Mobility of the Monomers in the Van der Waals Molecule \((N_2)_2\) Comparison with \(N_2\) Crystals

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The \(N_2-N_2\) intermolecular potential has been obtained from *ab initio* calculations and represented in two analytic forms: a spherical expansion and a site-site potential (with different sites for each contribution to the potential). It is shown that, in the range of the Van der Waals minimum, the short-range exchange repulsion is the dominant anisotropic contribution, not the multipole–multipole interactions; this repulsion is mainly responsible for the (crossed) equilibrium configuration of the \((N_2)_2\) dimer. Using this potential in lattice-dynamics calculations for solid \(N_2\) (in the ordered \(\alpha\) and \(\gamma\) phases) with the harmonic and self-consistent phonon methods, yields generally very good agreement with experimental data: lattice structure, cohesion energy, translational phonon frequencies and their pressure dependence, and pressure dependence of the librational frequencies. The values of the librational frequencies and their temperature dependence are less well reproduced, however, especially for the \(\alpha\)–\(\beta\) phase transition; this is probably due to the larger amplitudes of the librations in the crystal and the failure of the self-consistent phonon model to deal with these. The \((N_2)_2\) dimer, for which we have made preliminary (rigid-rotor–harmonic-oscillator) calculations is floppier than the crystal. The barriers to internal rotation are rather low (20 and 40 cm\(^{-1}\), dimer binding energy 125 cm\(^{-1}\)) and only one or two states in each internal-rotation direction correspond with "locked-in" \(N_2\) rotations (librations); the higher states will be (hindered) internal rotations.

1. INTRODUCTION

A Van der Waals molecule (dimer) is the smallest unit from a molecular crystal that is held together by the same forces that cause the cohesion of the crystal. Sometimes (also for \(N_2\)), this relation has been used to infer the equilibrium structure of Van der Waals molecules from the nearest-neighbour configurations in the crystal. This is too great a simplification, however, even when the interactions between the molecules are pairwise additive, since the surrounding of molecules in a crystal by several (nearest and further) neighbours will lead to optimum packing configurations which are generally different from the optimum dimer configuration. Still, knowing the structure and dynamical behaviour of the crystal can yield much information about the Van der Waals molecule and *vice versa*. The central role in such relations is, of course, played by the intermolecular potential.

The nitrogen solid, as one of the simplest typical molecular crystals, has been the object of many experimental and theoretical studies [for reviews see ref. (1) and (2)]. (Hydrogen is even simpler, of course, but very atypical because of the small anisotropy in the intermolecular potential and the very large rotational constant of the \(H_2\) molecule, leading to almost free \(H_2\) rotations in the solid.) Three crystal phases of solid \(N_2\) are known: the ordered \(\alpha\) and \(\gamma\) phases stable at low temperatures, the \(\gamma\) phase at pressures above 3.5 kbar, and the orientationally disordered \(\beta\) phase at temperatures above 35 K. Many experimental data are available; of particular
interest here are the structures,\textsuperscript{3} the cohesion energy,\textsuperscript{4} the phonon frequencies (at wavevector $q = 0$ from i.r. and Raman spectroscopy,\textsuperscript{5,6} for general $q$ from inelastic neutron scattering)\textsuperscript{7} and the temperature and pressure (or volume) dependence of these properties (Grüneisen parameters, etc.). Several empirical $N_2$--$N_2$ model potentials have been proposed\textsuperscript{2} and it is generally believed that the calculation of the equilibrium structure and the phonon frequencies of the crystal provides a very good check on these model potentials. In particular the frequencies of the librational phonon modes in the ordered $\alpha$ and $\gamma$ phases and the conditions for the orientational order--disorder, $\alpha$--$\beta$ phase transition should be sensitive to the anisotropy (the orientational dependence) of the intermolecular potential.

