Infrared spectra of the van der Waals molecule \((N_2)_2\)

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All bound states of the \((N_2)_2\) dimer are calculated by solving the ro-vibrational problem for the rigid monomer hamiltonian, using an \textit{ab initio} potential and a symmetrized product basis of angular momentum and associated Laguerre functions. Next we have evaluated the infrared line strengths for all the symmetry allowed bound-bound transitions, employing the empirical dipole function deduced from the collision induced far infrared spectrum and the \(N_2\) multipole moment and polarizability derivatives from \textit{ab initio} calculations. Thus we have generated the \((N_2)_2\) dimer far-infrared spectrum, corresponding to pure van der Waals vibrations and rotations, and the mid-infrared spectrum in the region of the monomer fundamental stretch \((2330\text{ cm}^{-1})\). Due to the strong anisotropy of the potential, on the one hand, but the lack of rigidness of the \((N_2)_2\) dimer, on the other, the spacing between vibrational levels and the shape of the rotational bands and, therefore, the appearance of the infrared spectra is very irregular.

1. Introduction

Knowledge of the intermolecular potential is crucial for understanding the properties of molecular gases, liquids and solids. Several of these properties, such as virial and transport coefficients in the fluid phases and phonon frequencies in solids, have been used to test and refine model potentials. Also potentials from \textit{ab initio} calculations, which are recently becoming available, have been tested via such properties [1–4]. With the experience gained [1–5], it is becoming clear, however, that the data which depend most sensitively on the detailed potential surface, in the physically important region around the van der Waals minimum, are given by the spectra of van der Waals molecules such as \((N_2)_2\). Except for atomic systems [5], it is generally impossible to extract the potential directly from the measured spectra. But, if potentials are available, from \textit{ab initio} calculations, for example, they can be used to calculate dimer spectra which can be compared with experimental ones. Thus, these potentials can be checked and improved.

The calculation of an infrared spectrum for the \((N_2)_2\) dimer, starting from an \textit{ab initio} \(N_2\)–\(N_2\) potential [6], is the purpose of this paper. As one will see, this is not an easy task. The number of bound states involved is very large [7] and the system does not comply with simple rules, which are given, for instance, by the harmonic oscillator/rigid rotor model or the free internal rotor model. In addition to the bound state ro-vibrational wavefunctions, one needs a dipole surface and the infrared transition intensities depend also on the details of this surface. Still,
we believe that the ro-vibrational spectrum can be calculated fairly accurately so that little information is lost and the comparison with experimental spectra indeed yields accurate data on the potential and dipole surfaces.

The method appropriate for solving the nuclear motion problem in van der Waals dimers originates in the close-coupling scheme [8]. An adaptation for atom–diatom systems, especially suitable for bound state calculations, was given by LeRoy and Van Kranendonk [9]; they expand their ro-vibrational wave functions as linear combinations of radial [10] and angular momentum function products (named LC–RAMP in [7]). For general dimers a formulation was presented by Brocks et al. [11] in a body-fixed reference frame. This approach has been extended to include (hyper)fine structure and Zeeman interactions [12–16]. A related, but more approximate, scheme involves the adiabatic (Born–Oppenheimer) separation between angular and radial motions (named BOARS [17–19]).

So far, most calculations have been done for atom–diatom systems: noble gas–H₂ [5, 9, 10, 20], ArHCl [17, 18], HeHF [21] and noble gas–O₂ [14–16]. Few studies have been made on diatom–diatom systems: (H₂)₂ [12, 13, 22], for which calculations are simplified by the near isotropy of the potential, and (HF)₂ in the BOARS approximation [19]. The present study on (N₂)₂ is an extension of the calculations by Tennyson and van der Avoird [7]. Including the contributions from all bound ro-vibrational van der Waals states, infrared spectra for (N₂)₂ are generated for both N₂ monomers in their vibrational ground states (far infrared spectrum) and for one monomer vibrationally excited (mid infrared spectrum).

2. Symmetry in (N₂)₂

Before discussing the dynamics of the (N₂)₂ dimer and the infrared transitions, it is important to consider the symmetry of this system. This simplifies the calculations and yields selection rules which are essential for interpreting the infrared spectrum. The most abundant (N₂)₂ species contains four identical ¹⁴N nuclei and the fundamental symmetry group to be used is the permutation–inversion (PI) group S₄ ⊗ I. However, the infrared experiments cannot induce the breaking of the intramolecular N₂ bonds and so we can restrict ourselves to the subspace of wave functions which describe stable monomers. The subgroup of S₄ ⊗ I which corresponds with this subspace is the group named G [23–25], PI(16) [26] or S₄' ⊗ C₁ [7]. This subgroup contains the so-called feasible PIs [23, 27]; it has also been called the molecular symmetry group [28].

The transformation of space-fixed coordinates under these PIs is straightforward [25, 26]. Before transforming body-fixed coordinates, however, one must define the transformation of the body-fixed frame first. In the case of van der Waals dimers such as (N₂)₂ it is convenient [11] to use a partially body-fixed frame with the z-axis lying along the vector R, which connects the centres of mass of the monomers (see figure 1). The direction of this vector is reversed by space inversion and by permutations which interchange the monomers and it is invariant under the permutations P₁₂ and P₃₄ (see figure 1). Maintaining a right-handed body-fixed frame and using the relationship between space- and body-fixed coordinates [11], one can easily derive the transformation of the latter. This
I.R. spectra of $(N_2)_2$

Figure 1. Body-fixed coordinate system, $\varphi = \varphi_A - \varphi_B$.

has been done by Tennyson and van der Avoird [7] (note the erratum with this paper). In brief, their results are summarized:

Space inversion, $E^*$, acts within the body-fixed frame as a reflection with respect to the $yz$-plane.

The permutation of monomers, $P_{13,24}$, acts as a twofold rotation around the body-fixed $x$-axis.

The permutations $P_{12}$ and $P_{34}$ act as inversions on the body-fixed coordinates of the monomers $A$ and $B$, respectively.

All other operations are easily deduced by multiplication.

If the $(N_2)_2$ dimer were a rigid $D_{2d}$ structured complex, the group of feasible PIs would be:

$$\text{PI}(D_{2d}) = \{E, P_{12,34}, P_{13,24}, P_{14,23}, P_{12}', P_{34}', P_{1324}', P_{1423}'\}.$$ 

When Eckart conditions are used to define the body-fixed frame for such a rigid molecule [29], an isomorphism between this PI group and the $D_{2d}$ point group of the rigid molecule is obtained [27, 28, 30]. This defines the PI operation as a product of a point group operation on the vibrational coordinates and a proper rotation of the Eckart frame. Thus, the $D_{2d}$ point group classification of vibrational functions is extended to a $\text{PI}(D_{2d})$ classification of the overall ro-vibrational states. The irreducible representations carried by the rotational functions are given in table 1. Together with table IV of Tennyson and van der Avoird [7], they yield the symmetry labels of the ro-vibrational functions with respect to $\text{PI}(D_{2d})$.

The dipole moment, being invariant under nuclear permutations and changing sign upon inversion, carries the representation $B_1$ of $\text{PI}(D_{2d})$, leading to the overall selection rules $A_{1,2} \leftrightarrow B_{1,2}$ and $E \leftrightarrow E$. If there is a good separation between the rotational and vibrational degrees of freedom, as in the rigid rotor/harmonic oscillator model, one can impose the usual selection rules on the rotational and vibrational transitions separately [28]. For instance, the internal dipole moment carries $D_{2d}$ representations $B_2(\mu_z)$ and $E(\mu_x, \mu_y)$, leading to additional vibrational selection rules. At the same time, the overall $\text{PI}(D_{2d})$ selection rules
Table 1. Symmetry assignment of the rotational wave functions $|JMk\rangle$ of a $D_{2d}$ molecule.

<table>
<thead>
<tr>
<th>Function†</th>
<th>Even</th>
<th>Odd</th>
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</thead>
<tbody>
<tr>
<td>$</td>
<td>JM\ 4n\rangle +</td>
<td>JM\ -(4n\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>JM\ 4n+2\rangle +</td>
<td>JM\ -(4n+2\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>JM\ 4n+2\rangle -</td>
<td>JM\ -(4n+2\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>JM\ 4n+4\rangle -</td>
<td>JM\ -(4n+4\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>JM\ 2n+1\rangle,</td>
<td>JM\ -(2n+1\rangle$</td>
</tr>
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</table>

† $n = 0, 1, 2, \ldots$

must be satisfied, which makes only specific rotational transitions allowed (see table 1), in combination with specific vibrational transitions.

