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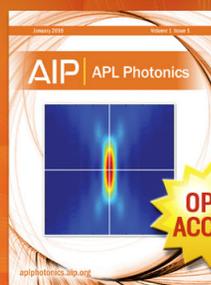
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Calculation of structural properties and vibrational frequencies of α - and γ -N₂ crystals

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The effects of the zero-point energy, residual forces and torques on the molecules, and molar density, on the calculated lattice frequencies and structural properties of solid α - and γ -N₂, are investigated. An intramolecular potential and a parametrized 12-6 atom-atom intermolecular potential are used to calculate lattice modes, intramolecular modes, sublimation energy, equilibrium unit cell parameters, Grüneisen coefficients, and P - V data. The second virial coefficient is also reasonably reproduced. The α -to- γ phase transition is not revealed by the employed intermolecular potential.

I. INTRODUCTION

Lattice dynamics studies of atomic and molecular solids make use of one of two approaches: (a) the F-G method^{1,2} and various shell models^{3,4} which use a parametric form to construct the force constant matrix and (b) the potential approach⁵⁻¹² which constructs the dynamical matrix from an explicit analytical form of the interaction potential. Only those physical properties which are determined by the second derivative of the potential with respect to atomic or molecular displacements (force constants), such as lattice frequencies, Grüneisen coefficients, vibrational heat capacity, etc. may be reproduced by employing a parametric form for the force constant matrix. The unit cell dimensions and the position of atoms inside the unit cell used by the parametric approaches to construct the dynamical matrix are assumed and not derived self-consistently from the employed model. On the other hand, the potential approach is capable also of predicting properties that are explicitly determined by the potential itself or its first derivatives, such as unit cell parameters (a , b , c , α , β , and γ), atomic positions, cohesion energy, P - V data, etc.

Lattice dynamics investigations of molecular solids have recently assumed a renewed interest due to the accumulation of extensive experimental data on both first and second derivatives dependent properties. Potential approach calculations on structural and dynamical properties of molecular solids have recently been carried out on simple molecular solids such as H₂,^{13a} OCS,^{13b} CO₂,^{12,14,15} N₂⁵⁻¹² and on more complicated organic crystals such as naphthalene and anthracene,¹⁶ paraffins,¹⁷ and pyrazine.¹⁸ In this paper we present the results of a potential approach calculation of lattice dynamics and related properties of α and γ nitrogen. The approximations usually assumed in previous potential approach calculations are first critically examined. These approximations are: (a) the neglect of zero-point effects in the determination of the equilibrium crystal structure, (b) the calculation of the dynamical matrix without completely relaxing the forces and torques on the molecules, and (c) the neglect of effects introduced by truncating

the lattice sums, on the calculated lattice frequencies and unit cell parameters. A detailed examination shows that these approximations may significantly influence the calculated results and that the basis on which proposed potentials have previously been accepted may be unjustified.

The elaborations presented here are used to suggest and test a refined potential for crystalline N₂. The experimental data used to test this potential are:

- (1) Raman^{19,20} and infrared^{11,21} lattice mode frequencies of α -N₂ and Raman²² frequencies of γ -N₂.
- (2) The intramolecular modes of α -N₂²³ and γ -N₂.²²
- (3) The Grüneisen coefficients of the optical modes of α -N₂²⁴ and γ -N₂.²⁵
- (4) The unit cell parameters of α -N₂²⁶ and γ -N₂.²⁷
- (5) The equilibrium position, at a given external pressure, of the atoms in the unit cell of α -N₂²⁶ and γ -N₂.²⁷
- (6) The low temperature isotherm of α -N₂.²⁸
- (7) The crystal cohesion energy of α -N₂.^{29,30}
- (8) The virial coefficient of N₂ gas.^{31,32}

Isotopic ¹⁴N/¹⁵N effects on structural and dynamical properties are also discussed.

Previous potential approach calculations (performed only on the α phase) employed one of the following forms of the potential:

- (1) Pure quadrupole-quadrupole (Q-Q) interaction. This was used by Goodings and Henkelman,⁷ Jacobi and Schnepf,⁸ and Raich⁹ to compute the librational frequencies. It was shown to represent the anisotropic forces in solid nitrogen reasonably well but since the Q-Q interaction forms only a small fraction^{7,33} of the total interaction potential, it is inadequate for computing the crystal cohesion energy. Also, since this potential lacks isotropic contributions, it cannot be used to reproduce translational lattice modes, crystal pressure, and equilibrium unit cell parameters, satisfactorily. Grüneisen coefficients are also poorly reproduced with this poten-

tial.²⁴

(2) Q-Q potential plus spherical (dumbbell model) Lennard-Jones 12-6 potential. This potential reproduces well the translational lattice modes¹¹ but fails to reproduce the librational modes unless the quadrupole moment is treated as an adjustable variable.¹⁹ The anisotropy of both the short-range repulsion and the long-range dispersion is not adequately represented by this potential.

(3) Q-Q potential plus parametric short-range repulsion plus dipole-dipole dispersive attraction.^{7,33} This potential, depending on four parameters, is physically very reasonable but has failed to reproduce lattice librations when gas phase data were used to adjust the parameters.

(4) Atom-atom anisotropic potential. This has been used by Donkersloot and Walmsley,⁵ Kuan, Warshel, and Schnepf,⁶ Jacobi and Schnepf,¹² and Ron and Schnepf¹⁰ to compute both structural and dynamical properties of α -N₂ and has so far yielded the best agreement with experiment. This potential form will consequently be used in this paper both for examining methods of calculation and for computing structural and dynamical properties.

In Sec. II of this paper the computational scheme employed will be presented. In Sec. III we examine some of the related approximations commonly used in the literature. Sections IV and V present the results obtained with our derived potential for α and γ nitrogen.

II. METHOD OF CALCULATION

The Born-Oppenheimer (B-O) surface for the ground electronic state of a molecular solid is a multidimensional function of the position vectors of the atoms in the unit cell ($\mathbf{r}_{s,t,l}$), where s runs over the molecules in the unit cell ($s = 1, 2, \dots, \sigma$), t runs over the different atoms in a molecule ($t = 1, 2, \dots, \tau$), and l indexes the unit cells ($l = 1, 2, \dots, N$). It is convenient to express the B-O surface as the sum of intermolecular (U_{inter}) and intramolecular (U_{intra}) potentials.

$$U(\{\mathbf{r}_{s,t,l}\}) = U_{\text{inter}} + U_{\text{intra}}. \quad (1)$$

If an atom-atom distance-dependent potential is adopted to express the intermolecular interactions, U_{inter} is given by

$$U_{\text{inter}} = \frac{1}{2\sigma} \sum_{s \neq s'} \sum_{t, t'} V_{\text{inter}}(D_{st',s't'}^{0,0}), \quad (2)$$

where $D_{st',s't'}^{0,0}$ is the distance between the atom t in the s molecule located in a central unit cell ($l = 0$) and atom t' in molecule s' ($t \neq t'$ if $s = s'$ and $l' = 0$) at the unit cell l' . U_{inter} is the interaction potential between atoms which belong to different molecules. The reference level for U_{inter} is infinite intermolecular separation. U_{intra} is given by

$$U_{\text{intra}} = \frac{1}{\sigma} \sum_{s=1}^{\sigma} V_s, \quad (3)$$

where

$$V_s = \sum_{t=1}^{\tau} \sum_{t'=1}^{\tau} V_{\text{intra}}(d_{s,t,t'}) \quad (4)$$

and

$$d_{s,t,t'} \equiv D_{st',st'}^{0,0},$$

where $d_{s,t,t'}$ is the intramolecular interatomic distance. The reference level for the intramolecular potential V_s is the ground electronic state of the isolated molecule at equilibrium. V_s determines the intramolecular vibrations of an isolated molecule. The crystal field U_{inter} may cause the removal of degeneracy in the intramolecular modes (site splitting), the coupling of the vibrations of the σ molecules in the unit cell (Davydov splitting), and also induce the infrared or Raman activity of normal modes.

In its most general form $U(\{\mathbf{r}_{s,t,l}\})$ depends on the translations and rotations of all the molecules in the unit cell, their internal conformation (in the case of a diatomic molecule this is reduced to the bond length), and the unit cell parameters a, b, c, α, β and γ ($3\sigma\tau + 6$ degrees of freedom in all). The treatment of the dynamics of molecular solids can be considerably simplified if, instead of introducing translational, rotational, and internal coordinates, the dynamical matrix is expressed as derivatives of the potential with respect to $3\sigma\tau$ atomic Cartesian coordinates $\{\mathbf{r}_k, k = 1 \dots \sigma\tau\}$.^{17,34} In this representation, the dynamical treatment can be simplified because the kinetic-energy matrix is given in the Cartesian system of coordinates as a simple function of atomic masses. The extra 6 degrees of freedom are the independent components of the lattice vectors $\{\mathbf{R}_p, p = 1 \dots 6\}$. The sets of $\{\mathbf{r}_k\}$ and $\{\mathbf{R}_p\}$ form a $(3\sigma\tau + 6)$ dimensional vector which will be denoted $\{\mathbf{p}\}$.

We now define the procedure of calculating the crystal unit cell parameters, lattice frequencies, crystal cohesive energy and atomic positions within the unit cell as a function of volume, as well as the method of calculating the crystal pressure and Grüneisen coefficients.

