ is the molecular reduced mass and ν_0 is the isolated molecular normal mode frequency. The contribution to the gas to solid frequency shift from the crystal-field perturbation is clearly $\delta\nu(0)$. In addition to this term, the physical shift also includes an expression involving the change in polarization between the two phases:

$$\Delta\nu(p) = \nu(p) - \nu(0) = A[r_c(p) - r_c(0)] + B[(\partial^2 U_{\text{inter}}/\partial r^2)|_{r_c(p)} - (\partial^2 U_{\text{inter}}/\partial r^2)|_{r_c(0)}] \quad (7)$$

is the frequency shift in the solid between zero and the pressure p . The second-derivative terms in equation (7) while small compared with the first term are not negligible at high pressures. Clearly, the calculation of $r_c(p)$ is the most important element in the analysis. The calculation proceeds by evaluating the total potential energy per molecule (equation (3)) for the appropriate crystal structure. Lattice sums are taken over the first shells until the contribution of additional shells to the value of the potential energy is negligible. The intramolecular separation r is then varied in equation (3) until it is minimized at $r = r_c$. Note that U_{inter} is a function of r as is the intramolecular potential because the force centres in the atom-atom potential are separated by r . This procedure is repeated at each molar volume until a mapping of r_c -volume relation is determined by taking the derivative $p = -\partial U_{\text{inter}}/\partial V$ of the energy U_{inter} , which has been fitted to power series in the volume.

From the calculated zero-temperature equation of state, an approximate high-temperature expression can be estimated using the quasiharmonic approximation

$$p(T) = p(0) + 3N_0k_B T\rho\gamma/M$$

where N_0 is Avogadro's number, T is the temperature, k_B is Boltzman's constant, ρ is the density, M is the molecular weight and γ is Grüneisen's parameter.

3. Calculation and results

3.1. Calculation of the nearest neighbours

The number of the nearest neighbours depends on the spatial distribution of the molecules. The space group of the α -phase of N_2 is $Pa\bar{3}$. The unit cell contains four molecules, each with its equilibrium axis ordered along one of the four body diagonals of the cube. This means that the centres of molecules 1, 2, 3 and 4 are located at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ as shown in figure 1 [6]. Calculation of the number of nearest

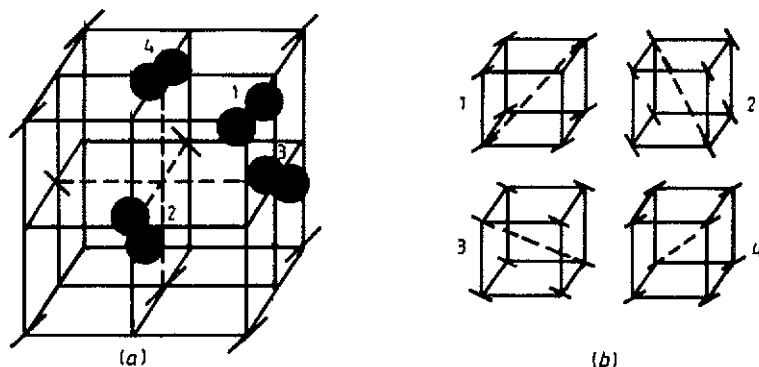


Figure 1. $Pa\bar{3}$ space group. (a) Spatial distribution of the molecular axes of the four inequivalent molecules; (b) division into sublattices.

neighbours is obtained for the first shells by using a simple computer program and the results are listed in table 1.

3.2. Calculation of the best orientation of the two molecules

Calculation has been carried out for five orientational geometries which are shown in

Table 1. Number of nearest neighbours (in units of the lattice constant) for the first shells.