The classification of the $(N_2)_2$ states in terms of $\text{PI}(16)$ is derived by noting that this group can be written as a direct product of $\text{PI}(D_{2d})$ and the space inversion group $I = \{E, E^*\}$. So, we can add + or − to the $D_{2d}$ labels, according to the inversion character. The dipole moment carries the representation $B_1^-$ of $\text{PI}(16)$, changing the exact selection rules to $A_1^+ \leftrightarrow B_1^0$ and $E^+ \leftrightarrow E^-$. The mechanism that makes inversion feasible can be explicitly introduced by assigning a large amplitude tunneling coordinate. Merer and Watson [24] have chosen the torsional coordinate as such (the angle $\phi$, see figure 1). By approximate separation of small (vibrations) and large (rotations, torsional tunnelling) amplitude motions, one can derive additional approximate selection rules for these motions separately. In the $(N_2)_2$ case, all motions except the monomer stretch vibrations must be considered as non-rigid, i.e. large amplitude motions. We have looked for approximate selection rules in the calculated spectra (see below), without success. Therefore, the only classification that applies to all the levels is the assignment of the monomer vibrational states and the classification of the complete ro-vibrational van der Waals states with respect to $\text{PI}(16)$ (see §3 and [7]).

If some small (Coriolis coupling) terms can be neglected (§3), one obtains an axially symmetric problem. The total angular momentum component $J_z$ relative to the body-fixed axis carries the representation $A_2^-$. The axial symmetry leads to the familiar two-fold degeneracy [31] of a symmetric top molecule for $|k| > 0$ states ($k$ being the eigenvalue of $J_z$). In the present case the degeneracy occurs between $A_{1,2}^+, |k|$ and $A_{2,1}^+, |k|$, between $B_{1,2}^+, |k|$ and $B_{2,1}^+, |k|$ and between $E^+, |k|$ and $E^-, |k|$ states with $k \neq 0$.

3. Theory

3.1. Potential and dynamics

The intermolecular potential is expressed, with respect to the body-fixed frame, in terms of a spherical expansion [32]

$$V(R, r_A, r_B, \theta_A, \theta_B, \phi) = 4\pi \sum_{L_A, L_B, L} v_{L_A, L_B, L}(R, r_A, r_B) \mathcal{Y}_{L_A, L_B}^{L} (\hat{r}_A, \hat{r}_B), \quad (1)$$

where the angular functions are the coupled spherical harmonics

$$\mathcal{Y}_{L_A, L_B}^{L} (\hat{r}_A, \hat{r}_B) = \sum_{M_A} \langle L_A, M_A; L_B, M - M_A | L, M \rangle Y_{L_A, M_A} (\hat{r}_A) Y_{L_B, M - M_A} (\hat{r}_B), \quad (2)$$
with \( \hat{r}_A = (\theta_A, \varphi_A), \hat{r}_B = (\theta_B, \varphi_B), \varphi = \varphi_A - \varphi_B \) (see figure 1). The large gap between the \( N_2 \) monomer fundamental stretch frequency, 2330 cm\(^{-1} \), and the frequencies of the van der Waals dimer vibrations, around 20 cm\(^{-1} \), indicates that the monomer vibrations can be decoupled from the dimer vibrations and rotations. This is confirmed by the very small shift, 0.1 cm\(^{-1} \), of the monomer stretch frequency in the \( (N_2)_2 \) dimer mid infrared spectrum [33]. When studying the dimer motions, one can average the expansion coefficients \( v_{L_A, L_B, l}(R, r_A, r_B) \) in equation (1) over the monomer stretch wave functions \( \phi_{v_A}(r_A)\phi_{v_B}(r_B) \). Moreover, since the \( N_2 \) average bond length hardly changes with the vibrational quantum number \( v_A \) for the lower \( v_A \) states [34], one can use the same effective potential for ground state \( v_A = v_B = 0 \) and excited \( v_A = 1, v_B = 0 \) dimers, with expansion coefficients

\[
v_{L_A, L_B, l}(R) = \langle v_{L_A, L_B, l}(R, r_A, r_B) \rangle_{v_A, v_B} \approx v_{L_A, L_B, l}(R, r_0, r_0). \tag{3}
\]

These coefficients have been obtained from \textit{ab initio} calculations on \( (N_2)_2 \) dimers [6], where \( r_0 \) was taken as the experimental ground state bond length \( r_0 = 1.094 \) Å. The resulting potential has a minimum at the crossed \( D_{2d} \) structure \( (\theta_A = \theta_B = \varphi = 90^\circ) \) with equilibrium van der Waals bond length \( R_c = 3.46 \) Å and well depth \( D_c = 122 \) cm\(^{-1} \). Rotational barriers through parallel \( (\theta_A = \theta_B = 90^\circ, \varphi = 0^\circ) \) and T-shaped \( (\theta_A = 90^\circ, \theta_B = 0^\circ) \) saddle points are in the range 20 to 40 cm\(^{-1} \) and another low lying configuration is the shifted parallel structure \( (\theta_A = \theta_B = 72^\circ, \varphi = 0^\circ, R_c = 3.64 \) Å, \( D_c = 108 \) cm\(^{-1} \)). This potential has been tested on several bulk properties: solid state data [2, 3], second virial coefficients [1] and transport properties [4]. The invariance of the potential under \( \text{PI}(16) \) operations leads to the following symmetry relations between the spherical expansion coefficients

\[
\begin{align*}
&v_{L_A, L_B, l}(R) = 0 \quad \text{unless } L_A, L_B, L \text{ are all even,} \\
v_{L_A, L_B, l}(R) = v_{L_B, L_A, l}(R). 
\end{align*} \tag{4}
\]

In general, van der Waals complexes can be classified according to the relative strength of the potential that couples various types of motion [35, 36]. Taking free internal monomer rotations as a zeroth order picture, the anisotropic potential couples free rotor states with \( \Delta_j = \Delta_jA \) and \( \Delta_jB \) even. The \( N_2 \) bond length \( r_0 = 1.094 \) Å, rotational constant \( b_0 = 2.0 \) cm\(^{-1} \), leads to a smallest separation between these monomer free rotor states of 12 cm\(^{-1} \). Comparison of this splitting with the barriers to internal rotation just mentioned, shows that the internal rotor states will be strongly coupled. This coupling will probably persist up to the dissociation limit since the density of free rotor levels does not significantly decrease and the potential remains fairly anisotropic [37] even at somewhat larger distances \( R \).

The length of the van der Waals bond \( R = 3.8 \) to 4 Å [7], as opposed to the monomer bond length \( r_0 = 1.094 \) Å, makes the end-over-end rotational constant \( B \approx 0.08 \) cm\(^{-1} \) an order of magnitude smaller than the rotational constant \( \frac{1}{2}b_0 = 1 \) cm\(^{-1} \) associated with the rotation around the van der Waals axis \( R \). There will be no rotation–vibration separation, since the latter constant has the same order of magnitude as the spacings between van der Waals vibrational levels [7]. These facts favour a nuclear dynamics calculation in the (partially) body-
fixed frame proposed by Brocks et al. [11], instead of the space-fixed approach which is suitable for the weakly coupled \( \text{H}_2 \) complexes [5, 9, 12, 13, 20, 22] or the Eckart approach appropriate for near-rigid molecules [29]. The vector \( \mathbf{R} \) between the monomer centres of mass defines the body-fixed \( z \)-axis; the body-fixed frame is obtained from the space-fixed one by rotation over the Euler angles \((\alpha, \beta, 0)\), where \((\beta, \alpha)\) are the polar angles of \( \mathbf{R} \) in the space-fixed frame.

The dimer hamiltonian can be written as

\[
H = b_0(J_A^2 + J_B^2) - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu R^2} (J^2 + J^2 - 2j \cdot \mathbf{J}) + V(R, \hat{r}_A, \hat{r}_B) \tag{5}
\]

where \( \mathbf{J} \) is the overall angular momentum, \( \mathbf{j} = J_A + J_B \) and \( j_A \) and \( j_B \) are the angular momenta associated with \((\theta_A, \varphi_A)\) and \((\theta_B, \varphi_B)\) and \( \mu \) is the dimer reduced mass. This rigid monomer hamiltonian can be derived from the exact Born–Oppenheimer hamiltonian for the nuclear motions when the monomer stretch vibrations are decoupled (see the discussion with equation (4)). Although the kinetic energy operator in equation (5) has a simple appearance and acts accordingly on the basis functions defined in equation (6), one must realize that some complications originate from the transformation to the (partially) body-fixed frame [11]. For instance, the explicit expression for \( J^2 \) deviates from the usual form [31] and the operators \( j \) and \( \mathbf{J} \) do not commute.