An initial crystal configuration is generated by assuming a set of unit cell parameters (a, b, c and α, β, γ) and the positions of the atoms in one reference molecule. The other molecules in the central unit cell are generated by applying factor group operations to the first molecule. The whole crystal is then generated by translations of the central unit cell.

Since the interaction potential $U(\{\mathbf{r}_{s,t,l}\})$ is usually anharmonic, the dynamical force constants matrix depends on the configuration of the atoms in the solid. For any given external hydrostatic pressure, the dynamics should be computed at the equilibrium positions of all atoms and unit cell parameters. At $T = 0^\circ$ this reduces to finding the minimum of the crystal internal energy

$$U_{\text{tot}} = U_{\text{stat}} + U_{\text{dyn}} \equiv (U_{\text{intra}} + U_{\text{inter}}) + U_{\text{dyn}} \quad (5)$$

as a function of the $3\sigma\tau + 6$ degrees of freedom. Here $(U_{\text{intra}} + U_{\text{inter}})$ [Eqs. (1)-(4)] is the static internal energy U_{stat} , while U_{dyn} is the excess zero-point energy (ZPE) in the solid, relative to the free molecule. It is given by the sum of $U_{\text{dyn}}^{\text{inter}}$ and $U_{\text{dyn}}^{\text{intra}}$ where (for a linear molecule)

$$U_{\text{dyn}}^{\text{inter}} = \frac{5}{2} \int_0^\infty G(\omega) \omega \, d\omega, \quad (6)$$

where $G(\omega)$ is the lattice frequency distribution, normalized to unity, and

$$U_{\text{dyn}}^{\text{intr}} = \frac{1}{2} \left[\int_0^\infty g(\omega) \omega d\omega - \sum_i \omega_i^0 \right]. \quad (7)$$

Here $g(\omega)$ is the distribution function of intramolecular modes and ω_i^0 is the free molecule vibrational frequencies of mode i .

The minimization procedure is performed in several steps:

(1) We first require that the net force on each atom will vanish and that the condition of uniform stress on the unit cell at static equilibrium is established at any given volume V . The first condition is achieved by solving the set of equations:

$$\nabla_{\mathbf{r}_k} U_{\text{stat}}(V) = 0 \quad k = 1, 2, \dots, \sigma\tau. \quad (8)$$

The second condition implies the diagonalization of the stress matrix

$$\begin{pmatrix} X_x & X_y & X_z \\ X_y & Y_y & Y_z \\ X_z & Y_z & Z_z \end{pmatrix} \quad (9)$$

at a given volume. The capital letter of the stress component indicates the direction of the force and the subscript indicates the normal to the plane to which this force is applied. The corresponding forces are related to derivatives of the static interaction energy $U_{\text{stat}}(V)$ with respect to the unit cell degrees of freedom and are given by $\nabla_{R_p} U_{\text{stat}}$.

To solve these equations, we employ the first derivative minimization steepest-descent method and the second derivative Newton-Raphson method.³⁵ The required derivatives are analytically computed from the chosen form of the interaction potentials. The summation in Eq. (2) is extended to 20 shells of interacting molecules. It should be stressed that we do not assume orthogonality ($\alpha = \beta = \gamma = 90^\circ$) of the unit cell axis or equality of some unit cell axes (e. g., $a = b = c$ or $a = b$). The iteration procedure is terminated when the difference between two derivatives in successive iterations does not exceed a required tolerance (usually 10^{-15} kcal/Å). The minimization of the stress components is performed for a range of unit cell volumes. At the termination of the minimization process of Eqs. (8) and (9) we calculate:

(i) The set of atomic coordinates for a given unit cell volume at static equilibrium $\{\mathbf{r}_k^{\text{eq}}\}$.

(ii) The static crystal interaction energy at static equilibrium positions of all atoms and unit cell variables for volume V , $U_{\text{stat}}^{\text{eq}}(V)$.

(iii) The static pressure $P_{\text{stat}}(V)$ at a given volume (from the numerical derivatives of the static energy).

(2) After the configuration of the minimum static energy has been reached for a given volume, the lattice frequencies $\omega_i(\mathbf{q})$ are computed for this configuration throughout a finite mesh of wavevector points in the Brillouin zone (BZ), by solving the secular equation

$$|\mathbf{F}(\mathbf{q}) - 4\pi^2\omega^2(\mathbf{q})\mathbf{M}| = 0. \quad (10)$$

Here $\mathbf{F}(\mathbf{q})$ is the $3\sigma\tau \times 3\sigma\tau$ dynamical matrix expressed by the second derivatives of $U_{\text{stat}}^{\text{eq}}(V)$ with respect to the dynamic variables $\{\mathbf{r}_k\}$ and evaluated at their equilibrium values $\{\mathbf{r}_k^{\text{eq}}\}$. \mathbf{M} is a diagonal matrix whose elements are the atomic masses of the atoms in the unit cell (in atomic units). From the dynamical calculation as a function of volume, we compute:

(i) The ZPE as a function of volume $U_{\text{ZPE}}(V) = U_{\text{dyn}}^{\text{intr}} + U_{\text{dyn}}^{\text{intr}}$ from Eqs. (6) and (7).

(ii) The dynamical contribution to the pressure $P_{\text{dyn}}(V)$ by numerically differentiating the zero-point energy with respect to volume.

Combining these results with the results of the previous step, we obtain both the calculated total crystal energy $U_{\text{tot}}(V)$ according to Eq. (5) and the calculated total pressure $P_{\text{tot}} = P_{\text{stat}}(V) + P_{\text{dyn}}(V)$ for a series of volumes corresponding to a series of different crystal configurations. The calculated frequencies at various volumes in the $\mathbf{q} = 0$ states are used to compute numerically the optical Grüneisen coefficients

$$\Gamma_i(\mathbf{q} = 0) = -d \ln \omega_i(\mathbf{q} = 0) / d \ln V \quad (11)$$

for the $5\sigma - 3$ optical lattice modes. Sufficiently small increments in V are considered and the standard error introduced by deviations from linearity of Γ_i at the volume range considered, is smaller than 0.05.

(3) We next turn our attention to the calculation of lattice parameters, atomic position coordinates, and lattice frequencies, which will be compared with experiment. For phases that are stable at zero pressure, we search for the volume for which our calculated total pressure satisfies: $P_{\text{tot}}(V) = 0$. The unit cell volume $V_{\text{eq}}(P_{\text{tot}} = 0)$ which satisfies this condition is taken to be the equilibrium zeropressure volume for this phase. The lattice parameters corresponding to this volume are computed from:

$$\nabla_{R_p} \{U_{\text{stat}} + U_{\text{dyn}}\}_{V=V_{\text{eq}}} = 0 \quad (12)$$

and compared with experiment.

For phases that are stable only at high pressures we require the calculated $P_{\text{tot}}(V)$ to satisfy the equation

$$P_{\text{tot}}(V) = P_{\text{exp}}(V), \quad (13)$$

where $P_{\text{exp}}(V)$ is the experimental pressure under which the desired property was measured (e. g., The unit cell parameters of γ -N₂ were measured under $P_{\text{exp}} = 4015 \pm 145$ atm²⁷ and the Raman spectrum was observed at $P_{\text{exp}} = 4500$ atm²²). This yields $V_{\text{eq}}(P_{\text{tot}} = P_{\text{exp}})$ and the lattice parameters $\{R_p, p = 1 \dots 6\}$ corresponding to this volume. The lattice parameters and lattice frequencies thus obtained are compared with experimental data.

The interaction potential employed in the calculation must yield the correct crystal class (e. g., $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ for α -N₂) within a tolerance of 0.01 Å and 0.5°. If it does not, the potential is rejected.

(4) For the unit cell configurations corresponding to the zero pressure phase and to the experimental pressure under which the lattice frequencies of the high pressure phase were measured, we minimize the energy with

respect to the atomic position coordinates:

$$\nabla_{\mathbf{r}_k} [U_{\text{stat}}(V_{0q}) + U_{\text{dyn}}(V_{0q})] = 0 \quad (14)$$

obtaining the set of equilibrium dynamical variables $\{\mathbf{r}_k\}$ at a given external pressure. At these configurations the lattice dynamics [Eq. (10)] of both phases is computed. The resulting frequencies are compared with the experimental results.

From the lattice frequencies evaluated at this step we also compute the ZPE $U_{\text{dyn}}(V_{0q})$ from Eqs. (6) and (7) and the static interaction energy $U_{\text{stat}}(V_{0q})$. The sum of these energies is compared with the cohesive energy found experimentally.

The final atomic positions computed from Eq. (14) are compared with those measured crystallographically at the corresponding pressure.