About the $(N_2)_2$ dimer much less is known. The only (experimental) study of this dimer (to our knowledge) has been made by Long et al.\textsuperscript{8} These authors describe the i.r. spectrum of $(N_2)_2$ in the region of the monomer stretch frequency ($v_1$) at 2329.7 cm$^{-1}$, measured at 77 K in the gas phase. This $N_2$ stretch transition is i.r.-forbidden in the free monomer, but it becomes weakly allowed (and shifted to the red, but only by 0.1 cm$^{-1}$) by the interactions in the dimer. (The same interactions lead to the collision-induced i.r. absorption from unbound $N_2$ complexes, which is observed as a broad band in the spectrum underlying the discrete dimer peaks.) From the $P$ and $R$ ($N_2$--$N_2$ end-over-end) rotational branches of this $v_1$ transition it is concluded, \textit{via} a model calculation that corrects for centrifugal distortion, that the $N_2$--$N_2$ equilibrium distance $R_0$ is ca. 3.7 Å. From the progression of the other observed side bands of the $v_1$ transition it is deduced that the $N_2$ monomers exhibit one libration at frequency $v_2 = 9.5$ cm$^{-1}$ (a “locked-in” monomer rotation), while the higher monomer rotations in the dimer are just slightly hindered, because they have energies equal to or higher than the barrier to internal rotation. They lead to a perturbed monomer rotational S band. The barrier to internal rotation is estimated to lie at 15-30 cm$^{-1}$. The equilibrium configuration of the $(N_2)_2$ dimer is not known, however, and the assignment of the spectrum \textsuperscript{8} is only tentative: it is based on the similarity with the $N_2$--$Ar$ and $O_2$--$Ar$ spectra and some model calculations for the latter systems.\textsuperscript{9,10} From the same parallel, Long \textit{et al.}\textsuperscript{8} conclude that the $(N_2)_2$ dimer might have a T-shaped equilibrium configuration ($O_2$--$Ar$ and $N_2$--$Ar$ are found to be T-shaped),\textsuperscript{9,10} which conclusion they support by looking at the crystal neighbour configurations and at the $N_2$-quadrupole--$N_2$-quadrupole interactions. (As we demonstrate below, these arguments are not conclusive, however.)

In order to make theoretical predictions about the structure and dynamical properties of the $N_2$ crystal and the $(N_2)_2$ Van der Waals molecule, one should know the intermolecular potential. One can try, nowadays, to extract this potential from \textit{ab initio} calculations. The danger of fitting empirical potentials to the experimental data is, namely, that this fitting is usually not direct, but involves intermediate models for the dynamics. For instance, in fitting the $N_2$--$N_2$ potential to the phonon frequencies of the solid, it has been assumed\textsuperscript{2} that the lattice modes are harmonic. One then obtains “effective” model potentials (from the “effective” harmonic force constants) which may not describe other experimental properties well. \textit{Ab initio} potentials do not have this drawback, but since the calculations are still difficult and the results contain inaccuracies, they must be checked by comparison with known experimental data. Berns and van der Avoird\textsuperscript{11} have calculated the $N_2$--$N_2$ potential; Luty \textit{et al.}\textsuperscript{12} have used it in lattice-dynamics calculations on solid $\alpha$- and $\gamma$-$N_2$ and directly compared the calculated properties of the crystal with measured data. Besides being a check on the calculated potential, this provides interesting information on the dynamical behaviour of solid $N_2$ itself (e.g. about the anharmonicity of the translational and librational motions of $N_2$ in the crystal). These calculations on solid $N_2$
are briefly described in section 3. We have also started detailed calculations on the
dynamics of (N₂)₂, using the same *ab initio* potential (see section 2). Some prelimi-

nary results are given in section 4.

2. N₂–N₂ POTENTIAL FROM *ab initio* CALCULATIONS

The *ab initio* calculations leading to the N₂–N₂ potential have been described in
ref. (11) and (13). The following contributions have been included: (first-order)
electrostatic multipole–multipole interactions, all $R^{-5}$, $R^{-7}$ and $R^{-9}$ terms; (second-
order) induction, multipole–induced–multipole interactions, all $R^{-8}$ and $R^{-10}$ terms;
(second-order) dispersion, induced-multipole–induced-multipole interactions, all
$R^{-6}$, $R^{-8}$ and $R^{-10}$ terms; (first-order) penetration and exchange effects due to overlap
between the monomer wavefunctions. The induction terms appear to be negligibly
small and, since these terms should provide the dominant three-body interactions
in a multimer (crystal), we expect the pairwise (molecule–molecule) potential to be a
good approximation (estimated deviation from pairwise additivity mainly due to
triple–dipole dispersion interactions and three-body exchange contributions: <10% of
the Van der Waals well depth).