The bound state problem for the hamiltonian (5) can be solved most conveniently in the following orthogonal basis:

\[
R^{-1} \chi_n(R) \varphi_{j_A, j_B}^n(\hat{r}_A, \hat{r}_B) \phi_{M, k}(\alpha, \beta, 0) \tag{6}
\]

where \( \chi_n(R) \) is an orthogonal basis of associated Laguerre functions [10], \( \varphi_{M, k}^n \) are rotation functions [38] normalized to unity and \( \varphi_{j_A, j_B}^n \) are coupled spherical harmonics (2). For a strong coupling case, the size of the resulting secular problem could become quite unmanageable without further approximations, such as the BOARS scheme used by Barton and Howard [19] in their calculation on \((\text{HF})_2\). In \((\text{N}_2)_2\) the PI(16) symmetry can be used to block-factorize the problem. Details can be found in [7].

The projection \( k \) of the overall angular momentum \( \mathbf{J} \) on the body-fixed \( z \)-axis can often be treated as a good quantum number [7, 19, 17–19]. The only terms in the hamiltonian (5) that couple states with different \( k \) are contained in the Coriolis operator \((2\mu R^2)^{-1}J \times J\cdot \mathbf{J}\), \( J \), viz. \( j_x J_x \text{ and } j_y J_y \), couple \( k \) with \( k \pm 1 \). Because of the length of the van der Waals bond, this coupling is rather small and neglect of these terms leads to an additional factorization of the problem. The hamiltonian (5) can be partitioned as

\[
H = H_{\text{vib}} + H_{\text{rot vib}} \tag{7}
\]

with

\[
H_{\text{vib}} = b_0(J_A^2 + J_B^2) - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu R^2} (J^2 - 2j_z J_z + V,
\]

\[
H_{\text{rot vib}} = \frac{1}{2\mu R^2} (J^2 - 2j_x J_x - 2j_y J_y)
\]

(note that \( J_z = j_z \) [11]).
In order to calculate all the bound states of the \((N_2)_2\) dimer and still keep the problem tractable, one can solve the vibrational problem with the Hamiltonian \(H_{vib}\) and the basis \((6)\). The effect of \(H_{rots}\) which corresponds with the end-over-end rotational structure, the Coriolis coupling and the centrifugal distortion, can then be introduced via perturbation theory [18, 19] or via an additional variational calculation using the eigenstates of \(H_{vib}\) as a basis. Up to first order perturbation theory \(k\) is conserved as a good quantum number and the two-fold degeneracy for \(k \neq 0\) remains, since \(H_{rots}\) couples \(k\) only with \(k \pm 1\).

Although the monomer stretch vibrations were assumed to be separable from the dimer vibrations and rotations, we must briefly consider the corresponding wave functions also, since they affect the \(\Pi(16)\) symmetry of the total wave functions and the infrared selection rules (see subsection 3.2). The total nuclear wave functions can be written as

\[
|v_A v_B^\pm\rangle|JMT\rangle, \tag{8}
\]

where \(|JMT\rangle\) denotes a van der Waals ro-vibrational state, i.e. an eigenstate of the dimer Hamiltonian \((5)\). The (approximate) calculation of these states has just been discussed, \(M\) is the projection of the overall angular momentum \(\mathbf{J}\) on the space-fixed \(z\)-axis and \(\Gamma\) is a \(\Pi(16)\) symmetry label. The symmetrized monomer stretch functions are given by

\[
|v_A v_B^\pm\rangle = \frac{1}{\sqrt{2}} [\phi_{va}(r_A)\phi_{vb}(r_B) \pm \phi_{vb}(r_A)\phi_{va}(r_B)] \quad \text{for } v_A \neq v_B
\]

\[
= \phi_{va}(r_A)\phi_{vb}(r_B) \quad \text{for } v_A = v_B \text{ (only + label occurs).} \tag{9}
\]

The \(\Pi(16)\) representations carried by these monomer stretch functions are \(A_1^+\) and \(B_2^+\) for the functions with the + and - labels, respectively. The separability reflected by equation \((8)\) leads to a degenerate set of levels for \(v_A \neq v_B\) with symmetry \(\Gamma \otimes A_1^+\) and \(\Gamma \otimes B_2^+\). This degeneracy would be lifted by introducing the dependence of the interaction potential on \(v_A\) and \(v_B\), which was assumed to be negligible in the case of \((N_2)_2\).

### 3.2. Dipole function, selection rules and infrared intensities

Just as the potential, the dipole function can be expressed with respect to the body-fixed frame in the form of a spherical expansion

\[
\mu_v(R, r_A, r_B) = 4\pi \sum \left| m_{\lambda A, \lambda B, \Lambda, \kappa}(R, r_A, r_B) \tilde{\alpha}_{\lambda A, \lambda B}(\tilde{r}_A, \tilde{r}_B) D^{(1)}_{\kappa\Lambda}(x, \beta, 0) \right|^2,
\]

with the coupled spherical harmonics \((2)\) and rotation functions \(D^{(1)}_{\kappa\Lambda}\) from [38]. It is more common [25, 39, 40] to write this expansion in space-fixed coordinates, but we can easily relate our expansion coefficients to those of Poll and Hunt [40]

\[
\left| m_{\lambda A, \lambda B, \Lambda, \kappa} \right|^2 = \sum_{L=\Lambda-1}^{\Lambda+1} \left( \frac{2L+1}{3} \right)^{1/2} \langle \Lambda, K; L, 0|1, K \rangle A_A(\lambda_A, \lambda_B, L). \tag{11}
\]

We consider the monomer stretch vibrations to be decoupled, as discussed in the previous section. The \((N_2)_2\) dimer will absorb in the far infrared region due to van der Waals vibrational and rotational transitions, while both \(N_2\) monomers...
remains in their vibrational ground states: \( v_A = v_B = 0 \). The effective dipole function for this part of the infrared spectrum is determined by the expansion coefficients

\[
M_{\lambda_A, \lambda_B, \Lambda, K}(R) = \langle 0 0 | m_{\lambda_A, \lambda_B, \Lambda, K}(R, r_A, r_B) | 0 0 \rangle.
\] (12)

The symmetry relations satisfied by these coefficients are

\[
M_{\lambda_A, \lambda_B, \Lambda, K} = 0 \quad \text{unless} \quad \lambda_A \text{ and } \lambda_B \text{ even},
\] (13a)

\[
M_{\lambda_A, \lambda_B, \Lambda, K} = (-1)^{\Lambda+1} M_{\lambda_B, \lambda_A, \Lambda, K},
\] (13b)

\[
M_{\lambda_A, \lambda_B, \Lambda, K} = (-1)^{\Lambda} M_{\lambda_A, \lambda_B, \Lambda, -K},
\] (13c)

and the PI(16) far infrared selection rules are (cf. §2)

\[
\begin{align*}
A_1^z & \leftrightarrow B_1^z, \\
A_2^z & \leftrightarrow B_2^z, \\
E^+ & \leftrightarrow E^-.
\end{align*}
\] (14)

The dipole of the \((N_2)_2\) dimer arises from different interactions between the monomers: multipole-induction, overlap (i.e. the effects of exchange and charge penetration [32]). The ‘long range’ multipole-induced dipole moments can be directly written in the spherical expansion form (10), the ‘short-range’ overlap contributions can also be expanded in that form [39, 40], see table 2. The interaction induced dipole moment gives rise to the collision induced (far) infrared absorption spectrum [41–42] of gaseous nitrogen. This spectrum has been interpreted by Poll and Hunt [40] using an effective isotropic potential [44] for the gas phase collisions at higher temperatures (124 K and 300 K). Each term in the spherical expansion of the dipole moment then leads to a separate absorption contribution to which one can attribute a specific line shape. Fitting the calculated spectrum to the measured one, Poll and Hunt have optimized the parameters which determine their dipole function. We use this empirical dipole function, see table 2, in order to calculate the far infrared spectrum of \((N_2)_2\)

<table>
<thead>
<tr>
<th>Table 2. Contributions to the (N_2-N_2) interaction induced dipole function for both monomers in the vibrational ground state.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism</td>
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<tr>
<td>Quadrupole induction via isotropic polarizability (\alpha)</td>
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<tr>
<td>Quadrupole induction via anisotropic polarizability (\gamma)</td>
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<tr>
<td>Hexadecapole induction via isotropic polarizability (\alpha)</td>
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<tr>
<td>Overlap</td>
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Empirical parameters from best fit [40]: quadrupole moment \(Q = -1.09 \text{e} \text{a}_0^2\), hexadecapole moment \(\Phi = -10.4 \text{e} \text{a}_0^3\), isotropic polarizability \((\alpha + 2 \alpha_1)/3 = \alpha = 11.92 \text{a}_0^3\), polarizability anisotropy \(\alpha_1 - \alpha_2 = \gamma = 4.76 \text{a}_0^3\), overlap parameters \(\sigma = 3.68 \text{A}, \rho = 0.11 \sigma, \lambda_1 = \pm 1.0 \times 10^{-3} \text{e} \text{a}_0, \lambda_3 = 1.0 \times 10^{-3} \text{e} \text{a}_0\).
I.R. spectra of \((\text{N}_2)_2\) dimers, corresponding to transitions between bound states. In discussing our results, in §4, we will also consider the effects of possible inaccuracies in the empirical dipole function.