It should be mentioned that at this step we neglected the indirect effect of the zero-point energy on the dynamical matrix. The latter was calculated from second derivatives of the *static* energy (evaluated at the static + dynamic equilibrium) and not of the *total energy*. This neglect of self-consistent phonon treatment³⁶⁻³⁸ does not cause serious errors in our case since it was verified that:

$$\frac{\partial^2 U_{\text{ZPE}}(V_{0q})}{\partial \mathbf{r}_k \partial \mathbf{r}_k} \ll \frac{\partial^2 U_{\text{stat}}(V_{0q})}{\partial \mathbf{r}_k \partial \mathbf{r}_k}. \quad (15)$$

On the other hand, the first derivatives of U_{ZPE} with respect to the unit cell vectors $\partial U_{\text{ZPE}}/\partial R_p$ are not negligible compared with the corresponding first derivative of the static energy $\partial U_{\text{stat}}/\partial R_p$ and therefore it is important to include zero-point effects when determining equilibrium unit cell parameters. The effect of $\partial U_{\text{ZPE}}/\partial R_p$ on the equilibrium unit cell parameters is composed of contributions both from intramolecular and intermolecular vibrations, the former being of importance only in molecular crystals made up of large molecules.

The zero-point energy has an important direct effect on the lattice frequencies since these change very significantly (see below) when they are computed at the minimum of U_{stat} (steps 1 and 2) instead of at the minimum of the total energy (step 4).

Recent computations^{9,8,39} examining the effects introduced by quantum lattice dynamics, suggest that the deviation of lattice frequencies calculated by classic dynamics is within 10%. Deviations from nonadditivity of pair forces in an isotropic solid were shown not to exceed 1%.⁴⁰ Multipole expansion of anisotropic potentials at large distances⁴¹ indicate that three center terms account for 10% of the corresponding contributions of the isotropic potential. Thus nonadditivity errors are expected not to exceed 1%. Our results are, therefore, to be considered within these limits of accuracy.

In previous computations of lattice dynamics and structural properties of molecular solids, one or more of the following approximations were usually adopted:

(i) The lattice dynamics were computed at values of unit cell parameters which minimize U_{stat} (step 2)^{5,6,12} and not U_{tot} (step 4).

(ii) The dynamics were computed without relaxing the forces and torques on the molecules [as in step 4, Eq. (14)] but rather at fixed positions of the atoms in the unit cell (usually the experimental).⁵ The atomic positions employed for the dynamical calculation are thus not consistent with the employed potential function. Since this potential is anharmonic, the resulting frequencies could be affected by this approximation.

(iii) The interaction radius (number of neighboring shells) used to minimize U_{stat} (step 1) with respect to unit cell parameters, was taken to be relatively small.¹²

The influence of these approximations on the lattice frequencies and equilibrium structure, will be examined in the following section.

During the computational work, it was found that the computing time could be considerably shortened without a significant loss in accuracy, if instead of solving the dynamical equation [Eq. (10)] for many points in the BZ [for computing $U_{\text{dyn}}(V)$], we solve only for $\mathbf{q} = 0$. The Einstein model is then adopted for the $5\sigma - 3$ optical modes [considering each optical branch i as an Einstein oscillator with different frequency $\omega_i(\mathbf{q} = 0)$ evaluated at $\mathbf{q} = 0$], and a Debye model is adopted for the 3 acoustical modes, employing an acoustical Debye frequency, equal to the lowest optical frequency at $\mathbf{q} = 0$

$$U_{\text{ZPE}}(\text{app}) = \frac{1}{2\sigma} \sum_{i=1}^{5\sigma-3} h\omega_i(\mathbf{q} = 0) + E_{\text{ZPE}}^{\text{Debye}}[\omega_i(\mathbf{q} = 0)], \quad (16)$$

where $\omega_i(\mathbf{q} = 0)$ are the optical frequencies and $\omega_1(\mathbf{q} = 0)$ is the lowest one. When U_{ZPE} was computed according to Eqs. (6) and (7) with a gross mesh of $30\mathbf{q}$ points along each principle direction, it was found that

$$|U_{\text{ZPE}}(\text{app}) - U_{\text{ZPE}}|/U_{\text{ZPE}} \quad (17)$$

did not exceed 5% for any volume examined. This is about 1% of the total energy and thus within the accuracy limit of our theoretical approach. Consequently, the calculations of Sec. III examining previous approximations are performed using the above-mentioned approximation, while in Secs. IV and V the ZPE was calculated according to Eqs. (6) and (7).

The interaction pair potential chosen in this work is of the form:

$$V_{\text{inter}}(D_{st,rs,t'}) = \epsilon \left| \left(\frac{\sigma}{D_{st,rs,t'}} \right)^{12} - \left(\frac{\sigma}{D_{st,rs,t'}} \right)^6 \right|, \quad (18)$$

where σ and ϵ are two adjustable parameters and $D_{st,rs,t'}$ is the nonbonded interatomic distance. It should be mentioned that the choice of power 12 to express the repulsive part of the potential has no theoretical justification but is customary in these studies. As a matter of fact, other powers from 7 to 14 are being considered with the aim of elucidating their effects on pressure-dependent properties (Grüneisen coefficients, P - V data, α -to- γ phase transition, etc.).

For the intramolecular part of the potential we chose either a simple harmonic potential:

$$V_{\text{intra}} = \frac{1}{2} K(b - b_0)^2, \quad (19)$$

where K and b_0 are parameters determining the funda-

mental frequency and molecular bond length of the isolated molecule, or a more complex form taken from R-K-R fittings of the full vibrational frequencies of N₂⁴²:

$$U_{\text{int ra}} = D_i \{ [1 - (b_0/b)] (e^{-\beta(b-b_0)^p} - e^{-\beta(b_0-b)^p}) \}^2, \quad (20)$$

where D_i is the dissociation energy and β and p are adjusted parameters.

III. CRITICAL EXAMINATION OF APPROXIMATIONS

One of the purposes of calculating static and dynamical properties of molecular crystals is to arrive at a set of potential functions and parameters which adequately reproduce the experimental data and which can thus be used to predict other properties. Some of the approximations that have usually been adopted in these calculations (see last section) can lead to the choice of a parametric potential which yields a poor fit to experimental results if the above mentioned approximations are not made. Accepting various of the previously suggested atom-atom potentials for α -N₂ we investigate in this section the effect introduced by each approximation.

A. Zero-point effects

The calculation of Jacobi and Schnepf¹² employing their 12-6 potential (JS-I, see Table I) has been repeated for a series of different unit cell volumes. The consequences of neglecting zero-point effects in their calculation on lattice equilibrium, conformation, and frequencies were investigated by performing the calculations both at the minimum of the static energy (steps 1-2, in Sec. II) and the minimum of the total energy (steps 1-4). Figure 1 shows the dependence of both the static and the total energy at the equilibrium position of the atoms as a function of volume per molecule. It can be seen that due to the anharmonic character of the intermolecular interaction the effect of the zero-point energy is to shift the equilibrium volume to considerably higher values. The calculated sublimation energy, unit cell parameters and lattice mode frequencies at the minimum of the total energy, are given in Table II, where they are compared to the experimental results as well as to the calculated properties at the static minimum. The sublimation energy in the "static energy minimum" column in Table II was computed by adding the static and the dynamic contributions at the static equilibrium unit cell volume instead of the minimum of total energy (column 4). It is

TABLE I. Parameters for the 12-6 potential employed in different studies.

Authors	ϵ^a (kcal/mole)	σ (Å)	b_0 (Å)
Jacobi and Schnepf ¹² (JS-I)	0.264	3.406	1.030
Jacobi and Schnepf ¹² (JS-II)	0.377	3.319	1.038
Kuan, Warshel, and Schnepf ⁶ (KWS)	0.295	3.346	1.098
Donkersloot and Walmsley ⁵ (DW)	0.265	3.385	1.098
Present work	0.310	3.300	1.098

^a ϵ and σ are the parameters defined in Eq. (18). b_0 is the effective bond length of the N₂ molecule used in the calculations.

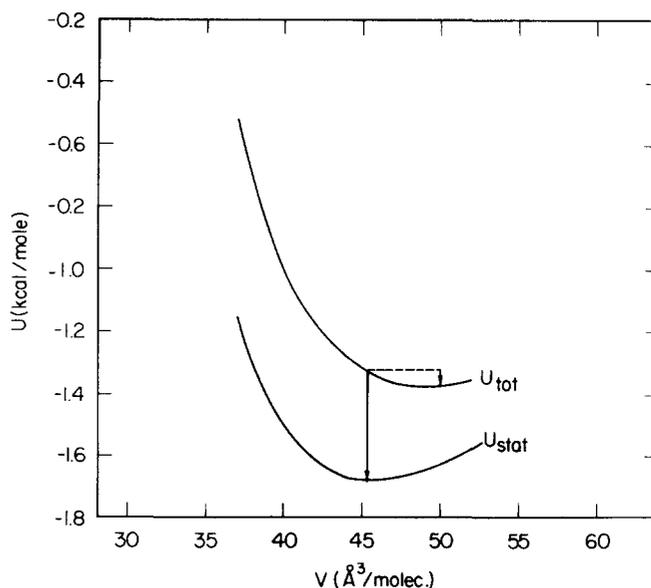


FIG. 1. Total energy U_{tot} [Eq. (5)] and static energy U_{stat} [Eqs. (2)-(4)] of α -N₂ as calculated with the potential of Jacobi and Schnepf¹² (JS-I, Table I). The minimum in the corresponding curves is indicated by arrows.

evident from the table that the agreement with experiment becomes considerably worse when the calculation is carried out at the dynamical minimum yielded by the employed potential.