In order to express the potential and to formulate dynamical equations (section 4),
we have to choose a dimer coordinate system. The geometry of the dimer is deter-
mined by the vector $R$ pointing from the centre-of-mass of molecule A to that of mole-
cule B and by the vectors $r_A$ and $r_B$ defining the orientations of the monomer axes (the
lengths of the vectors $r_A$ and $r_B$ are the monomer internuclear distances; these are
assumed to be fixed, see below). These vectors can be expressed with all angles given
either relative to an arbitrary space-fixed frame:

$$
R = (R, \tilde{R}) = (R, \Theta^s, \Phi^s) \\
r_A = (r_A, \tilde{r}_A) = (r_A, \theta_A^s, \varphi_A^s) \\
r_B = (r_B, \tilde{r}_B) = (r_B, \theta_B^s, \varphi_B^s)
$$

or relative to a body-fixed frame attached to the dimer, e.g. with the $z$-axis lying along
$R$ and molecule B in the $xz$-plane, so that

$$
R = (R, 0, 0) \\
r_A = (r_A, \theta_A, \varphi_A) \\
r_B = (r_B, \theta_B, 0).
$$

This body-fixed frame itself can be obtained from the space-fixed frame by rotations
over three Euler angles

$$(\alpha, \beta, \gamma) = (\Phi^s, \Theta^s, \varphi_B^s).$$

Since the potential depends only on the internal dimer angles ($\theta_A, \theta_B, \varphi_A$), we can write,
for rigid monomers:

$$V(R, \tilde{r}_A, \tilde{r}_B, \tilde{R}) \equiv V(R, \theta_A, \theta_B, \varphi_A). \quad (1)$$

Two different analytic representations of the *ab initio* potential have been given.¹¹

(a) A site–site potential (*i.e.* a generalized atom–atom potential with the force
centres shifted away from the nuclei), fitted to 36 interaction-energy values, calculated
for six values of $R$ ($3 \leq R / \AA \leq 4.4$) and six combinations of angles ($\theta_A, \theta_B, \varphi_A$). This
site–site potential has the form

$$V_{AB} = \sum_{i \in A} \sum_{j \in B} [q_i q_j r_{ij} \tilde{r}_{ij} + A \exp(-B r_{ij}) - C r_{ij}^6] \quad (2)$$
where \( r_{ij} \) are the distances between sites on the molecules A and B. The positions of these sites along the N-N axes are optimized for each term in the potential (2) separately, and the parameters \( q_1, A, B, C \) are determined by separate fits of the three different terms to the corresponding \textit{ab initio} contributions.

(b) A spherical expansion:

\[
V_{AB} = (4\pi)^{3/2} \sum_{L_A L_B L} v_{L_A L_B L}(R) A_{L_A L_B L}(\hat{r}_A, \hat{r}_B, \vec{R})
\]

where \( r_{ij} \) are the distances between sites on the molecules A and B. The positions of these sites along the N-N axes are optimized for each term in the potential (2) separately, and the parameters \( q_1, A, B, C \) are determined by separate fits of the three different terms to the corresponding \textit{ab initio} contributions.

The long-range contributions have been obtained \textsuperscript{11} directly from the multipole expanded electrostatic and dispersion energies.\textsuperscript{13} The short-range coefficients have been calculated \textsuperscript{11} at \( R = 3 \text{ Å} \) from \textit{ab initio} results at 105 different angle combinations \((\theta_A, \theta_B, \phi_A)\) by numerical integration (Gauss–Legendre and Gauss–Chebyshev quadrature), while they have been assumed to vary with distance as \( \exp(-a - bR - cR^2) \). All parameters are given in ref. (11).