The \((\text{N}_2)_2\) dimer also absorbs in the mid infrared region when the dimer vibrational and rotational transitions are combined with vibrational excitation of one of the monomers. This part of the dimer infrared spectrum will be mainly centred around the monomer fundamental stretch frequency, at 2330 cm\(^{-1}\). The effective dipole function for describing such dimer transitions is determined by the expansion coefficients:

\[
N_{\lambda A, \lambda B, \Lambda, K}^\pm (R) = \langle 0 | m_{\lambda A, \lambda B, \Lambda, K}(R, r_A, r_B) | 1 0^\pm \rangle, \tag{15}
\]

where the monomer vibrational functions for the ground state \(|0 0\rangle\) and the excited state \(|1 0^\pm\rangle\) are defined by equation (9). These coefficients satisfy symmetry relations analogous to equations (13a) and (13c), but equation (13b) has to be replaced by:

\[
N_{\lambda A, \lambda B, \Lambda, K}^\pm = \pm (-1)^{\Lambda + 1} N_{\lambda A, \lambda B, \Lambda, K}^\pm. \tag{16}
\]

The effective dipole function now carries the representations \(B_1^- = B_1^- \otimes A_1^+\) and \(A_2^- = B_1^- \otimes B_2^+\) of \(\Pi(16)\) and the corresponding selection rules for dimer transitions are

\[
\begin{align*}
A_{1,2}^+ &\leftrightarrow B_{1,2}^+, \\
E^+ &\leftrightarrow E^-,
\end{align*}
\]

for the + component \((B_1^-)\)

\[
\begin{align*}
A_1^+ &\leftrightarrow A_2^+, \\
B_1^+ &\leftrightarrow B_2^+, \\
E^+ &\leftrightarrow E^-.
\end{align*}
\]

The \(B_1^-\) transitions are allowed in the far infrared also, cf. equation (14), the \(A_2^-\) transitions (17) are additional. The expansion coefficients (15) are not known, but we can proceed by expanding the \(r_A\) and \(r_B\) dependence of the coefficients \(m(R, r_A, r_B)\) in a Taylor series in \(\Delta r_A = r_A - r_{A,e}\) and \(\Delta r_B = r_B - r_{B,e}\) [25]. Substituting this expansion into equation (15) and using the result [45] that the \(\text{N}_2\) monomer stretch functions \(\phi_{\nu A}(r_A)\) and \(\phi_{\nu B}(r_B)\) may be well replaced by harmonic oscillator functions, we obtain the following expression, correct up to and including second order:

\[
N_{\lambda A, \lambda B, \Lambda, K}^\pm (R) = \frac{1}{\sqrt{2}} \langle 0 | \Delta r | 1 \rangle \\
\times \left[ \frac{\partial m_{\lambda A, \lambda B, \Lambda, K}(R, r_A, r_B)}{\partial r_A} \pm \frac{\partial m_{\lambda A, \lambda B, \Lambda, K}(R, r_A, r_B)}{\partial r_B} \right]_{r_A = r_B = r_{e}}. \tag{18}
\]

The derivatives required to evaluate equation (18) are still not known in general, but if we use our experience from the far infrared spectrum (see §4) that the transition intensities are dominated by the ‘long range’ multipole-induced dipole contributions, we can express these derivatives in terms of monomer multipole moments, polarizabilities and their derivatives, see table 3. The latter are known for \(\text{N}_2\) from \textit{ab initio} calculations [45–47].
Table 3. Contributions to the \( \text{N}_2 - \text{N}_2 \) interaction induced dipole function for an excited \((v = 1)\) and a ground state \((v = 0)\) monomer.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>( \lambda_A )</th>
<th>( \lambda_B )</th>
<th>( \Lambda )</th>
<th>( K )</th>
<th>( N_{\lambda_A, \lambda_B, \Lambda, K}(R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole induction via isotropic polarizability ( \alpha )</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>((9\frac{ij_0}{(T_0)})^{1/2}) (\frac{d}{dr_B} \pm \alpha_B \frac{d}{dr_A} ) (R^{-4}\langle \Delta r \rangle_{01})</td>
</tr>
<tr>
<td>Quadrupole induction via anisotropic polarizability ( \gamma )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>(-\frac{(3\frac{ij_0}{(T_0)})^{1/2}}{2}) (\frac{d}{dr_B} \pm \gamma_B \frac{d}{dr_A} ) (R^{-4}\langle \Delta r \rangle_{01})</td>
</tr>
<tr>
<td>Hexadecapole induction via isotropic polarizability ( \alpha )</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>((\frac{2\varphi_5}{(T_0)})^{1/2}) (\Phi_A \frac{d}{dr_B} \pm \alpha_B \frac{d}{dr_A} ) (R^{-6}\langle \Delta r \rangle_{01})</td>
</tr>
<tr>
<td>Hexadecapole induction via anisotropic polarizability ( \gamma )</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>(-\frac{\varphi_5^{1/2}}{2}) (\Phi_A \frac{d}{dr_B} \pm \gamma_B \frac{d}{dr_A} ) (R^{-6}\langle \Delta r \rangle_{01})</td>
</tr>
</tbody>
</table>

The \( \text{N}_2 \) monomer transition moment \( \langle \Delta r \rangle_{01} = \langle \phi_0(r)|\Delta r|\phi_1(r)\rangle \) has been replaced by its harmonic oscillator expression \((h/2\mu v)^{1/2}\), with reduced mass \( \mu = 7 \) amu and fundamental frequency \( v = 2330 \text{ cm}^{-1} \). 

Ab initio parameters [46]

\[
\begin{align*}
\left( \frac{dQ}{dr} \right)_{res} &= 1.15 e a_0^2 \\
\left( \frac{d\Phi}{dr} \right)_{res} &= -2.53 e a_0^3 \\
\left( \frac{dz}{dr} \right)_{res} &= 5.8 a_0^2 \\
\left( \frac{d\gamma}{dr} \right)_{res} &= 6.5 a_0^3
\end{align*}
\]

The infrared absorption coefficient, in the dipole approximation, is given by the familiar first order perturbation expression [48]

\[
A(\omega) = N Z^{-1} [\exp (-E_i/kT) - \exp (-E_f/kT)] S_i S_{if} \delta(\omega - \omega_{if})
\]

where \( E_i \) and \( E_f \) are the lower and upper energy levels, \( Z \) is the partition function, \( N \) the number density of the dimers, \( \omega_{if} = (E_f - E_i)/\hbar \) the transition frequency, \( S_i \) the spin statistical weight and \( S_{if} \) the line strength:

\[
S_{if} = \sum_{j,l,v} |\langle (J_i, \Gamma_i)| \mu_v |(J_f, \Gamma_f)\rangle|^2.
\]

The labels \( j \) and \( l \) run over all degenerate ro-vibrational \( i \) and \( f \) levels, \( v \) over all components of the (monomer stretch averaged) dipole moment. Writing \( \mu \) in spherical tensor form and applying the Wigner–Eckart theorem [31] yields the selection rule \( \Delta J = 0, \pm 1 \). If \( k \) is treated as a good quantum number we have the additional rule \( \Delta k = 0, \pm 1 \) (for \( k = 0 \to 0, \Delta J = 0 \) is forbidden).