A similar check was performed on the potential proposed by Kuan, Warshel, and Schnepf⁶ (KWS in Table I) and the results indicate a similar trend. The equilibrium unit cell parameters are increased from 5.62 to 5.86 Å. This has a marked influence on the calculated lattice frequencies, lowering them by an average of 14 cm⁻¹.

An increase in the calculated unit cell dimensions introduced by the vibrational energy through zero-point effects has also been noted in the study of paraffins¹⁷ and the rare gas solids.^{5,43} In the latter, however, because of the lack of librational contributions and the smaller number of translational branches, this increase is smaller.

TABLE II. Results obtained with the Jacobi and Schnepf potential (JS-I in Table I) at the minimum of the static energy (column 2) or of the total energy (column 4), compared with experimental results.

Property	Static energy minimum	Experimental	Total energy minimum
Sublimation energy (kcal/mole)	1.524	1.655 ^a	1.3517
a_{ex} (Å)	5.664	5.644 ^b	5.848
Lattice frequencies (cm ⁻¹):			
A_u	42.26	Inactive	34.04
E_u	54.61	Inactive	39.98
$T_u(Q_2)$	48.29	48.8 ^c	35.45
$T_u(Q_1)$	74.08	70.0 ^c	53.12
E_f	35.48	31.5 ^d	26.53
$T_f(Q_2)$	49.87	60.0 ^e	36.61
$T_f(Q_1)$	39.86	36.0 ^e	29.61

^aReference 29, 30.

^bReference 26.

^cReference 21, 11.

^dReference 20.

^eReference 19.

It should be mentioned that in solids composed of large molecules, the zero-point energy is a relatively small fraction of the total interaction energy and therefore its exact calculation is not essential to the evaluation of the sublimation energy. However, even in this case the ZPE seems to be important in the determination of the equilibrium unit cell parameters. Its effect should be considered if equilibrium lattice dynamics calculations are to be performed at molar volumes which are consistent with the employed potential.

B. Residual forces and torques

In crystals with more than one atom in the unit cell, it is not sufficient to arrive at the minimum of the crystal energy with respect to the unit cell parameters [Eq. (9)]; also, forces and torques on the molecules should be relaxed [Eqs. (8) and (14)]. This implies that it is necessary to minimize the energy with respect to translations and rotations of the molecules in the unit cell, or equivalently in our computational scheme, to minimize the crystal energy with respect to the $3\sigma\tau$ Cartesian coordinates of all the atoms in the unit cell. Even though the relaxation of forces and torques is usually accomplished by extremely small changes in the positions of the molecules, the effects on the dynamical matrix, and thus on the calculated frequencies, are of major importance when the potential is strongly anharmonic. To demonstrate this point we repeated the calculation of Donkersloot and Walmsley⁵ on the normal modes of α -N₂ at zero pressure, with their 12-6 atom-atom potential (DW, see Table I), under different "stress" conditions on the molecules. The results are shown in Table III. In column 2, we present the results obtained after completely minimizing the lattice sum as a function of the six unit cell parameters and the $3\sigma\tau$ positional coordinates (step 1 in Sec. II). Column 3 presents the results obtained when only the unit cell parameters were used as minimization variables [Eq. (9)], as performed with our program, and column 4 presents the authors' results.

Both types of calculations have been carried out with our 12-6 potential also (see Sec. IV) and the results are presented in Table III, columns 6, 7 for α -N₂ and in Table IV for two different unit cell volumes of γ -N₂.

From Tables III and IV it can be seen that relaxation of forces and torques on the molecules causes a slight shift in the translational mode frequencies and a much stronger decrease in the librational modes. At larger unit cell volumes the effect is less pronounced since the residual forces and torques are smaller. This implies that in calculating volume dependent dynamical properties and internal energy as a function of volume for different phases, an appropriate energy minimization must be performed.

The relaxation of forces and torques on the molecules is not as important in the study of lattice dynamics of metals and heavy ionic solids since they do not exhibit librational modes and their translational frequencies should be affected only slightly due to the heavy masses of the atoms involved.

C. Interaction radius

It has been shown previously⁴⁴ that the calculated lattice frequencies of benzene are already at their convergence limit if the lattice sums are extended up to an interatomic distance of 5 Å. This behavior characteristic of the relatively short range interaction of Van der Waals molecular solids, is also obtained for α -N₂ (Fig. 2). In cases where long range interactions may be important (as in molecular ions or in noncentrosymmetric molecules) more sophisticated methods for performing the lattice sum may be required.^{44b} The frequencies were calculated as a function of the radius of interaction with the Jacobi and Schnepf "one-shell" potential,¹² (JS-II, see Table I), which was selected by these authors to yield a good fit to experimental data through a dynamical calculation, including the interactions up to only one molecular shell. The calculations presented in Fig. 2

TABLE III. Comparison of α -N₂ lattice frequencies at $q=0$ as calculated with complete Cartesian coordinates minimization [Eq. (8)] (column 2) and without relaxing forces and torques on the molecules in the unit cell (column 3). The results of Donkersloot and Walmsley⁵ (column 4) and experimental results (reference for experimental data in Table II) are also given. The calculations are performed with the DW (Table I) potential at unit cell constants which yield a minimum to the static energy. The second part of the table shows similar results obtained with the 12-6 potential of the present work at unit cell parameters dimensions at which the total crystal energy is at the minimum.

Frequency (cm ⁻¹)	DW potential ⁵ ($\alpha = 5.66$ Å)		Ref. 5	Experimental	12-6 potential of this work ($\alpha = 5.63$ Å)	
	Complete minimization (this work)	No relaxation of forces and torques (this work)			Complete minimization	No relaxation of forces and torques
Translations						
A_u	45.9	48.9	49	Inactive	43.7	43.7
E_u	54.5	57.3	58	Inactive	51.8	51.8
$T_u(Q_2)$	49.2	51.4	52	48.8	47.0	46.7
$T_u(Q_1)$	73.3	77.1	77	70.0	69.5	69.0
Librations						
E_g	35.9	49.0	49	31.5	34.5	43.7
$T_g(Q_2)$	49.3	60.8	61	60.0	47.5	54.2
$T_g(Q_1)$	40.4	53.5	53	36.0	38.5	47.2

TABLE IV. Comparison between γ -N₂ calculated lattice frequencies with and without relaxation of forces and torques on the molecules for two molar volumes employing the 12-6 potential of this work. Experimental data for $V=39.4 \text{ \AA}^3/\text{molecule}$ from Medina and Daniels.²²

Frequency (cm ⁻¹)	$V=39.4 \text{ \AA}^3/\text{mol.}$		Exptl. $V=39.4$ $\text{\AA}^3/\text{mol.}$	$V=43.8 \text{ \AA}^3/\text{mol.}$	
	No relaxation of forces and torques	Complete minimization		No relaxation of forces and torques	Complete minimization
Translations					
B_{1u}	110.4	110.4	Inactive	78.3	78.3
E_u	66.1	66.1	...	47.8	47.8
Librations					
A_{2g}	102.4	91.0	Inactive	72.8	65.1
B_{1g}	114.4	107.3	103.6	81.2	74.4
E_g	72.6	55.4	58.4	51.9	40.5

were performed at a fixed value of the unit cell parameters ($a=b=c=5.66 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$) corresponding to the structure found experimentally at atmospheric pressure. In the same figure, we present the derivative with respect to the unit cell parameter $\partial U_{\text{stat}}/\partial a$ evaluated at these unit cell dimensions, as a function of the number of shells included in the calculation of U_{stat} [Eqs. (2)–(4)]. It can be seen that although the truncation of the lattice sum at 3–4 shells introduces only small errors in the computed frequencies, the deviation of the unit cell from static equilibrium (given by the value of $\partial U_{\text{stat}}/\partial a$) depends strongly on the interaction radius. This implies that the calculated unit cell parameter, a , corresponding to the static equilibrium at zero pressure (where $\partial U_{\text{stat}}/\partial a=0$) depends appreciably on the interaction radius employed. It is also evident from Fig. 2 that the JS-II potential predicts an increasing instability ($|\partial U_{\text{stat}}/\partial a|$ increasing) of the α structure in its experimental unit cell dimensions when the number of interacting shells is increased. The limiting value of $\partial U_{\text{stat}}/\partial a$ obtained when interactions of up to 40 shells are included, reveals the existence of a force that tends to increase the unit cell parameter a . (A further increase would result from the imposition of the condition of equilibrium for the *total*, rather than *only* static, energy). This variation in the computed value of a_{eq} as a function of interaction radius should also be manifested in the lattice frequencies.