Distance squared d^2	Number of nearest neighbours	Distance squared d^2	Number of nearest neighbours
0.5	8	5	24
1	6	5.5	16
1.5	16	6	24
2	12	6.5	40
2.5	16	7	0
3	8	7.5	16
3.5	32	8	12
4	6		
4.5	24		

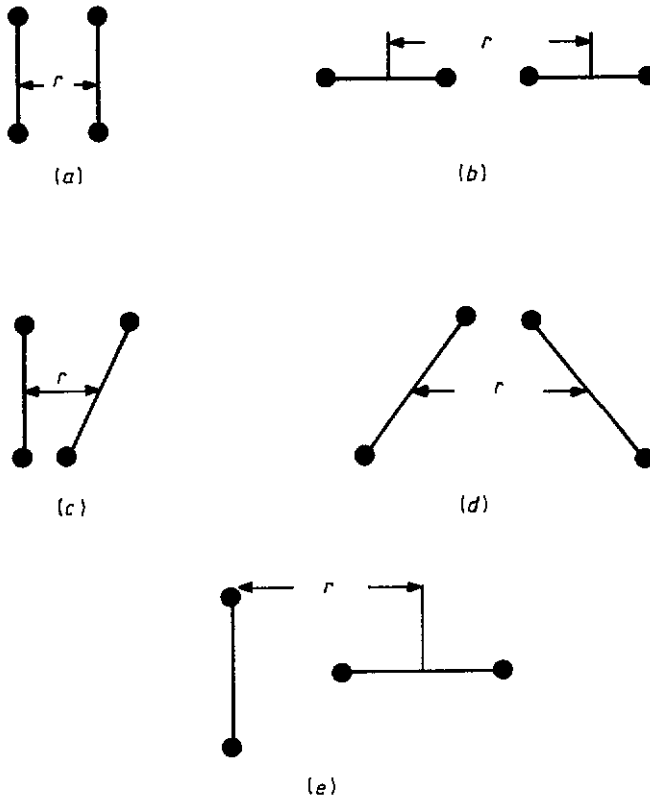


Figure 2. Orientational geometries of two molecules (gas phase): (a) H; (b) L; (c) X; (d) I; (e) T.

figure 2 [8]. Using the Lennard-Jones potential [9]

$$U = \sum_{ij} \epsilon \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]$$

with $\epsilon = 0.31 \text{ kcal mol}^{-1}$ and $\sigma = 3.3 \text{ \AA}$ to find the best orientation which gives the minimum potential energy. From figure 3, the best orientations are X and H geometries.

3.3. Calculation of the bond length r_c and corresponding minimum potential U_c

Our crystal potential consists of a 6-12-type potential between atoms of different molecules and an intramolecular harmonic potential [10]. The values of r_c and U_c are obtained and figure 4 shows the relation between the molar volume V and the minimum potential U_c in the molar volume range $16\text{--}28.4 \text{ cm}^3 \text{ mol}^{-1}$.

3.4. Equation of state

At each molar volume V we calculate the corresponding pressure p by two methods.

(i) *The first method: lattice sum.* Using the definition $p = -\partial U / \partial V$ and representing

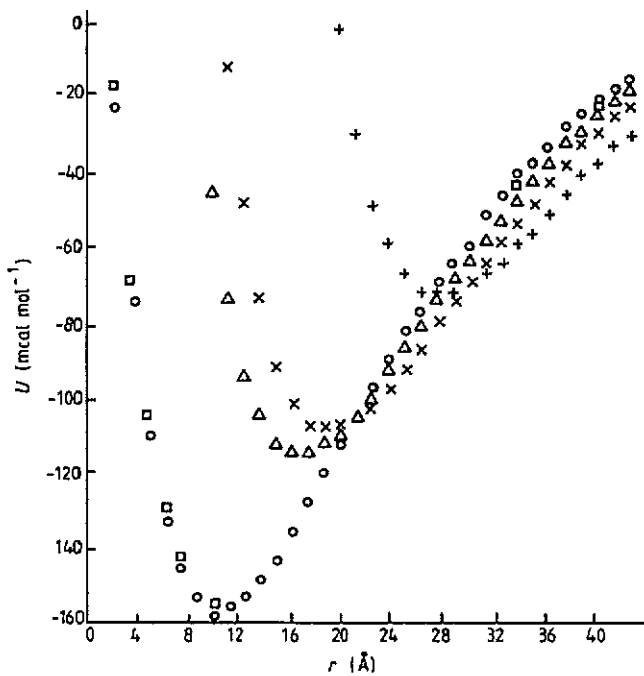


Figure 3. The intermolecular potential for nitrogen in typical orientations, where r is the centre-to-centre distance: +, L geometry; ×, T geometry; □, H geometry; ○, X geometry; △, I geometry.