The eigenstates \(|JMf\rangle\) of the hamiltonian (5) are given as linear combinations of (symmetrized) basis functions (6). Using the dipole expansion (10), the calculation of matrix elements (20) is straightforward. They are expressed in products of vector coupling coefficients (3-\(j_s\)s and 9-\(j_s\)s) and radial integrals; all of these have been met already in the matrix elements over the potential (1) [7, 11].
4. Results

4.1. Test calculations

For all nuclear dynamics calculations we have used the basis set of Tennyson and van der Avoird [7]. As this basis was specially designed to converge the lower levels, it behaves accordingly. The ground state level at $-74.945 \text{ cm}^{-1}$ has converged to within 0.002 cm$^{-1}$. We have also tested the higher bound states, however. The convergence with respect to the size of the angular basis is good for all bound states; actually, one can expect the largest basis to be needed for describing the more rigid lower states. The quality of the radial basis decreases with increasing radial excitation. For most levels between the ground state and $-10 \text{ cm}^{-1}$ an accuracy of 0.2 cm$^{-1}$ may be claimed; states that are strongly radially excited are converged only to within 1.5 cm$^{-1}$. Since the associated vibrational excitation energy is higher than the librational energies, these states are relatively unimportant for the lower energy part of the spectrum. Levels that are less than 10 cm$^{-1}$ below the dissociation limit become increasingly unreliable. These inaccuracies might not be acceptable when looking at detailed ro-vibrational spectra, such as found for H$_2$ dimers [12, 13, 22]. In the case of (N$_2$)$_2$ only a coarse structured spectrum has been measured, however [33]. Moreover, the potential [6] and the dipole function [40] are not expected to be sufficiently accurate as to justify increased computational effort at the moment.

Even so, a full calculation including the Coriolis terms would be an immense task for higher $J$ states. Making the separation (7) and treating $H_{\text{rot vib}}$ as a perturbation operator, the off-diagonal Coriolis terms affect the end-over-end rotational constant $B$ only in second and higher order perturbation theory [18, 19]. In order to generate the complete infrared spectrum, we have chosen, therefore, to calculate all bound states of the hamiltonian (5) with $J = k$, while neglecting the off-diagonal Coriolis terms. These bound states go up to $k$ quantum numbers as high as $k = 8$. The end-over-end rotational ladders are then generated by taking $B = \langle (2\mu R^2)^{-1} \rangle$. This approach is equivalent with the separation (7), while treating $H_{\text{rot vib}}$ to first order in the Coriolis terms, but to order infinity in the centrifugal distortion for $J = k$. Exact solution of the full $J = 1$ secular problem, including Coriolis interactions, shows that the effect of these terms is strongly state dependent. For most levels, the rotational constant $B$ is perturbed by less than 10 per cent. However, in some cases the changes are larger, due to near degeneracy effects. The Coriolis perturbations are always larger than in (HF)$_2$ [19] and ArHCl [18], because of the higher density of states. The centrifugal distortion constant $D_J$ was found to be at least four orders smaller than $B$, so centrifugal distortion will be negligible, except for very high $J$ values.

For tests on the empirical dipole function [40] we have used the exact $J = 0$ and $J = 1$ eigenstates of the hamiltonian (5). Table 4 shows a typical series of line strengths for $J = 0 \rightarrow 1$ transitions from the $A_1^+$ ground state. It is clear that several transitions from the ground state obtain comparable intensity, in contrast with more rigid systems with near harmonic vibrations, where practically all intensity goes into the fundamentals. A second observation is that individual line strengths are substantially modified by overlap contributions to the dipole moment, especially through interference with the long range multipole-induction contributions. For comparison, we note that in the continuous collision induced infrared spectrum these interference terms reduced the quadrupole intensity con-
Table 4. Transition strengths |⟨i|μ|f⟩|^2 in 10^{-6} e^2 a_0^2 for A_1^+(J = 0) → B_1^+(J = 1) transitions from the ground A_1^+ state (−74.95 cm^{-1}) in ortho N_2-ortho N_2 dimers.

<table>
<thead>
<tr>
<th>B_1^+ level number</th>
<th>Q^2†</th>
<th>Φ^2†</th>
<th>(λ_1, λ_3)^2‡‡</th>
<th>2Q . Φ†</th>
<th>2(λ_1, λ_3) . Q‡‡</th>
<th>2(λ_1, λ_3) . Φ‡‡</th>
<th>Total without overlap</th>
<th>Total‡</th>
<th>Δk§</th>
<th>¯ν/(cm⁻¹)‖</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.2</td>
<td>0.8</td>
<td>0.0/0.7</td>
<td>−10.2</td>
<td>−0.61/−9.5</td>
<td>−0.1/1.5</td>
<td>22.8</td>
<td>23.3/15.5</td>
<td>1</td>
<td>22.1</td>
</tr>
<tr>
<td>2</td>
<td>5.85</td>
<td>0.25</td>
<td>0.13/0.0</td>
<td>−2.43</td>
<td>−1.78/0.16</td>
<td>0.37/−0.03</td>
<td>3.67</td>
<td>2.40/3.80</td>
<td>0</td>
<td>25.1</td>
</tr>
<tr>
<td>3</td>
<td>0.567</td>
<td>0.0</td>
<td>0.001/0.039</td>
<td>0.017</td>
<td>0.039/−0.299</td>
<td>0.001/−0.004</td>
<td>0.584</td>
<td>0.624/0.320</td>
<td>1</td>
<td>33.1</td>
</tr>
<tr>
<td>4</td>
<td>8.37</td>
<td>0.94</td>
<td>0.0/0.38</td>
<td>−5.61</td>
<td>0.17/−3.56</td>
<td>−0.06/1.19</td>
<td>3.70</td>
<td>3.81/1.71</td>
<td>1</td>
<td>42.0</td>
</tr>
<tr>
<td>5</td>
<td>5.46</td>
<td>1.47</td>
<td>0.16/0.0</td>
<td>−5.67</td>
<td>−1.88/−0.29</td>
<td>0.98/0.15</td>
<td>1.26</td>
<td>0.522/1.13</td>
<td>0</td>
<td>46.5</td>
</tr>
<tr>
<td>6</td>
<td>0.0953</td>
<td>0.0619</td>
<td>0.0216/0.0551</td>
<td>−0.1536</td>
<td>0.0908/−0.1449</td>
<td>−0.0732/0.1168</td>
<td>0.00358</td>
<td>0.0428/0.0305</td>
<td>1</td>
<td>47.5</td>
</tr>
<tr>
<td>7</td>
<td>0.115</td>
<td>0.0</td>
<td>0.0/0.009</td>
<td>−0.004</td>
<td>0.004/−0.063</td>
<td>0.0/0.001</td>
<td>0.111</td>
<td>0.115/0.0579</td>
<td>1</td>
<td>53.9</td>
</tr>
</tbody>
</table>

† Contributions from: pure quadrupole induction (Q^2), pure hexadecapole induction (Φ^2), pure overlap terms (λ_1, λ_3)^2, quadrupole–hexadecapole interference terms 2Q . Φ, quadrupole–overlap interference terms 2(λ_1, λ_3) . Q, hexadecapole–overlap interference terms 2(λ_1, λ_3) . Φ.

‡‡ Results for λ_1 = −1.0 × 10^{-5} e a_0 and λ_1 = 1.0 × 10^{-3} e a_0, respectively. (The sign of λ_1 was undetermined, see [40].)

§ Approximate labelling.

‖ Transition frequency.
tribution by not more than 10 per cent. The hexadecapolar and pure overlap contributions to the gas phase spectrum were found [40] to be 5 per cent and 1 per cent, respectively. In the bound state spectrum of \((N_2)_2\), also the hexadecapolar contribution is relatively more important, through interference with the quadrupole contribution. In general, we can conclude that interference terms are relatively more pronounced in the \((N_2)_2\) spectrum, because the bound states are more sensitive to the anisotropy of the potential than the continuum states and this anisotropy couples all different \(\lambda_A, \lambda_B\) contributions to the induced dipole moment. Thus, a more detailed induced dipole model could, in principle, be deduced from the dimer spectrum by looking at the intensities of individual lines (Poll and Hunt [40] were not able to determine the sign of their parameter \(\lambda_1\), for example).

Although the short range overlap contributions are important, we can still conclude that the line strengths can be calculated for all more intense transitions to within a factor of two from the long range multipole-induction terms alone. Until more detailed experimental information [33] becomes available, this is sufficient for our purpose. Only the quadrupole and hexadecapole induced dipole contributions were included in our further calculations. Moreover, this enabled us to construct a dipole function for the mid infrared spectrum corresponding with the same multipolar induction mechanisms (see §3.2 and table 3).

The effect of neglecting the off-diagonal Coriolis terms on the line strengths is shown in table 5 for some typical far infrared transitions. The results demonstrate that this neglect is tolerable in view of the approximations already made. For \(k = 0 \rightarrow 0\) transitions the \(\Delta J = 0\) component becomes forbidden; comparison for \(J = 1\) (table 6) shows that the 'exact' line strengths of such components are at least two orders of magnitude smaller than the stronger ones in table 5.