To demonstrate this behavior we solved the dynamical problem with potential JS-II for different interaction radii, evaluating, each time, the dynamical matrix at the volume corresponding to the absolute static minimum ($\partial U_{\text{stat}}/\partial a < 10^{-4} \text{ kcal/\AA}$) for this interaction range. The results of a_{eq} , U_{stat} and the calculated frequencies are presented in Fig. 3. It can be seen that only for a relatively large interaction radius (15–20 shells), the equilibrium unit cell parameters level off and so only then the lattice frequencies and lattice energy level off. Comparing Figs. 2 and 3, it can be seen that the relative order of the T_g and T_u lattice frequencies is changed depending upon whether calculations are done at equilibrium (Fig. 3) or nonequilibrium (Fig. 2) for the same interaction radius. Moreover, the relative order of the lattice modes depends on the interaction radius even if the calculations are done at equilibrium (see crossing of T_g and T_u modes in Fig. 3). The effect of the interac-

tion radius on the equilibrium static energy, U_{stat} , is pronounced, and only at a large interaction radius (~ 20 shells) U_{stat} reaches convergence. This factor must be considered when investigating volume dependence of total crystal energies of various phases in a search for possible phase transitions.^{45,46}

VI. RESULTS

Taking into account the considerations discussed in the last section, we searched for the 12-6 atom-atom potential that would best fit the available experimental data on α -N₂, cited in Sec. I. This includes the lattice parameters, cohesive energy, ir and Raman lattice fre-

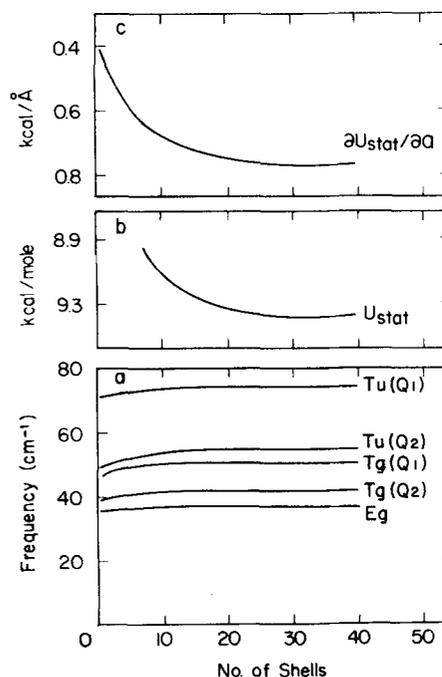


FIG. 2. The dependence of lattice mode frequencies (a), static energy U_{stat} (b), the derivative of static energy with respect to unit cell parameter $\partial U_{\text{stat}}/\partial a$ (c), on the number of employed interacting molecular shells. The potential used for these calculations was the potential JS-II (Table I) of Jacobi and Schnepf¹² used by these authors to compute lattice properties in a 1-shell approximation. The values are computed at constant unit cell dimensions $a=b=c=5.66 \text{ \AA}$ as was done by these authors in their calculation.

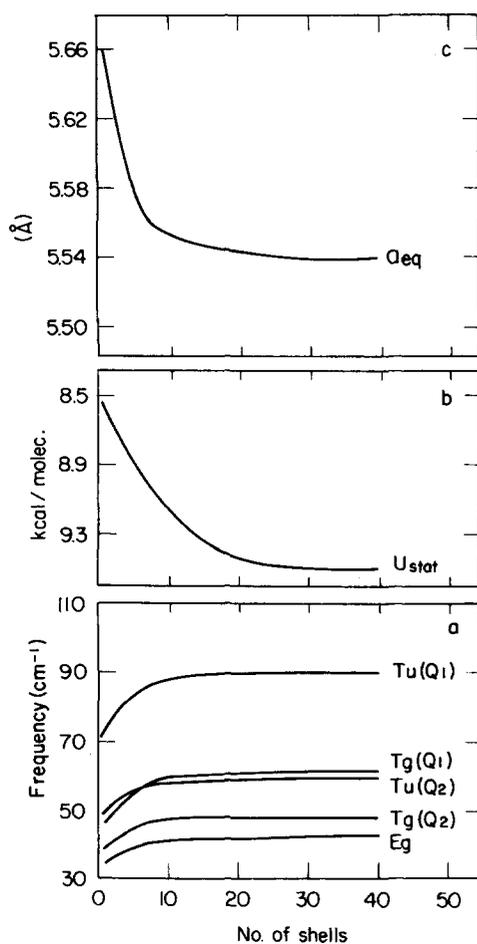


FIG. 3. Dependence of lattice mode frequencies (a), static energy U_{stat} (b), and equilibrium lattice constant (c), on the number of employed interacting molecular shells. The calculation is carried out with potential JS-II (Table I) under conditions of static equilibrium ($\partial U_{\text{stat}}/\partial \rho = 0$) for the given number of interacting shells.

quencies, atomic positions in the unit cell, the intramolecular modes, and also the N-N stretching frequency of the isolated (gas phase) N₂ molecule.

Parameters were changed from run to run by a least squares iteration scheme. Lattice sums were extended to 20 molecular shells thus assuring the stability of the calculated frequency within 0.1 cm⁻¹ and the calculated energies within 0.02 kcal/mole. Each calculation was performed at the lattice equilibrium configuration, keeping $\partial U_{\text{tot}}/\partial R_p < 10^{-6}$ kcal/Å and $\partial U_{\text{tot}}/\partial r_x < 10^{-8}$ kcal/Å. This usually required 5–10 steepest-descent iterations and 2–3 Newton-Raphson iterations. The zero-point energy was obtained by sampling 2160 points in the BZ. The calculations for both α and γ phases were extended over the volume range of 34–65 Å³/molecule. At the convergence of the least squares procedure, the following parameters were obtained for the interatomic potential [Eq. (18)]:

$$\epsilon = 0.310 \text{ kcal/mole}, \quad (21)$$

$$\sigma = 3.300 \text{ Å},$$

and

$$K = 3244.18 \text{ kcal/Å}^2$$

for the harmonic intramolecular potential [Eq. (19)]. The molecular bond length b_0 was not treated as a parameter but set at the experimental N-N bond length of 1.098 Å.⁴⁷ The anharmonic form of V_s suggested by Levine,⁴² Eq. (20), was also used without changing its parameters.

A. α -N₂

The calculated unit cell parameters, sublimation energy, and $q = 0$ lattice mode frequencies of α -N₂ are presented in Table V. The shift in the lattice constant introduced by zero-point effects is 0.132 Å for our potential.

The experimental heat of sublimation was computed by Kelly³⁰ from the experimental data of Giauque and Clayton²⁹ which includes the heat capacity of α -N₂, β -N₂, liquid N₂, and gaseous N₂ as a function of temperature, the α to β transition enthalpy, the β -N₂ fusion enthalpy, and the liquid-gas evaporation enthalpy. Corrections for deviations from ideal gas behavior were introduced by a simple equation of state. We estimate the experimental errors to total approximately 100 cal/mole.

The calculated lattice mode frequencies agree well with experimental Raman and ir results, the largest deviation being from the high $T_g(Q_1)$ mode. A similar discrepancy for this mode, was previously obtained in the calculation of Kuan *et al.*,⁶ Jacobi and Schnepf,¹² and Anderson *et al.*¹⁹ Kuan *et al.* and Jacobi and Schnepf introduced a third adjustable parameter (the effective bond length, b_0) into their potential to overcome this discrepancy and Anderson *et al.* treated the molecular quadrupole moment as an adjustable parameter for the same purpose.

The results for the volume dependence of the pressure at $T = 0^\circ\text{K}$ are shown in Fig. 4 and compared with the

TABLE V. Properties of $Pa3 \alpha$ -N₂ calculated with the 12-6 potential of the present work as compared with experimental data. Calculation carried out through steps 1-4 as indicated in Sec. II.

Property	Calculated	Experimental
Unit cell parameters a, b, c (Å)	$a = b = c = 5.63$	5.644 ^a
Unit cell angles α, β, γ (deg.)	$\alpha = \beta = \gamma = 89.8^\circ$	90° ^a
Sublimation energy (kcal/mole)	1.582	1.655 ^b
Translational modes (cm ⁻¹) ^c		
A_u	43.7	Inactive
E_u	51.8	Inactive
$T_u(Q_1)$	69.5	70.0
$T_u(Q_2)$	47.0	48.8
Librational modes (cm ⁻¹)		
E_g	34.5	31.5
$T_g(Q_1)$	47.5	60.0
$T_g(Q_2)$	38.5	36.0

^aReference 26.

^bReference 29, 30.

^cFor references on the lattice vibrations see Table II.

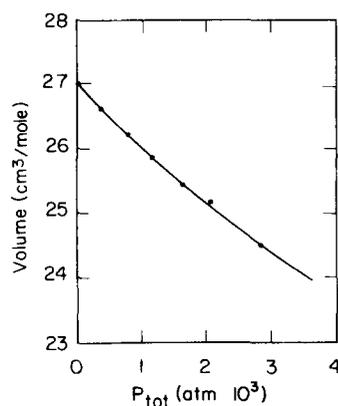


FIG. 4. Calculated and experimental²⁸ isotherm for α -N₂. — Experimental. Calculated.

4.2 °K isotherm measured by Swenson.²⁸ Thermal contributions to the pressure at this temperature were estimated to be smaller than the experimental error and were neglected in the calculation.

The volume dependence of the calculated α -phase lattice mode frequencies is shown in Fig. 5 for a large volume range. From these calculations the Grüneisen coefficients for the $q=0$ modes were computed (Table

VI) in the volume range of 40–55 Å³/molecule. At this range the graph of $d \ln \omega_i$ vs $d \ln V$ was practically linear as can be seen from the small standard deviation to this fit. Around the volume corresponding to the solid α -N₂ to the liquid transition ($V = 57.5$ Å³/mole) the frequency-volume curves of different modes began to cross and this region was excluded from the range where Grüneisen coefficients were computed. The calculated Grüneisen coefficients are compared with the experimental data of Medina and Daniels²⁴ and Thiery *et al.*²⁵ (Table VI). There is probably a large uncertainty in the experimental results due to the use of P - V data²⁵ to establish the "experimental" volume and due to errors in the measured pressure (± 150 atm). However discrepancies between the experimental works^{24,25} are smaller than those between our calculated values and experimental values.