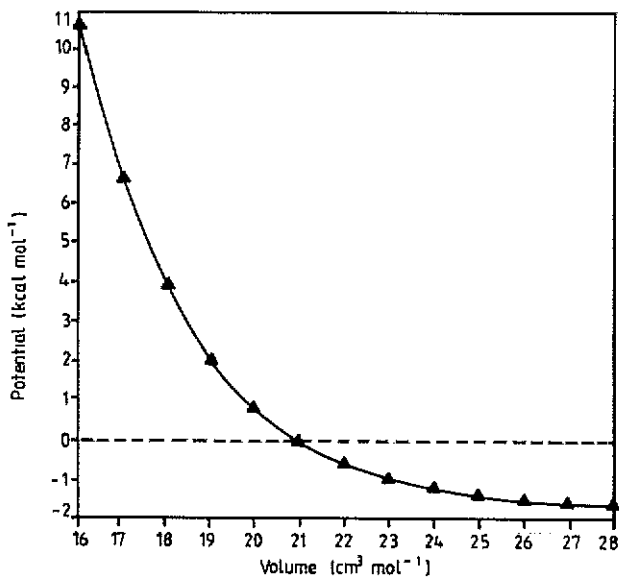


Figure 4. The calculated minimum potential versus molar volume.

U by the Lennard-Jones potential

$$U = \sum_{ij} \epsilon \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]$$

we get

$$\frac{\partial U}{\partial V} = \sum_{ij} \beta \left[2 \left(\frac{\sigma}{R_{ij}} \right)^{13} - \left(\frac{\sigma}{R_{ij}} \right)^7 \right] \frac{\partial R_{ij}}{\partial V}$$

where $\beta = -6\epsilon/\sigma$. By writing $\partial R_{ij}/\partial V = (\partial R_{ij}/\partial a)(da/dV)$ and $V = ca^3$ where $C = N_0/4$ then $da/dV = (a/3)V$ which depends on the lattice constants a [11, 12]. Figure 5 shows the p - V curve.

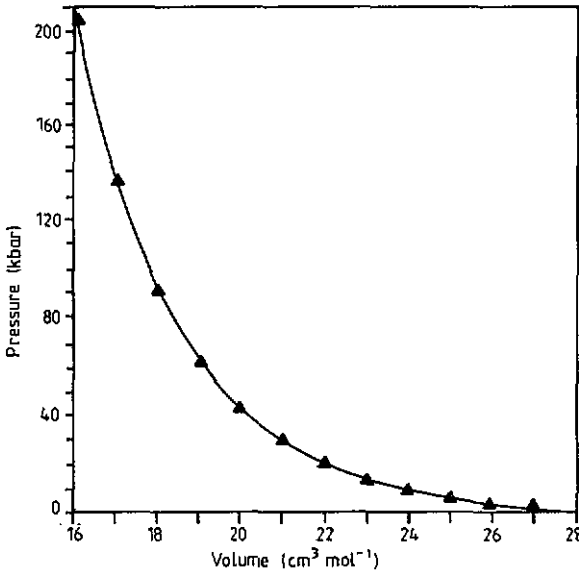


Figure 5. The calculated pressure versus molar volume (α -phase).

(ii) *The second method: curve fitting.* *U* can be fitted to the series in the volume *V* given by

$$U = F(V) = \sum_n \frac{a_n}{V^n}$$

and the pressure is determined by the relation

$$p = -\frac{dF(V)}{dV} = \sum_n \frac{na_n}{V^{n+1}}$$

We find that the best fitting can be obtained from the following:

$$U = A/V^2 + B/V^3 + C/V^4 + D/V^5 - 0.26$$

$$p = 2A/V^3 + 3D/V^4 + 4C/V^5 + 5D/V^6.$$

The values of the constants in these equations are

$$A = 1000.56 \quad B = -52\,406.21 \quad C = 860\,483.76 \quad D = 15\,190\,694.03.$$

We can obtain the value of the volume which gives the minimum potential ($p = 0$) by solving the equation

$$2AV^3 + 3BV^2 + 4CV + 5D = 0.$$

The results obtained with this method are almost the same as obtained with the first method.