If \(k\) is treated as a good quantum number, table 7 illustrates that the line strengths within a given rotational envelope are controlled by the factor

\[
(2J + 1)(2J' + 1)
\left( \frac{J}{k'} \frac{1}{k' - k} \frac{J'}{k} \right)^2.
\]

This can be seen as another manifestation of negligible centrifugal distortion. So, the computation of one line for each transition between van der Waals vibrational levels is sufficient to generate the complete end-over-end rotational envelopes.

<table>
<thead>
<tr>
<th>(B_1^{-}) level number</th>
<th>(\Delta k)†</th>
<th>Line strength with Coriolis</th>
<th>(\bar{v}/(\text{cm}^{-1}))‡</th>
<th>Line strength without Coriolis</th>
<th>(\bar{v}/(\text{cm}^{-1}))‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>22.8</td>
<td>22.14</td>
<td>21.0</td>
<td>22.16</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3.67</td>
<td>25.10</td>
<td>5.35</td>
<td>25.09</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.584</td>
<td>33.13</td>
<td>0.634</td>
<td>33.13</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>3.70</td>
<td>42.04</td>
<td>3.35</td>
<td>42.06</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.26</td>
<td>46.54</td>
<td>1.52</td>
<td>46.60</td>
</tr>
</tbody>
</table>

† In the case with Coriolis terms, approximate labelling.
‡ Transition frequency.
Table 6. Transition strengths in $10^{-6} e^2 a_0^2$ for $A_2^−(J = 1, k = 0) \rightarrow B_2^+(J = 1, k = 0)$ transitions from the lowest $A_2^−(J = 1, k = 0)$ state ($−74\text{–}78\text{ cm}^{-1}$), with long range multipole-induced dipole contributions only, showing the effect of the Coriolis interactions; these transitions are forbidden without off-diagonal Coriolis terms.

<table>
<thead>
<tr>
<th>Level number</th>
<th>Line strength $\vec{v}/(\text{cm}^{-1})$</th>
<th>Line strength $\vec{v}/(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0376</td>
<td>19.11</td>
</tr>
<tr>
<td>2</td>
<td>0.000401</td>
<td>38.49</td>
</tr>
<tr>
<td>3</td>
<td>0.000950</td>
<td>46.15</td>
</tr>
<tr>
<td>4</td>
<td>0.000234</td>
<td>60.19</td>
</tr>
<tr>
<td>5</td>
<td>0.00105</td>
<td>66.98</td>
</tr>
</tbody>
</table>

Furthermore, the states with $k \neq 0$ are always doubly degenerate, as mentioned in §2. For each transition between degenerate levels only one of the two allowed components has to be calculated.

Still, a large number of individual lines must be evaluated in order to generate the complete spectrum. The potential well is found to support about 260 independent $k \neq 0$ and 80 $k = 0$ van der Waals vibrational levels (i.e. not counting degeneracy and the individual levels in the end-over-end rotational ladders). This leads to about 5600 independent transitions in the far infrared and 11 600 in the mid-infrared. The majority of these are very weak, but, depending on the temperature, there are still many that have appreciable intensity. The total amount of bound states in the potential well is estimated at 8000–8500, using an end-over-end rotational constant $B = 0.075\text{ cm}^{-1}$.

4.2. Nature of the ro-vibrational states of $(N_2)_2$; dominant dipole transitions

The ground $(k = 0)$ state of the $(N_2)_2$ complex is fairly localised around the $D_{2d}$ potential minimum, but it is split by torsional tunneling through the $\phi$

Table 7. Line strengths in $10^{-6} e^2 a_0^2$ for transitions within one rotational envelope, with long range multipole–induced dipole contributions only and with neglect of Coriolis interactions.

<table>
<thead>
<tr>
<th>Level number</th>
<th>Line strength $a$</th>
<th>Line strength $b$</th>
<th>Line strength $c$</th>
<th>Line strength $d$</th>
<th>Line strength $a$</th>
<th>Line strength $b$</th>
<th>Line strength $c$</th>
<th>Line strength $d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.7</td>
<td>5.35</td>
<td>5.37</td>
<td>10.8</td>
<td>−25.18</td>
<td>−25.09</td>
<td>−24.77</td>
<td>−24.58</td>
</tr>
<tr>
<td>2</td>
<td>49.7</td>
<td>24.8</td>
<td>24.8</td>
<td>50.0</td>
<td>−8.40</td>
<td>−8.29</td>
<td>−7.98</td>
<td>−7.81</td>
</tr>
<tr>
<td>3</td>
<td>28.6</td>
<td>14.4</td>
<td>14.3</td>
<td>28.4</td>
<td>−3.31</td>
<td>−3.19</td>
<td>−2.88</td>
<td>−2.70</td>
</tr>
<tr>
<td>4</td>
<td>36.8</td>
<td>18.4</td>
<td>18.4</td>
<td>36.7</td>
<td>7.98</td>
<td>8.11</td>
<td>8.41</td>
<td>8.57</td>
</tr>
<tr>
<td>5</td>
<td>35.3</td>
<td>17.6</td>
<td>17.6</td>
<td>35.3</td>
<td>14.70</td>
<td>14.83</td>
<td>15.12</td>
<td>15.27</td>
</tr>
</tbody>
</table>

† For a transition $I \rightarrow II$ the lowest level of I is taken; level number indicates II levels:

- $a \ B_2^+(J = 2, k = 0)$ ($−49.58\text{ cm}^{-1}$) $\rightarrow A_2^−(J = 1, k = 0)$,
- $b \ B_2^−(J = 1, k = 0)$ ($−49.86\text{ cm}^{-1}$) $\rightarrow A_2^+(J = 0)$,
- $c \ B_2^+(J = 0)$ ($−50.00\text{ cm}^{-1}$) $\rightarrow A_2^−(J = 1, k = 0)$,
- $d \ B_2^−(J = 1, k = 0)$ ($−49.86\text{ cm}^{-1}$) $\rightarrow A_2^+(J = 2, k = 0)$.

According to equation (21) the line strengths should be: $(a) = (d) = 2 \times (b) = 2 \times (c)$.
I.R. spectra of $(N_2)_2$

barrier between the two equivalent $D_{2d}$ minima. Assuming separation between vibrations and rotations, as outlined in §2, the combination of such a pair of vibration-tunneling states with the $k \neq 0$ rotations around the axis R leads to a rotational ladder. The first column of table 8 shows that such a ladder of states with the correct symmetries is actually found in the calculations. Indeed, all the states of this ladder have nearly the same vibrational wave function, which is shown in figure 2 for the ground state. The level structure for a $\varphi$-tunneling $(A_2)_2$ system is explained by Merer and Watson [24].

According to the general selection rules, pure end-over-end rotational transitions are forbidden in ortho-ortho and para-para dimers ($A, B$ symmetry), but they are allowed in mixed ortho-para dimers, i.e. between degenerate $E^+$ and $E^-$ $|k| > 0$ levels. Their line strengths are small, however, e.g. for the $E^+(J = 1, k = 1) \rightarrow E^-(J = 1, k = 1)$ ground state transition the line strength is $0.0114 \times 10^{-6} e^2 a_0^2$. Dividing this value by the rotational factor (21), the vibrationally average dipole moment for ortho-para dimers is estimated to be $\langle \mu_\varphi \rangle = 8.7 \times 10^{-5} e a_0$. This small value of the dipole moment indicates that the asymmetry which is present in the ortho-para dimer (the ortho $N_2$-molecule has only even $j_A$ states and the para $N_2$ only odd $j_B$ states) is not reflected in the ground state wave function. The latter is very similar to the ortho-ortho and para-para ground states. This confirms the fairly rigid $D_{2d}$ structure of the $(N_2)_2$ ground state.