Isotopic effects on lattice parameters and lattice mode frequencies were investigated by repeating the minimization procedure for the total energy of the α phase of ¹⁵N. The lattice parameters a, b, c for this phase were found to be 0.0217 Å smaller than the corresponding parameters in the ¹⁴N α phase. The sublimation energy of the

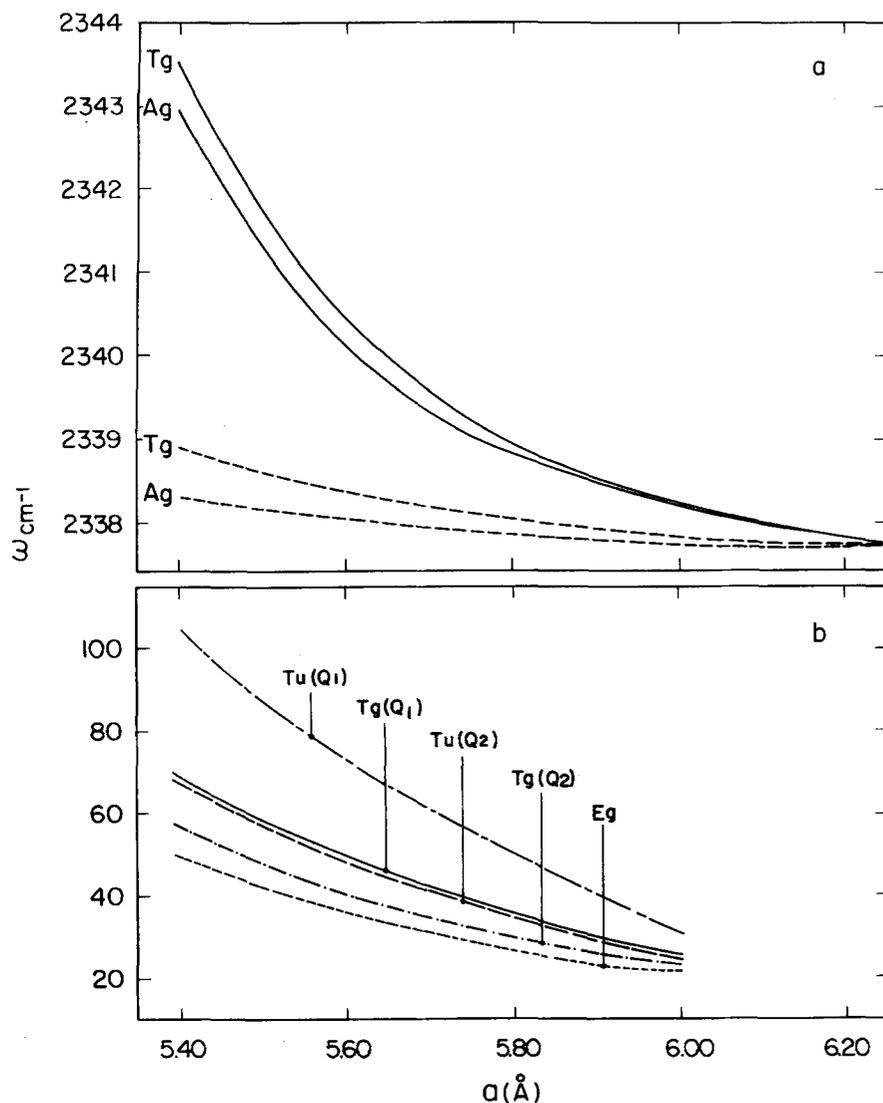


FIG. 5. ir and Raman active frequencies of α -N₂ as a function of unit cell dimension calculated with the 12-6 potential of the present work. (a) Intramolecular frequencies calculated with — anharmonic intramolecular potential [Eq. (20)] with parameters of Levine,⁴² --- Harmonic intramolecular potential [Eq. (19)]. (b) Lattice modes.

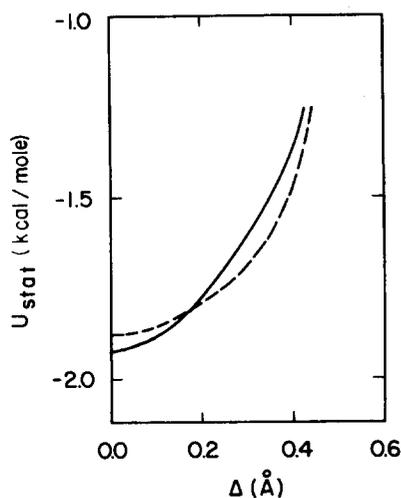


FIG. 6. Crystal energy of the $P2_13$ structure as a function of the displacement Δ of the centers of the molecules along the body diagonals. $\Delta=0$ corresponds to the $Pa3$ structure. — $\alpha=5.35$ Å. ---- $\alpha=5.63$ Å.

¹⁵N α phase was found to be similar to the ¹⁴N sublimation energy (1.598 kcal/mole for ¹⁵N compared with 1.582 kcal/mole for ¹⁴N).

X-ray^{48,49} and electron diffraction^{50,51} studies on polycrystals have indicated that α -N₂ crystallizes in a $Pa3$ centrosymmetric structure with four molecules per unit cell. From single crystal x-ray measurements⁵² and piezoelectric resonance experiments⁵³ it has been concluded that the correct structure is the non-centrosymmetric $P2_13$, in which the center of each molecule is displaced along the cube diagonal by 0.1 to 0.2 Å. The absence of uv absorptions violating the centrosymmetric selection rules,⁵⁴ shows that the $P2_13$ structure could not be detected spectroscopically. On the other hand, the coincidence of ir and Raman spectra,^{21b} suggests the $P2_13$ structure.

The potential function derived in this work was also used to test the stability of the $P2_13$ structure. We first calculated the static energy per molecule as a function of the displacement Δ of the molecules along the body diagonals (Fig. 6) ($\Delta=0$ corresponds to the $Pa3$ structure and $\Delta=0.17$ to the $P2_13$ structure). The centrosymmetric $Pa3$ structure is seen to be more stable. The

TABLE VI. Calculated and experimental Grüneisen coefficients for α and γ nitrogen. Mean standard deviation for the fit to calculated α -N₂ coefficients: 0.05; for γ -N₂: 0.04.

Mode	α -N ₂		Mode	γ -N ₂	
	Calculated	Experimental		Calculated	Experimental
A_u	3.076		A_u	3.268	
E_u	3.116		E_u	3.072	
$T_u(Q_1)$	3.310		B_{1g}	3.184	2.22 ^b
$T_u(Q_2)$	3.114		A_{2g}	3.160	
E_g	2.918	2.09 ^a -2.13 ^b	E_g	2.970	2.316 ^b
$T_g(Q_1)$	3.158	1.70 ^a -2.12 ^b			
$T_g(Q_2)$	3.000	1.74 ^a -1.90 ^b			

^aReference 24 measured at 8 °K.

^bReference 25 measured 4.2 °K. The corresponding volume used to calculate the Grüneisen coefficients were taken from the 20 °K isotherm of Swenson.²⁸

ratio of static energies between $P2_13$ and $Pa3$ structures at equilibrium unit cell dimensions ($a=5.63$ Å) is $U_{P2_13}^{stat}/U_{Pa3}^{stat}=0.964$.

At smaller unit cell volumes ($a=5.53$ Å), the $P2_13$ structure is more stable than the larger volume $P2_13$ structure for $\Delta \leq 0.17$ Å but is still metastable relative to the $Pa3$ structure.

Since the static energy difference between the phases is small, zero-point effects on the relative stability have to be examined. It is not possible to perform complete relaxation of forces and torques on the molecules in the $P2_13$ structure since its static energy is unstable relative to the $Pa3$ static energy and thus only approximate calculation of the lattice dynamics can be performed (see Sec. IIIB). A reference calculation to estimate the error in zero-point energy introduced by doing the lattice dynamics calculation without relaxation of forces and torques was performed on the stable $Pa3$ structure. This indicated that the neglect of relaxation effects causes an overestimation of the zero-point energy by less than 8% or less than 2% of the total energy. A nonrelaxed lattice dynamics calculation on the $P2_13$ and $Pa3$ structure revealed that the former has a zero-point energy larger by ~30% than the corresponding one for the $Pa3$ structure at equilibrium. Zero-point effects thus further increase the relative stability of the $Pa3$ structure ($U_{P2_13}^{tot}/U_{Pa3}^{tot}=0.9426$).