Looking at the orientational \((\theta_A, \theta_B, \phi_A)\) dependence of the \textit{ab initio} potential (in both representations) we observe the following remarkable features (see fig. 1). The multipole–multipole interactions (led by the quadrupole term) are indeed most attractive for a T-shaped dimer \((\theta_A = 90^\circ, \theta_B = \phi_A = 0^\circ)\), but the minimum for a shifted parallel dimer \((\theta_A = \theta_B \approx 45^\circ, \phi_A = 0^\circ)\) is equally deep. The anisotropy in the dispersion interactions, although these are always attractive, is just as important as the anisotropy in the multipole-multipole interactions, however. The dispersion term would favour a linear geometry \((\theta_A = \theta_B = \phi_A = 0^\circ)\), for given distance \( R \), the long-range terms together would favour the T-shape or shifted parallel configurations. However, at the distance \( R = 4 \text{ Å} \), which is about the equilibrium distance in the isotropic potential, the dominating anisotropic effect is caused by the short-range overlap effects (mainly exchange repulsion). So the exchange repulsion is most important in determining the dimer equilibrium configuration (as has been found empirically by Henderson and Ewing\textsuperscript{9,10} for the \( \text{N}_2-\text{Ar} \) and \( \text{O}_2-\text{Ar} \) dimers, which are T-shaped). In the case of \((\text{N}_2)_2\), however, the requirement of minimum exchange repulsion favours the crossed structure \((\theta_A = \theta_B = \phi_A = 90^\circ)\) or the parallel one \((\theta_A = \theta_B = 90^\circ, \phi_A = 0^\circ)\). The quadrupole–quadrupole interaction is more repulsive in the latter case, so that the minimum in the potential occurs for the crossed configuration (see fig. 2).

3. STRUCTURE AND LATTICE DYNAMICS OF SOLID \textit{N}_2

Performing lattice summations with the \textit{ab initio} \( \text{N}_2-\text{N}_2 \) potential in its site–site representation, Luty \textit{et al.} \textsuperscript{12} have calculated the crystal equilibrium structure (\textit{i.e.}
optimized the lattice constants within the given space group \textit{Pa}3 for \(\alpha\) nitrogen with 4 molecules in the unit cell and \textit{P}4\_2/m\textit{mm} for \(\gamma\) nitrogen with 2 molecules in the unit cell), by minimizing the total internal energy (or, in the self-consistent phonon model, the Gibbs free energy at given temperature and pressure). Nearest-neighbour pairs in the crystal correspond to dimer configurations: \(\theta_A = 90^\circ\), \(\theta_B = 35^\circ\) and \(\phi_A = 55^\circ\) in the \(\alpha\) phase (fixed by symmetry) and \(\theta_A = 90^\circ\), \(\theta_B = 42^\circ\) and \(\phi_A = 90^\circ\) in the \(\gamma\) phase. So the nearest-neighbour configurations, which apparently lead to a minimum in the total lattice energy, do not correspond to the energy minimum for each indi-

![Graph showing orientational dependence of different long-range (multipole) and short-range (exchange and penetration) contributions to the N\textsubscript{2}-N\textsubscript{2} potential at \(R = 4\) Å; (---) spherical expansion (3) and (---) site-site (2) representations of the potential.]

After optimizing the structure, lattice dynamics calculations have been carried out \textsuperscript{12} by the harmonic \textsuperscript{16} and self-consistent phonon \textsuperscript{17} models. The self-consistent phonon method had originally been developed for light noble-gas (i.e. atomic)
crystals (He in particular) with a large zero-point vibrational energy.\textsuperscript{17} It corrects the lattice modes for the effects of anharmonicity in the potential by using effective force constants which are derived by minimizing the first-order expression for the Gibbs (or Helmholtz) free energy of the crystal (\textit{i.e.} the canonical ensemble average of the “exact” anharmonic potential over harmonic oscillator states). This minimization leads to an expression for the effective force constants: the second derivatives of the potential, Fourier transformed for a given wavevector $q$, averaged over the molecular displacements. Also this average is a canonical ensemble mean value, \textit{i.e.} one has to take quantum-mechanical expectation values (for all wavevectors $q$) weighted by Boltzmann factors (for a given temperature $T$): in practice, this is performed \textit{via} the displacement-displacement correlation function. Since this correlation function depends on the lattice vibration functions (the phonon eigenvectors) and thereby on the effective force constants again, the calculation has to be carried out self-consistently. In each self-consistent phonon cycle also the structure of the crystal has been optimized \textsuperscript{12} by minimizing the free energy; after convergence this results in the average lattice structure at given temperature and pressure. Also the phonon frequencies, and all thermodynamic properties derived \textit{via} the statistical partition function, become functions of $T$ and $p$. Wasiutynski \textsuperscript{18} has generalized the self-consistent
phonon formalism to molecular crystals, by dealing explicitly with the librational phonon modes, making the assumption that these modes have small amplitudes, however. Luty et al. have used the computer program written by him. Results for the $\alpha$ phase, where most experimental data are available, are shown in table 1; the $\gamma$ phase results are similar. The increase of the phonon frequencies (at $q = 0$) with pressure can be observed in fig. 3. It appears that the calculated results