Although this estimated value for the dipole moment of the ortho-para dimer is probably too small to measure the rotational spectrum of this dimer in microwave spectroscopy, we still calculate its rotational constants in order to further characterize the ground state. As mentioned in the previous section, one has to include the Coriolis effects. Introducing these effects by treating $H_{\text{rot vib}}$ (7) as a perturbation is in general not satisfactory. For the ground state it is feasible,

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$J$</th>
<th>$k$</th>
<th>$\epsilon/(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1^+$</td>
<td>0</td>
<td>0</td>
<td>-74.945</td>
</tr>
<tr>
<td>$A_1^-$</td>
<td>0</td>
<td>0</td>
<td>-72.543</td>
</tr>
<tr>
<td>$E^+/E^-$</td>
<td>1</td>
<td>1</td>
<td>-72.763</td>
</tr>
<tr>
<td>$B_2^+/B_2^-$</td>
<td>2</td>
<td>2</td>
<td>-67.877</td>
</tr>
<tr>
<td>$B_2^+/B_2^+$</td>
<td>2</td>
<td>2</td>
<td>-70.056</td>
</tr>
<tr>
<td>$E^+/E^-$</td>
<td>3</td>
<td>3</td>
<td>-63.392</td>
</tr>
<tr>
<td>$A_1^+/A_2^-$</td>
<td>4</td>
<td>4</td>
<td>-56.157</td>
</tr>
<tr>
<td>$A_1^-/A_2^+$</td>
<td>4</td>
<td>4</td>
<td>-54.222</td>
</tr>
<tr>
<td>$E^+/E^-$</td>
<td>5</td>
<td>5</td>
<td>-45.188</td>
</tr>
<tr>
<td>$B_2^+/B_2^-</td>
<td>6</td>
<td>6</td>
<td>-31.831</td>
</tr>
<tr>
<td>$B_2^-/B_2^+$</td>
<td>6</td>
<td>6</td>
<td>-33.584</td>
</tr>
<tr>
<td>$E^+/E^-$</td>
<td>7</td>
<td>7</td>
<td>-18.403</td>
</tr>
</tbody>
</table>

Table 8. Rotational excitations for the van der Waals ground state and first $\theta$-excited state. The level structure for the ground state can be explained on the basis of a prolate symmetric top and torsion ($\varphi$) tunnelling. This model is not appropriate for the first $\theta$-excited vibrational state.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$J$</th>
<th>$k$</th>
<th>$\epsilon/(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^+$</td>
<td>0</td>
<td>0</td>
<td>-60.792</td>
</tr>
<tr>
<td>$E^-$</td>
<td>0</td>
<td>0</td>
<td>-53.685</td>
</tr>
<tr>
<td>$A_1^+/A_2^-$</td>
<td>1</td>
<td>1</td>
<td>-58.032</td>
</tr>
<tr>
<td>$A_1^-/A_2^+$</td>
<td>1</td>
<td>1</td>
<td>-54.612</td>
</tr>
<tr>
<td>$B_2^-/B_2^+$</td>
<td>1</td>
<td>1</td>
<td>-52.535</td>
</tr>
<tr>
<td>$E^+/E^-</td>
<td>2</td>
<td>2</td>
<td>-54.158</td>
</tr>
<tr>
<td>$A_1^-/A_2^+$</td>
<td>3</td>
<td>3</td>
<td>-47.621</td>
</tr>
<tr>
<td>$A_1^-/A_2^+$</td>
<td>3</td>
<td>3</td>
<td>-42.280</td>
</tr>
<tr>
<td>$B_2^-/B_2^+$</td>
<td>3</td>
<td>3</td>
<td>-42.962</td>
</tr>
<tr>
<td>$E^+/E^-</td>
<td>4</td>
<td>4</td>
<td>-37.133</td>
</tr>
</tbody>
</table>
Figure 2. Cuts through ro-vibrational wave functions with $R$ and $\varphi$ fixed at the values specified below. The contours correspond with 10, 30, 50, 70 and 90 per cent of the maximum amplitude (solid curves for positive and dashed curves for negative amplitude). The states are labelled $\Gamma(k, n)$, where $\Gamma$ is the PI(16) symmetry label, $k$ the angular momentum around the intermolecular axis $R$ and $n$ a sequence number for the levels belonging to the same $\Gamma$ and $k$. Shown are the ground state $A^+_1(0, 1)$ ($R = 7.0 \, \text{a.u.,} \ \varphi = 90^\circ$) and the excited levels for which transitions from the ground state are strongest; near-infrared: shifted parallel structure $A^+_2(1, 1)$; mid infrared: $T$-structure $B^+_1(0, 1)$ and $\theta$-excited state $B^+_1(1, 1)$.

Table 9. Rotational and centrifugal constants for $E^+$ and $E^-$, $k = 1$ lowest states from second order perturbation theory.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$B_{k+1}^+$/(MHz)</th>
<th>$B_{k-1}^+$/MHz</th>
<th>$B_1^+$(MHz)</th>
<th>$D_{1j}^+$(kHz)</th>
<th>$B_{k-1}^-$(MHz)</th>
<th>$B_1^-(MHz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$-23.35$</td>
<td>$-53.45$</td>
<td>$2476.50$</td>
<td>$17.78$</td>
<td>$-26.93$</td>
<td>$2503.01$</td>
</tr>
<tr>
<td>20</td>
<td>$-24.49$</td>
<td>$-54.44$</td>
<td>$2474.36$</td>
<td>$18.18$</td>
<td>$-27.33$</td>
<td>$2501.47$</td>
</tr>
<tr>
<td>30</td>
<td>$-25.05$</td>
<td>$-54.62$</td>
<td>$2473.62$</td>
<td>$18.34$</td>
<td>$-27.43$</td>
<td>$2500.81$</td>
</tr>
<tr>
<td>40</td>
<td>$-25.28$</td>
<td>$-54.73$</td>
<td>$2473.27$</td>
<td>$18.43$</td>
<td>$-27.48$</td>
<td>$2500.55$</td>
</tr>
<tr>
<td>50</td>
<td>$-25.35$</td>
<td>$-54.82$</td>
<td>$2473.12$</td>
<td>$18.46$</td>
<td>$-27.47$</td>
<td>$2500.47$</td>
</tr>
</tbody>
</table>

† Number of levels included in perturbation calculation.
‡ Contribution from Coriolis coupling with $k + 1$ states; first order $B^{(1)} = 2553.29 \text{ MHz}$.
§ Idem from coupling with $k - 1$ states.
|| Other columns are the same as for $E^+$. 
however, since this state is sufficiently well separated. Table 9 lists the ground state rotational and centrifugal distortion constants calculated by second order perturbation theory [18, 19].

The picture of a more or less localized $D_{2d}$ structured complex which is tunneling through the $\phi$ barrier, breaks down for the vibrationally excited states. The second column of table 8 shows the energy levels which should correspond with the first $\theta$-bending excited state, in a harmonic oscillator/rigid rotor model according to their symmetry (assuming vibration–rotation separation). However, the large splittings cannot be explained by $\phi$-tunnelling only. Coupling of the various modes becomes important. In general, one might expect the higher states to more and more resemble free internal rotor states. Examining the eigenstates does not confirm this free rotor character, though; the monomer angular momentum states $j_A, j_B$ are strongly mixed. So, the free internal rotor or weak coupling limit does not hold either. The lack of a simple zeroth order picture for $(N_2)_2$ implies that one cannot make reasonable qualitative predictions about its infrared spectrum; all the allowed transitions have to be calculated quantitatively.

### 4.3. Far infrared spectrum

Figure 3 shows the absorption coefficients (19) at low temperature ($T = 2$ K) as a function of frequency using the dipole model of table 2. The calculation included all the allowed transitions as outlined in the previous sections. A Lorentz shape (width parameter $\Gamma = 0.04 \text{cm}^{-1}$) was assumed for each individual line and the Lorentz distributions were summed to obtain the absorption coefficient.

A number of general remarks can be made. The transitions in the para–para dimer are unimportant because of the small statistical weight (see table VI of [7]). Transitions are strongest for $k = 0, 1$ and their intensities decrease rapidly for higher $k$ states. The rotational envelopes are strongly asymmetric, as compared with the ro-vibrational spectra of more rigid molecules. This is a result of

![Figure 3. Calculated far infrared spectrum of the $(N_2)_2$ dimer at low temperature ($T = 2$ K) and high resolution, including the end-over-end rotational structure. The Lorentz line width of each individual line is set at 0.04 cm$^{-1}$; the absorption coefficient is given in arbitrary units. The most intense transitions with their individual rotational branches are labelled as explained in figure 2.](image-url)
Figure 4. Calculated far infrared spectrum of the \((\text{N}_2)_2\) dimer at \(T = 25\,\text{K}\) and low resolution (Lorentz line width 0.2 cm\(^{-1}\)). The complicated structure arises from the (partial) overlap of many individual lines.

the considerable variation of the end-over-end rotational constant \(B\) from state to state (in the range 0.069 to 0.086 cm\(^{-1}\)). In some cases one even observes the band heads familiar from electronic spectra [34]. The irregular structure of the far-infrared spectrum is a result of this phenomenon, together with the irregular spacings between the van der Waals levels.

At low temperature, only transitions from (near) ground state levels are important. In figure 3 one can observe that the strongest transitions are located around 22 cm\(^{-1}\) and 43 cm\(^{-1}\). Figure 2 shows the wave functions for some of the states involved. These excited states can be classified as \(\theta\)-excited or \(T\)-structured states. It is plausible that such states are relatively important for the infrared spectrum since the induced dipole moment adopts its maximum values at those structures.