3.5. The ν - p relation

From the r_c - V and p - V relations we can obtain the change in r_c with p using the equation

$$\Delta\nu_p = \nu(p) - \nu(0) = A[r_c(p) - r_c(0)] + B[(\partial^2 U_{\text{inter}}/\partial r^2)|_{r_c(p)} - (\partial^2 U_{\text{inter}}/\partial r^2)|_{r_c(0)}]. \quad (7)$$

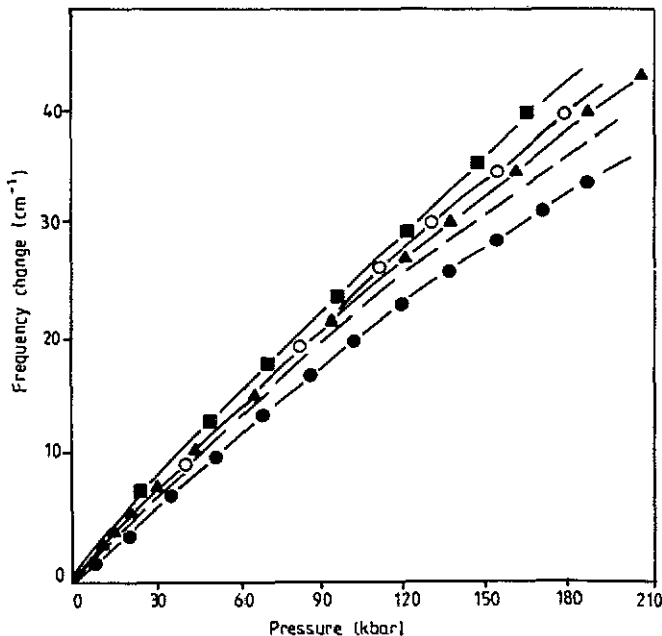


Figure 6. Frequency change versus pressure for N_2 : \blacktriangle , calculated points; ---, Berns-Van der Avoird [13] potential; — · —, potential of Murthy *et al* [10]; \blacksquare , 6-12 potential [14]; \circ , experimental data [4].

Neglecting the second term and for $A = 3285.1 \text{ cm}^{-1} \text{ \AA}^{-1}$ we obtain the pressure dependence of frequency as shown in figure 6. Our potential agrees very well with experiment [13]. The Berns-Van der Avoird potential [13] and other potentials [10, 14] as shown in figure 6 give very poor results.

3.6. Evaluation of bulk modulus

The bulk modulus is given by

$$B_m = -V(\partial p/\partial V)_T.$$

This can be obtained from the curve fitting calculated before; the pressure is

$$p = \sum_n \frac{na_n}{V^{n+1}}$$

and therefore the bulk modulus B_m is

$$B_m = \sum_n \frac{n(n+1)a_n}{V^{n+1}} = \frac{6A}{V^3} + \frac{12B}{V^4} + \frac{20C}{V^5} + \frac{30D}{V^6}.$$

From this relation the bulk modulus at any molar volume can be obtained and hence the pressure dependence of the zero-absolute-temperature compressibility for N_2 can be estimated.

4. Discussion and conclusions

The quality of the results for $\Delta\nu$ depends on the quality of intermolecular potential that characterize the solid. The intramolecular interaction can be described by the properties of an isolated molecule. The crystal field is then assumed to act as a small perturbation on internal modes. An atom-atom 6-12 potential has been used to investigate the pressure dependence of intramolecular mode frequencies in solid nitrogen. Using this potential the sublimation energy is calculated and is in good agreement with experiment. Our results have been calculated at zero temperature using the appropriate $T = 0$ K crystal structures. We see also that different crystal structures do not seriously change the pressure dependence of the intramolecular vibrational modes at low pressures. The results of this work indicate that the low-pressure model of compressed molecular solids, discussed earlier, is correct. The good agreement with experiment implies that no substantial charge transfer is occurring; this demonstrates that charge transfer is not responsible for the fact that $d\nu(p)/dp$ becomes a decreasing positive quantity in solid N_2 .

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