**Table 1.---$\alpha$-N$_2$ crystal data at zero pressure and $T = 15$ K**

<table>
<thead>
<tr>
<th></th>
<th>calculated $^a$</th>
<th>experimental $^b$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>harmonic</td>
<td>self-consistent phonon</td>
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<tr>
<td>lattice constant/Å</td>
<td>5.611</td>
<td>5.763</td>
</tr>
<tr>
<td>cohesion energy / kJ mol$^{-1}$</td>
<td>6.43</td>
<td>6.48</td>
</tr>
<tr>
<td>(at $T = 0$ K, including zero-point motions) / cm$^{-1}$</td>
<td>536</td>
<td>540</td>
</tr>
<tr>
<td>phonon frequencies/cm$^{-1}$ / K</td>
<td>772</td>
<td>778</td>
</tr>
<tr>
<td>$\Gamma (0, 0, 0)$</td>
<td>{ $E_g$, $T_g$, $T_u$ }</td>
<td>{ $A_u$, $T_u$ }</td>
</tr>
<tr>
<td>librations</td>
<td>42.4</td>
<td>41.1</td>
</tr>
<tr>
<td>$T_g$</td>
<td>52.9</td>
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<tr>
<td>$T_u$</td>
<td>77.7</td>
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<tr>
<td>$A_u$</td>
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<tr>
<td>$E_u$</td>
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</tr>
<tr>
<td>$T_u$</td>
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<td>73.3</td>
</tr>
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<td>{ $M_{12}$, $M_{12}$ }</td>
<td>{ $M_{12}$, $M_{12}$ }</td>
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</tr>
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</tr>
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<td>$M_{12}$</td>
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<td>$M_{12}$</td>
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<td>$R_{12}$</td>
<td>58.1</td>
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</tr>
<tr>
<td>$R_{12}$</td>
<td>61.0</td>
<td>58.4</td>
</tr>
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</table>

$^a$ Results from ref. (12), harmonic values with potential B (best site-site potential), self-consistent phonon corrections with potential A (slightly simplified site-site potential). $^b$ Results from ref. (4) and (7).

[lattice constants, cohesion energy, phonon frequencies and their pressure dependence (or volume dependence: Grüneisen parameters)] are in good agreement with the measured data. This is the more satisfactory if one considers that no adjustments of the potential to the experimental data have been made. [The usual (semi-)empirical potentials are fitted to these data.] Looking in particular at the dynamical properties, one observes that the phonon frequencies which correspond to translational vibrations of the N$_2$ molecules in the crystal are in almost perfect agreement with the neutron scattering results (only 2 cm$^{-1}$ too high on the average); the correction for anharmonicity by the self-consistent phonon method is essential to reach this agree-
Fig. 3.—Pressure dependence of the phonon frequencies (for $q = 0$) in solid $N_2$, $\alpha$ and $\gamma$ phases, calculated $^{12}$ by the self-consistent phonon method at $T = 12$ K. Solid lines: librational modes; dashed lines: translational modes.