With increasing temperature, the pattern of the spectrum broadens due to the strong mixing of the various higher excited modes. Figure 4 displays the far infrared spectrum at \(T = 25\,\text{K}\). The occupation at \(-10\) cm\(^{-1}\) and the dissociation limit is then 3 per cent and 1 per cent, respectively, of the ground state occupation, so it is not allowed to use the present calculations for higher temperature spectra. Up to now, no experimental data have been reported on the discrete structure in the far infrared spectrum of nitrogen, which would correspond with the bound dimer transitions. Experiments on collision induced far infrared absorption have been performed at \(T = 124\,\text{K}\) [43] and \(T = 300\,\text{K}\) [41–43]. These temperatures are too high to discriminate the specific contributions from the weakly bound van der Waals dimers. An early attempt to detect \((\text{N}_2)_2\) dimers in molecular beams [49] has failed because the electric dipole moment was found too small to deflect such dimers.

4.4. Mid infrared spectrum

Figure 5 shows the absorption coefficient (19) at low temperature \((T = 2\,\text{K})\) in the region of the monomer stretch frequency (assumed at 2330 cm\(^{-1}\)), using the dipole model of table 3. Compared with figure 3, this spectrum has an intense
end-over-end rotational PQR band. (The spectrum is shown only for frequencies above 2330 cm\(^{-1}\), so only the QR-bands are visible.) These bands are not seen in figure 3 because the Boltzmann factors in equation (19) for the pure end-over-end rotational transitions are nearly equal. If these transitions are accompanied by a monomer stretch transition, \(v = 0 \rightarrow 1\), which is set at 2330 cm\(^{-1}\). The most intense transitions are labelled (see figures 2, 3).

Table 10. Transition strengths in \(10^{-9} e^2 a_0^2\) for \(A_i^+(J = 0) \rightarrow B_j^-(J = 1)\) and \(A_i^+(J = 0) \rightarrow A_j^- (J = 1)\) transitions from the lowest \(A_i^+\) state in ortho \(N_2 (v = 1)\)-ortho \(N_2 (v = 0)\) dimers.

<table>
<thead>
<tr>
<th>Level number</th>
<th>(Q^2)</th>
<th>(\Phi^2)</th>
<th>(2Q \cdot \Phi)</th>
<th>Total</th>
<th>(\Delta k)</th>
<th>(\tilde{\nu}/(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_1^-)</td>
<td>1</td>
<td>9·4</td>
<td>0·8</td>
<td>5·4</td>
<td>15·6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3·97</td>
<td>0·25</td>
<td>1·99</td>
<td>6·21</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1·10</td>
<td>0·0</td>
<td>-0·02</td>
<td>1·08</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2·38</td>
<td>0·92</td>
<td>2·97</td>
<td>6·27</td>
<td>1</td>
</tr>
<tr>
<td>(A_2^-)</td>
<td>1</td>
<td>524</td>
<td>0</td>
<td>-20</td>
<td>505</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>227</td>
<td>0</td>
<td>-14</td>
<td>214</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1·30</td>
<td>0</td>
<td>0·09</td>
<td>1·39</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18·7</td>
<td>0</td>
<td>-1·1</td>
<td>17·6</td>
<td>0</td>
</tr>
</tbody>
</table>

† Contributions as in table 4.

‡ Absolute wavenumber = 2330 ± \(\tilde{\nu}\).
NEAR IR T=25K

Figure 6. Calculated mid infrared spectrum of the (N₂)₂ dimer at \( T = 25 \text{ K} \) and low resolution (Lorentz line width 0.2 cm\(^{-1}\)). The monomer stretch transition \( v = 0 \rightarrow 1 \) is set at 2330 cm\(^{-1}\).

The strongest transitions lie around 17 cm\(^{-1}\). One of the states involved can be classified as a shifted parallel structure (see figure 2). Another strong transition from the ground state goes to the \( A_2^\lambda(J = 1, k = 0) \) state, which has the same doubly \( \phi \)-excited vibrational wave function as the first excited \( A_1^\lambda(J = 0, k = 0) \) state (see figure 4 of [7]). These transitions are forbidden in the far infrared spectrum. Just as the latter spectrum, the pattern broadens and complicates with increasing temperature. Figure 6 shows the mid infrared spectrum at \( T = 25 \text{ K} \).

A gas phase mid infrared spectrum has been measured by Long et al. [33] at \( T = 77 \text{ K} \). The discrete structure on top of the broad collision induced absorption band has been interpreted as the ro-vibrational spectrum of the (N₂)₂ dimer. This spectrum is rather different from figure 5, however. The intense \( P-R \) end-over-end rotation band is clearly observed, but the peak at 9.5 cm\(^{-1}\), which has been assigned [33] to a librational excitation, and the series of bands starting at 25 cm\(^{-1}\), which were ascribed to internal rotations, cannot be seen in figure 5. On the other hand, the experimental spectrum does not show the \( Q \)-band and the structure around 17 cm\(^{-1}\). Several explanations for this discrepancy may be given. First of all, of course, the considerably higher temperature of the measurement, which leads to the population of many higher vibrational and rotational states. The \( Q \)-band at 2330 cm\(^{-1}\) in figure 6 results mainly from the (rotationally excited) van der Waals ground state (see table 8). The occupancy of this state will be less at higher temperature and with the experimental resolution of 1 cm\(^{-1}\) [33] this \( Q \)-band may well become unobservable. At 77 K the occupation number at the dissociation level of (N₂)₂ is estimated to be 25 per cent of the ground state occupation. So, we expect that even continuum states contribute to the experimental spectrum. The high frequency bands go up to 85 cm\(^{-1}\), which is higher than the calculated dissociation energy, thus pointing to the contribution of bound-continuum and, possibly, continuum-continuum transitions. Such contributions may considerably change the appearance of the low temperature spectra (figures 5 and 6). On the other hand, we have found, during our calculations, that changes in the assumed dipole function and especially in the potential will have a strong influence on the calculated spectrum. Both may have to be improved in order to reach agreement with the measured spectrum.
5. Conclusions

The present calculations demonstrate that the infrared spectra of van der Waals dimers, such as \((N_2)_2\), contain detailed information both on the intermolecular potential and on the (interaction induced) dipole moment function. The \((N_2)_2\) dimer has a large number of irregularly spaced ro-vibrational levels. The picture of more or less localized vibrations, separable from the rotations, only applies to the ground state. The amplitudes of vibration are rather large and tunnelling between two different \(D_{2h}\) equilibrium configurations is important even there. In the vibrationally excited states all the normal modes are mixed and coupling, especially with the rotations around the dimer axis \(R\), becomes considerable. On the other hand, higher excited states are still not described by the weak coupling limit of free internal monomer rotations, which applies to \(H_2\)-rare gas and \((H_2)_2\) complexes. A simple picture lacking, the infrared spectrum, can only be obtained from a full calculation including all possible transitions between ro-vibrational states. The errors in the resulting spectrum have three possible sources. First, the intermolecular potential has inaccuracies both in the short range (exchange, charge penetration) \([6]\) and long range (multipole interaction, dispersion) \([37]\) regions. A set of more accurate long range coefficients for \(N_2-N_2\) is already available from recent \(ab\) \(initio\) calculations \([50]\); work on the short range repulsion is in progress \([51]\). Secondly, one must look at the interaction induced dipole moment, especially at the short range overlap contributions which have been determined \([40]\) rather crudely. \(Ab\) \(initio\) calculations may be helpful here too, but they must be pressed hard if the results are to be sufficiently reliable. Fortunately, it seems possible to calculate the most important transition intensities to within a factor of two from the long range multipole-induced dipole moment alone. Finally, there are errors in the dynamical calculations which result from the incomplete bases and the neglect of off-diagonal Coriolis terms. When the experimental data require this, the calculations can be refined, however, as outlined in §3.

The only experimental (mid infrared) spectrum of \((N_2)_2\), which was measured more than ten years ago \([33]\), was taken at rather low resolution (1 cm\(^{-1}\)) and high temperature (77 K). Only one peak was assigned to a localized libration and one series of bands to free internal rotations. From our calculations we expect that actually much more structure should be visible. Furthermore, the experimental spectrum probably contains a substantial contribution from the continuum which will be hard to calculate. We hope that the present study might encourage experimentalists to measure the \((N_2)_2\) infrared, Raman or hyperfine spectrum, preferably at higher resolution and lower temperature, possibly in molecular beams.

References

[34] Herzberg, G., 1950, Spectra of Diatomic Molecules (Van Nostrand).