Since the neglect of the relaxation of forces and torques causes only a small change in the translational modes (see Table III), it is possible to compare these modes in the two structures with reasonable accuracy. Table VII shows the frequency of these modes for both $P2_13$ and $Pa3$ structures. It is evident that "no relaxation" errors do not exceed 0.015% in the $Pa3$ structure. The three translational modes $2T_u+A_u$ of the $Pa3$ structure are transformed to $2T+A$ modes in the $P2_13$ structure. At $q=0$, these are almost pure translation at the latter structure and are all shifted to larger frequencies with respect to their counterparts in the $Pa3$ structure. A_u mode undergoes a very small shift, possibly due to the fact that the movement of the molecules in this translational mode is along the body diagonals. This is the direction in which they would move to undergo the $Pa3$ to $P2_13$ transition. Therefore, in the $Pa3$ to $P2_13$ transition the A_u normal coordinate can be considered as a kind of "reaction coordinate," and hence the least affected by it. Both T_u modes have a larger shift, the low frequency mode exhibiting the highest shift due to its higher vibrational amplitude.

The intramolecular frequencies of the α -phase (T_g

TABLE VII. Translational frequencies for $Pa3$ and $P2_13$ structures for $a=5.63$ Å.

Mode	$Pa3$ relaxed	$Pa3$ unrelaxed	$P2_13$ unrelaxed	Frequency shift
A_u	43.7	43.7	44.5	0.8
$T_u(Q_1)$	69.5	69.0	74.2	5.2
$T_u(Q_2)$	47.0	47.7	58.1	10.4

and A_g modes) were computed using both an harmonic intramolecular potential [Eq. (19)] and the experimentally adjusted⁴² anharmonic form [Eq. (20)]. The volume dependence of the intramolecular modes is shown in Fig. 5. At large unit cell volume the T_g - A_g splitting disappears and both modes collapse into a fourfold degenerate mode having the frequency of the isolated N₂ molecule. The Davydov splitting of the $q=0$ internal modes is increasing from zero at $V \geq 60 \text{ \AA}^3/\text{mole}$ to 0.6 cm^{-1} at $V = 40 \text{ \AA}^3/\text{mole}$. Experimental evidence^{19,23} indicate a splitting of $\sim 1 \text{ cm}^{-1}$ at equilibrium volume under atmospheric pressure. The anharmonic potential exhibits somewhat smaller splitting than the corresponding results for the harmonic potential.

The $q=0$ Grüneisen coefficients of the internal modes are very low as expected: for the harmonic potential, only field induced anharmonicity causes volume dependence in the frequencies ($\gamma_{T_g} = 2.015 \times 10^{-3}$, $\gamma_{A_g} = 1.07 \times 10^{-3}$) while for the anharmonic intramolecular potential, both field and internal anharmonicity contribute to the Grüneisen coefficients ($\gamma_{T_g} = 1.18 \times 10^{-2}$, $\gamma_{A_g} = 1.06 \times 10^{-2}$). The internal anharmonicity is larger than the field anharmonicity, the latter contributing only 10%–18% to the total Grüneisen coefficient.

Mixing between internal and lattice modes is negligible in solid nitrogen due to the very strong intramolecular bond in N≡N molecule resulting in a high stretching frequency. In other molecular crystals having "softer" bonds, this mixing could be of importance.⁴⁴ The weakness of the intermolecular interactions relative to the intramolecular ones also causes a very small dispersion in the intramolecular modes (less than 0.2 cm^{-1} over the entire Brillouin zone).

B. γ -N₂

The properties of the γ phase of N₂ were investigated experimentally only to a limited extent. The unit cell

TABLE VIII. Experimental and calculated results for γ -N₂ employing the 12-6 potential of this work.

Property	Experimental	Calculated
Unit cell dimensions (Å)	$a = 3.957^a$ $c = 5.109$	$a = 3.940$ $c = 5.080$
Unit cell angles (deg.)	$\alpha = \beta = \gamma = 90^\circ$ ^a	$\alpha = \beta = \gamma = 90^\circ$
Sublimation energy (kcal/mole)	...	1.282
Translational modes (cm ⁻¹)		
B_{1u}	Inactive	110.4
E_u	...	66.1
Librational modes (cm ⁻¹)		
A_{2g}	Inactive	91.0
B_{1g}	103.6 ^b	107.3
E_g	58.4 ^b	55.4
Internal modes (cm ⁻¹)		
A_{1g}	2331 ^b	2331.35
B_{2g}		2330.80

^aReference 27.

^bReference 22, $T = 8^\circ\text{K}$, $V = 39.4 \text{ \AA}^3/\text{mol}$.

parameters were measured by Schuch and Mills²⁷ and recently the Raman spectrum of this high pressure phase was measured by Medina and Daniels²² and Thiery *et al.*²⁵ Our potential, chosen to fit experimental data of α -N₂ was applied without further elaboration to calculate γ phase properties. Table VIII summarizes the experimental and calculated results for γ -N₂. The unit cell parameters were calculated for an external pressure of 4100 atm under which the experimental data were obtained. The unit cell axes a and c were independently varied to minimize the crystal energy. The minimum of the total energy was obtained at $c/a = 1.291$ (compared with the experimental value of 1.29.²⁷ Figure 7 shows the c/a dependence of both static and total crystal energy for two selected volumes. The c/a ratio

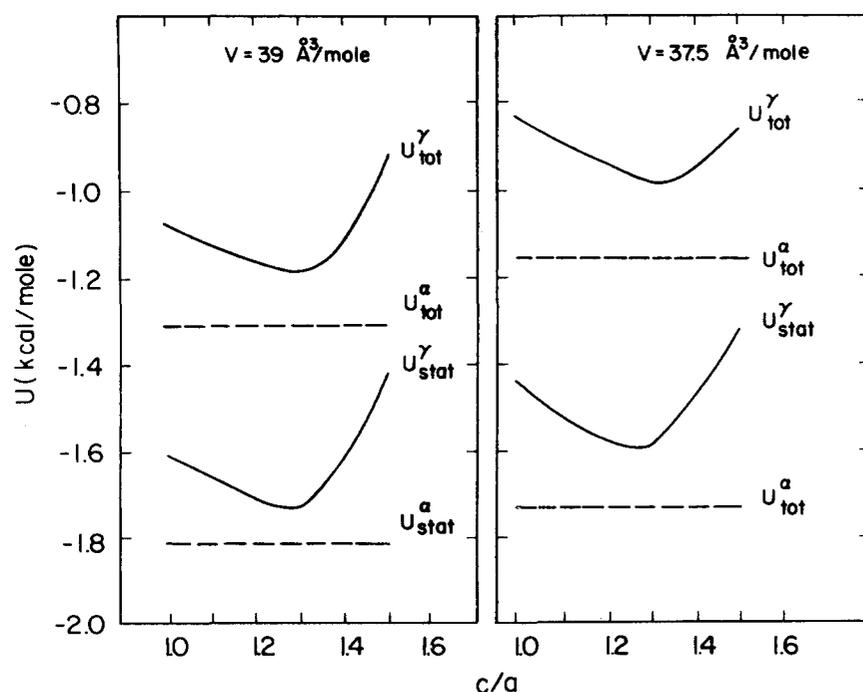


FIG. 7. Dependence of U_{tot} and U_{stat} of γ -N₂ on c/a ratio, as compared with the corresponding values for α -N₂ at two volumes. — γ -N₂. ---- α -N₂.

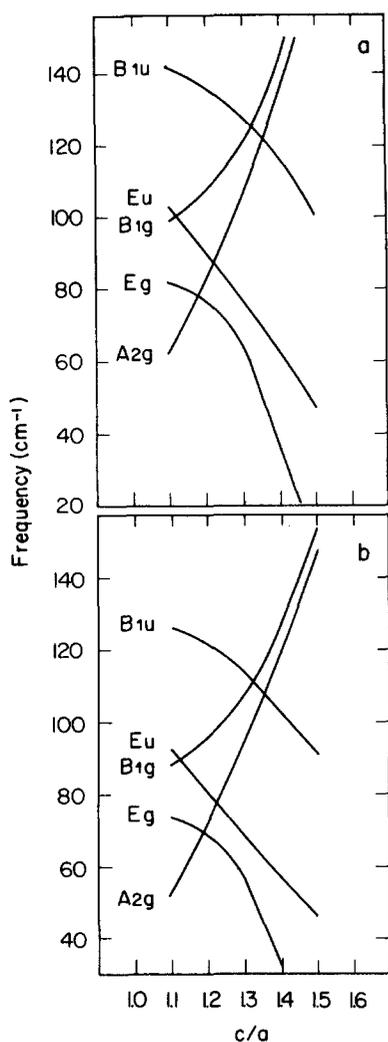


FIG. 8. The dependence of γ -N₂ lattice modes on c/a ratio for two volumes: (a) $V=37.5 \text{ \AA}^3/\text{molecule}$, (b) $V=39.0 \text{ \AA}^3/\text{molecule}$. Calculated with the 12-6 potential of the present work.

for which the energy is a minimum is negligibly affected by zero-point effects, and is practically independent of the molar volume. The lattice mode frequencies were found to depend strongly on the c/a ratio even at constant volume. Figure 8 describes the γ -phase lattice modes as a function of c/a ratio, for two selected volumes.

It is plausible that the potential yields the correct c/a value and reproduces well the experimental Raman frequencies of the γ phase.

The calculated lattice constants at external pressure of 4100 atm, agree well with the experimental values.