ment (the harmonic frequencies are 6 cm$^{-1}$ too high). For the pure librational modes the agreement is less good; these are too high by 12 cm$^{-1}$, on the average, although the self-consistent phonon corrections work in the right direction (harmonic frequencies are 14.5 cm$^{-1}$ too high). These corrections are too small, however, which must probably be ascribed to the fact that the self-consistent phonon method,$^{17}$ in particular its generalization to molecular crystals,$^{18}$ does not sufficiently correct for anharmonicity in the case of the librations, which actually have rather large amplitudes (ca. 15°) even at low temperature. At higher temperatures close to the $\alpha$-$\beta$ phase transition [remember that in the $\beta$ phase the librations pass into (hindered) rotations], the self-consistent phonon method fails even more in following the observed softening of the librations (see fig. 4 for a typical librational mode). Of course, it may also be that the orientational dependence of the potential is less accurate than its $R$-dependence (which should be almost perfect, judged by the values of the translational mode frequencies), but the agreement of several calculated properties (e.g. the Grüneisen parameters, also for the librational modes) and the theoretical failure of the self-consistent phonon method$^{18}$ to account for larger amplitude librations, point to the conclusion that it is the dynamical (self-consistent phonon) model which must be refined in the first place, at least for the librations. We expect that the calculations
A. VAN DER AVOIRD

4. STRUCTURE AND DYNAMICS OF (N$_2$)$_2$

As we have seen in section 2, the \textit{ab initio} calculations predict that the equilibrium configuration of the (N$_2$)$_2$ dimer is a crossed one ($\theta_A = \theta_B = \phi_A = 90^\circ$) with $R_e = 3.5$ Å and binding energy $\Delta E = 1.5$ kJ mol$^{-1} = 125$ cm$^{-1} = 180$ K. The barriers to internal rotation are rather low: \textit{ca.} 20 cm$^{-1}$ for a rotation over $\phi_A$ through the parallel structure (with $\theta_A = \theta_B = 90^\circ$; $\phi_A = 0^\circ$ and almost the same $R_e = 3.6$ Å); \textit{ca.} 40 cm$^{-1}$ for a rotation over $\theta_A$ or $\theta_B$ through the T-shaped structure ($\theta_A = 90^\circ$; $\theta_B = \phi_A = 0^\circ$; $R_e = 4.2$ Å). These results are in good agreement with the quantities obtained from the i.r. spectrum: \textit{ca.} 3.7 Å and a barrier to internal rotation of 15-30 cm$^{-1}$ (in one direction), even though the equilibrium configuration is different from the T-shaped structure predicted by Long \textit{et al}.\textsuperscript{8} According to our calculations a T-shaped structure would lead to a much larger equilibrium distance: $R_e = 4.2$ Å.

Knowing the complete anisotropic N$_2$–N$_2$ potential [see section 2, the spherical expansion (3) is especially convenient here], we can solve the dynamical problem for the dimer, assuming that the N$_2$ molecules can be considered as rigid rotors (length $r_0$). Actually the N$_2$ stretching frequency (2329.7 cm$^{-1}$) is so much higher than the dimer vibrational frequencies (see below) that this approximation should hold very well. The hamiltonian for the dimer then becomes, in space-fixed coordinates:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Temperature dependence of the $E_g$ librational frequency $\Delta \omega$ in $\alpha$-N$_2$; $\Delta \omega = \omega(T) - \omega(T = 0)$.}
\end{figure}
MOBILITY IN (N\textsubscript{2})\textsubscript{2} AND N\textsubscript{2} CRYSTALS

\begin{equation}
H = -\frac{\hbar^2}{2\mu_d} R^{-1} \frac{\partial^2}{\partial R^2} R + \frac{\mu^2}{2\mu_d R^2} + \frac{j_A^2}{2\mu_{0_d}^2} + \frac{j_B^2}{2\mu_{0_0}^2} + V(R,\hat{r}_A,\hat{r}_B,\hat{R})
\end{equation}

where \( l, j_A \) and \( j_B \) are the angular momentum operators associated with the angles \( \hat{R}, \hat{r}_A \) and \( \hat{r}_B \), respectively, and \( \mu_d = m \) and \( \mu = m/2 \) are the dimer and monomer reduced masses (\( m \) is the nitrogen nuclear mass). One can solve for the bound states of this hamiltonian by the close-coupling secular-equation method, formulated for atom–diatom systems by Le Roy et al.\textsuperscript{19} For a diatom–diatom dimer one has to use a basis:

\begin{equation}
R^{-1} \chi_{nl}(R) \left[ \sum_{m_A,m_B} \left( \sum_{j_A,m_A} Y_{j_A,m_A}^{*}(\hat{r}_A) Y_{j_B,m_B}(\hat{r}_B)(j,m_j|j_A,m_A;j_B,m_B) \right) \times Y_{1,m}(\hat{R})(J,M_J|j,m_j;l,m) \right]
\end{equation}

The expressions in parentheses (\ldots) are Clebsch–Gordan coefficients. The radial part of the problem, i.e. the generation of the (numerical) basis functions \( \chi_{nl}(R) \) from a pseudo-diatomic problem with the potential \( V(R) \), which may be the isotropic potential \( v_{0,0,0}(R) \), and the calculation of the radial matrix elements, is just the same as for the atom–diatom problem \textsuperscript{19} using the spherical expansion (3) for the anisotropic potential. The angular matrix elements lead to generalized Percival–Seaton\textsuperscript{20} coefficients, which contain \( 9-j \) and \( 6-j \) symbols.

It is more convenient to use the body-fixed coordinate system, however, and to transform the hamiltonian (5) into the form

\begin{equation}
H = -\frac{\hbar^2}{2\mu_d} R^{-1} \frac{\partial^2}{\partial R^2} R + \frac{(J - j_A - j_B)^2}{2\mu_d R^2} + \frac{j_A^2}{2\mu_{0_d}^2} + \frac{j_B^2}{2\mu_{0_0}^2} + V(R,\theta_A,\theta_B,\varphi_A - \varphi_B)
\end{equation}

where the angular momentum vectors \( J, j_A \) and \( j_B \) are now associated with the body-fixed * angles \( (\alpha,\beta) \), \((\theta_A,\varphi_A)\) and \((\theta_B,\varphi_B)\) (see section 2). \( J \) is the overall angular momentum; one should remember that the components of \( J \) with respect to the body-fixed frame obey the converse of the usual angular-momentum-commutation relations. For this hamiltonian (7) one can use the basis

\begin{equation}
R^{-1} \chi_{nl}(R) \left( \sum_{m_A,m_B} Y_{j_A,m_A}(\theta_A,\varphi_A) Y_{j_B,m_B}(\theta_B,\varphi_B)(j,k|j_A,m_A;j_B,m_B) \right) D_{k,M_J}^{l}(\alpha,\beta,0)
\end{equation}

where \( D_{k,M_J}^{l} \) are symmetric top eigenfunctions. The angular matrix elements with the potential (3) are simpler (although they still contain a \( 9-j \) symbol).

In order to get an initial idea about the positions of the vibrational levels in the (\( N\textsubscript{2} \))\textsubscript{2} dimer, we have solved for the eigenstates of the body-fixed hamiltonian (7) in the rigid-rotor–harmonic-oscillator approximation. Neglecting the rotation–vibration coupling terms \( J j_A \) and \( J j_B \) and assuming infinitesimal displacements from the equilibrium coordinates \( R_e, \theta_{Ac}, \theta_{Be}, (\varphi_A - \varphi_B)_e \), the body-fixed hamiltonian (7) easily yields the expressions for the Wilson \( G \) matrix\textsuperscript{21} in terms of internal-displacement coordinates \( R, \theta_A, \theta_B \) and \((\varphi_A - \varphi_B)\). [This \( G \) matrix can also be derived by the methods of ref. (21), using the Eckart conditions, but this is much more elaborate.] The force-constant matrix \( F \), which contains all second derivatives of the potential (3) with respect to \( R, \theta_A, \theta_B \) and \((\varphi_A - \varphi_B)\), has been derived using formulae from ref. (22). Instead of the spherical potential (3), we have also used the site–site potential (2) and derived the expressions for the \( F \) and \( G \) matrices in terms of the atom–atom

* Actually, this coordinate system is not completely body-fixed. The third Euler angle \( (\gamma = \varphi_B^e \text{, section 2}) \), which should rotate molecule B into the \( xz \) plane, is not used. Instead, one uses \( \varphi_B \) as an "internal" angle. One must realize that the motions with \( \varphi_A = \varphi_B \) are in fact overall rotations, however, while the internal angle is \( \varphi_A - \varphi_B \). This distinction is usually not made explicitly in the literature.
distances $r_{ij}$. [Note that these are different from the site–site distances; the methods of ref. (21) can be generalized to deal with this problem, however.] The results of both rigid-rotor–harmonic-oscillator calculations are listed in table 2.