The volume dependence of the calculated γ -N₂ lattice modes is shown in Fig. 9(a) and the relevant Grüneisen coefficients are summarized in Table VI. The Raman spectrum of γ -N₂ was recently measured at several molar volumes.²⁵ The Grüneisen coefficients deduced from these measurements are given in Table VI together with the calculated parameters. The agreement between calculated and experimental results seems to be quite poor.

The Davydov splitting between $q=0$ internal modes in γ -N₂ is larger than the corresponding splitting in α -N₂. Experimentally²² only one Davydov component was observed in the intramolecular Raman spectrum. A shoulder of this peak, that could not be separated from the main peak, was assigned to the second Davydov component, and suggests that the splitting is 1 cm^{-1} (Table VIII). As in the case of α -N₂, the anharmonic potential [Eq. (20)] reveals a larger volume dependence of the intramolecular modes than the harmonic potential [Eq. (19), Fig. 9].

Isotopic effects on the γ phase are slightly larger than on the α phase due to the greater relative importance of zero-point effects in the more compressed γ phase. Keeping the c/a ratio at its ¹⁴N minimum energy value, the unit cell parameters of the ¹⁵N γ phase are 0.0161 \AA smaller than the corresponding value for the ¹⁴N γ phase.

A search for an α -to- γ phase transition with the employed potential was unsuccessful, as the α phase was calculated to be more stable than the γ phase over the investigated volume range. Figure 7 demonstrates that zero-point energy effects reduce the relative stability of the γ phase, the γ -to- α energy difference increasing upon introducing the ZPE. Variation of c/a up to the extreme case of a cubic ($c/a=1.0$) lattice was performed (Fig. 7) but still the α phase remained more stable than the γ phase. The same result was obtained by Raich⁴⁵ with the 12-6 potential of Kuan *et al.*⁶ employing a simplified form for the zero-point energy contribution. The minimum total energy difference between α and γ phases is 0.08 kcal/mole at $V=39 \text{ \AA}^3/\text{molecule}$ (which is the experimental transition volume) and is 6% and 5% of the total energy of the γ and α phases, respectively, at this volume.

Finally, a gas phase property was calculated with our 12-6 potential. Using the general statistical mechanics results of Sweet and Steele⁵⁵ for an atom-atom 12-6 potential, we computed the second virial coefficient of N₂ in the temperature range of $250^\circ\text{--}440^\circ\text{K}$. The standard error of the fit between calculated and measured^{31,32} results was 8.7 cm^3 in this temperature range. The order of magnitude of the error should be compared with the results obtained by Dows and Hsu⁵⁶ for CO₂ for a 12-6 potential that was calibrated to yield a good fit, for crystal data on CO₂⁵⁷ of 31 cm^3 and with the deviation of 2 cm^3 ,⁵⁶ obtained with the potential that fits best the second virial coefficient of CO₂.

V. CONCLUSIONS

Zero-point energy effects, the relaxation of forces and torques on the molecules, and the calculation of intermolecular interactions up to a long intermolecular distance seem to be important factors in the calculation of equilibrium unit cell dimensions and lattice frequencies of crystalline nitrogen. Relatively small changes in the unit cell dimensions at which the calculation of the lattice dynamics is carried out were shown to lead to quite different results for the calculated frequencies.

The incomplete release of the forces and torques on the molecules also influences the results, especially for

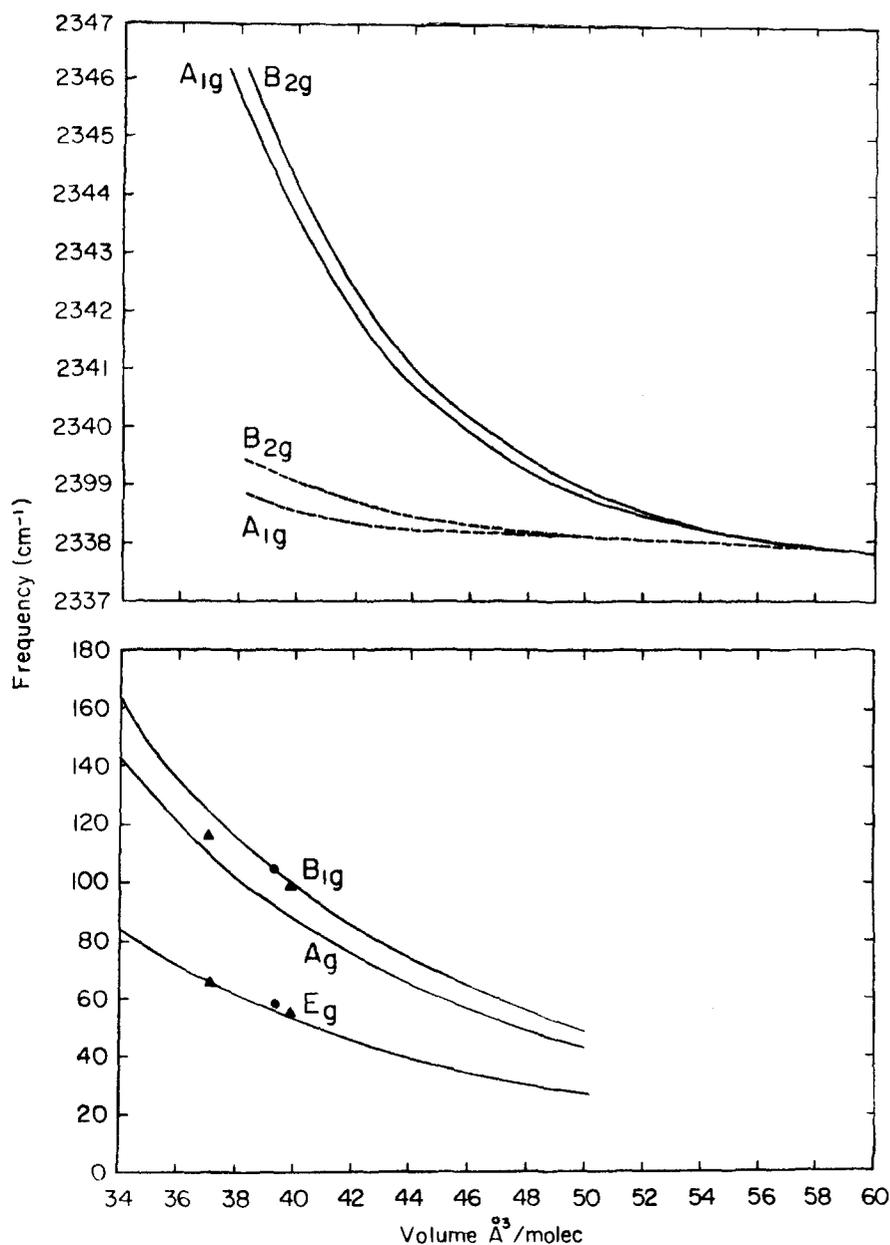


FIG. 9. Raman active frequencies of γ -N₂ as a function of unit cell dimension calculated with the interatomic 12-6 potential of the present work. (a) Intramolecular frequencies calculated with — anharmonic intramolecular potential [Eq. (19)]. (b) Lattice modes. ● Raman frequencies measured by Medina and Daniels²⁴ at 8°K. ▲ Raman frequencies measured by Thiery *et al.*²⁵ at 4.2°K.

the librational lattice modes; the frequencies are much higher than when the calculations are carried out under equilibrium conditions. These observations seem to be of a general nature and should probably be considered in the study of other molecular crystals.

The representation of the molecular interaction through a simple 12-6 atom-atom potential has been shown to predict correctly many of the static and dynamic properties of α and γ nitrogen. However, this potential fails to reveal a phase transition between these structures, and also predicts the $Pa3$ structure to be more stable than the $P2_13$ whose existence seems to be experimentally confirmed.^{57b} The calculated Grüneisen coefficients are quite high with respect to the measured quantities (see Table VI). This points to the possibility that the 12 power on the repulsive part of the atom-atom potentials may be too high. Other powers on the repulsive potential seem to fit the properties of molecular crystals at a given pressure equally well.⁵⁸ On the other

hand, the calculation of static and dynamical properties as a function of pressure seems to be quite sensitive to the repulsive power. These studies are, therefore, especially appropriate to the elucidation of the character of the intermolecular interactions in the repulsive range of the potential.⁵⁹

Both the inability of the simple potential adopted here to reproduce the α -to- γ transition and the overestimation of the Grüneisen coefficients, suggest that a more sophisticated form for the interaction should be considered. Perhaps the most promising method is that recently adopted for rare-gas interactions. In this method, the repulsive segment of the potential taken from either theoretical Thomas-Fermi-Dirac,^{60,61} or Hartree-Fock⁶² closed shell calculations or from experimental scattering data,⁶³⁻⁶⁵ is joined by a Spline^{66,63} or quintic Hermite⁶⁷ interpolation, with the attractive section calculated from accurate empirical values.⁶⁷ Sufficient experimental data on rare gases is available

to construct such potentials.⁶³⁻⁶⁷ However, both the reliability of the potential and the values of its free parameters have been determined only in relation to fluids and condensed gases (viscosity, second virial coefficients, vibrational frequencies of dimers, etc.) where the important anisotropic interactions are hardly manifested. It is hoped that the experimental data needed to construct such potentials for nitrogen and other simple crystals will be made available in the future so that both structural and dynamical properties relating various solid modifications could be better understood.

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