**Table 2.—Harmonic frequencies for (N$_2$)$_2$**

<table>
<thead>
<tr>
<th>Normal coordinate</th>
<th>Symmetry</th>
<th>$\nu$/cm$^{-1}$</th>
<th>Site–site potential (2)</th>
<th>Spherical potential (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_A + r_B$</td>
<td>$A_1$</td>
<td>2329.7</td>
<td>($R_c = 3.6$ Å)</td>
<td></td>
</tr>
<tr>
<td>$r_A - r_B$</td>
<td>$B_2$</td>
<td>2329.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>$A_1$</td>
<td>38.9</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>$\theta_A, \theta_B$</td>
<td>$E$</td>
<td>27.7</td>
<td>22.1</td>
<td></td>
</tr>
<tr>
<td>$\varphi_A - \varphi_B$</td>
<td>$B_1$</td>
<td>15.2</td>
<td>13.9</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental monomer value,* assuming to be unchanged for dimer.

Although we do not expect the rigid-rotor–harmonic-oscillator model to be valid for a floppy molecule such as N$_2$–N$_2$, we can still draw the following conclusions. (Henderson and Ewing$^9,10$ have shown in their calculations for N$_2$–Ar and O$_2$–Ar that the harmonic-oscillator model is not too bad an approximation for the lowest levels.) In the first place, it is reassuring to observe that the two different analytic representations of the *ab initio* potential produce frequencies which are reasonably close to each other. These frequencies are clearly lower than the frequencies of the translational and librational phonon modes in the N$_2$ crystal (table 1), so we may conclude that the Van der Waals molecule (N$_2$)$_2$ is floppier than solid N$_2$. Just as for the crystal (cf. table 1), we expect that the anharmonic effects will further lower the frequencies in the dimer. For the internal rotations in the $\varphi$-direction (barrier $\approx 20$ cm$^{-1}$) we can expect just one or two librational states (‘locked-in’ N$_2$ rotations): the ground state at ca. 7 cm$^{-1}$ from the bottom of the well and possibly another state near the top of the barrier (fundamental transition frequency $\lesssim 14$ cm$^{-1}$), whereas all the higher states are (hindered) internal rotations. For the internal rotations in the $\theta_A$ and $\theta_B$ directions (barrier ca. 40 cm$^{-1}$) we expect a similar picture with higher frequencies: zero-point energy ca. 12 cm$^{-1}$, fundamental transition frequency $\lesssim 25$ cm$^{-1}$. The bending/internal-rotation coordinates $\theta_A$, $\theta_B$ will probably mix rather strongly with the stretching coordinate $R$, because of the significant shift in $R_c$ when going from the crossed equilibrium structure to the saddle point in the T-shaped configuration. Generally, the picture obtained from the calculations agrees well with the type of internal motions deduced from the (N$_2$)$_2$ i.r. spectrum by Long *et al.*$^8$ A more detailed interpretation of the spectrum can be made when we have solved the complete dynamical problem in the (N$_2$)$_2$ dimer in the close-coupling secular-equation formalism.

Looking at the dimer properties for non-zero temperature will also be useful for understanding the dynamics of the solid. At very low temperatures only the librational states in the dimer will be populated; at higher temperatures an increasing fraction of dimers will become orientationally disordered with (hindered) internal N$_2$ rotations. The transition should resemble the $\alpha$–$\beta$ phase transition in the solid, although it will probably occur at lower temperature.
MOBILITY IN (N$_2$)$_2$ AND N$_2$ CRYSTALS

I thank Drs Fred Mulder, Rut Berns and Tadeusz Luty for their contributions to the calculation of the N$_2$–N$_2$ potential and to the lattice dynamics calculations on solid N$_2$, Maarten Claessens and Theo van der Lee for their assistance with the rigid-rotor-harmonic-oscillator calculations on (N$_2$)$_2$ using the site–site potential, and Drs Paul Wormer, Jonathan Tennyson, Brian Sutcliffe and Wim Briels for useful discussions.