CONTRIBUTION OF BOUND DIMERS, \((N_2)_2\), TO THE
INTERACTION INDUCED INFRARED SPECTRUM OF NITROGEN

Geert Brocks and Ad van der Avoird

Institute of Theoretical Chemistry
University of Nijmegen
Toernooiveld 6525 Ed Nijmegen, The Netherlands

ABSTRACT

Using the ro-vibrational wave functions from a recent \textit{ab initio} quantum dynamical calculation in combination with an empirical dipole function deduced from the collision induced far infrared spectrum of gaseous nitrogen, we have calculated the intensities of far infrared transitions in \((N_2)_2\) dimers. Employing, moreover, the multipole moment and polarizability derivatives from \textit{ab initio} calculations on \(N_2\) monomers, we have estimated intensities of near infrared transitions. It is demonstrated that the dimer infrared spectra depend sensitively, not only on the intermolecular potential, but also on the different contributions to the \(N_2-N_2\) interaction induced dipole function.

INTRODUCTION

Part of the intensity in collision-induced infrared absorption (CIA) and collision-induced light scattering (CIS) spectra is due to the contributions from bound dimers (Prengel and Cornall, 1976; Birnbaum et al., 1983; Frommhold et al., 1976) or so-called Van der Waals molecules (Blaney and Ewing, 1976). This paper is concerned with the \((N_2)_2\) dimer contributions to the well-known CIA spectra of gaseous nitrogen, both in the far (Bosomworth and Gush, 1965; Dagg et al., 1974; Buontempo et al., 1975) and near (Sheng and Ewing, 1971) infrared regions. Just as is collision induced absorption, dimer absorption is caused by the dipole moment induced via intermolecular interactions. The dimer spectrum should exhibit
a more specific and detailed structure, however, since the monomer rotations and (relative) translations causing the rather broad and featureless bands in collision induced spectra are replaced by discrete dimer vibrations (and overall rotations). In most spectra, which were taken at rather high temperatures, this structure is not visible. In the near infrared nitrogen gas spectrum of Long et al. (1973) it has been resolved, however.

In principle, the structure found in such dimer spectra contains detailed information on the intermolecular potential energy surface and the interaction induced dipole function or the interaction induced polarizability changes. In simpler cases, such as rare gas dimers, (Godfried and Silvera, 1982), rare gas-\(\text{H}_2\) and \(\text{H}_2-\text{H}_2\) complexes (Mc Kellar, 1982; Mc Kellar and Welsh, 1971), where the spectra are well resolved and can be more easily interpreted, it has actually been demonstrated (LeRoy and Van Kranendonk, 1974; LeRoy and Carley, 1980; Verberne and Reuss, 1980, 1981; Waaier et al., 1981; Danby and Flower, 1983) that the positions of the peaks in this spectrum are a most sensitive probe of the potential in the Van der Waals well. Even in these simple systems, it was not possible, though, to deduce the complete intermolecular potential from the infrared spectrum alone, so in a more complex system as \(\text{N}_2-\text{N}_2\) this will be practically excluded. Information from other sources, such as \textit{ab initio} calculations (Van der Avoird et al., 1980), will have to be used. A beautiful example of the application of such calculations has recently been given by Schäfer and Meyer (1984), who have generated the complete low temperature CIA spectrum of \(\text{N}_2-\text{H}_2\). For \(\text{N}_2-\text{N}_2\), a complete intermolecular potential is available from \textit{ab initio} calculations (Berns and v.d. Avoird, 1980; Mulder et al., 1980). The accuracy of this potential has now been tested for several bulk properties: solid state data (Luty et al., 1980), liquid properties (Allnatt, 1983) and virial coefficients (Van Hemert and Berns, 1982), transport properties, depolarized Rayleigh line widths and rotational relaxation coefficients of gaseous \(\text{N}_2\) (Nylund et al., 1984). Recently, this potential has been used by Tennyson and Van der Avoird (1982) to calculate bound ro-vibrational states of \((\text{N}_2)_2\) dimers. In the present paper, we point out how the wave functions resulting from this calculation can be used, together with an empirical dipole function that Poll and Hunt (1981) have extracted from the collision induced far infrared spectrum of gaseous \(\text{N}_2\) (Bosomworth and Gush 1965; Dagg et al., 1974; Buontempo et al., 1975), to compute the far infrared absorption intensities for the \((\text{N}_2)_2\) dimer. Using, moreover, polarizability and multipole moment "derivatives from \textit{ab initio} calculations on \(\text{N}_2\) monomers (Svendsen and Oddershede, 1979; Amos, 1980; Langhoff et al., 1983), we can even estimate the intensities in the near infrared spectrum of \((\text{N}_2)_2\).
(N₂)₂ QUANTUM DYNAMICAL MODEL

The model which has been employed to calculate the bound ro-vibrational states of (N₂)₂ has been described extensively in (Tennyson and v.d. Avoird, 1982). It starts from a Hamiltonian which is exact, with the Born-Oppenheimer separation of electronic and nuclear motion, except by assuming that the monomer stretch vibrations can be decoupled from the dimer "Van der Waals" vibrations. Given the large gap between the monomer fundamental stretch frequency of 2333 cm⁻¹ and the dimer vibration frequencies lying around 20 cm⁻¹ (Tennyson and v.d. Avoird, 1982), this assumption seems to be justified. It is confirmed by the very small shift, 0.1 cm⁻¹, of the monomer fundamental frequency in the (N₂)₂ dimer spectrum (Long et al., 1973). Further justification of the decoupling assumption is provided by explicit tests (Tennyson and Sutcliffe, 1983) on the Van der Waals dimer, He-HF. On the other hand, it proved to be necessary (Tennyson and v.d. Avoird, 1982) for such a "floppy" system as (N₂)₂, to include the centrifugal distortion and Coriolis terms which couple the dimer vibrations and overall rotations.

It was found convenient, for the calculation of matrix elements, to express the Hamiltonian in a body-fixed coordinate system (Brocks et al., 1983) with the z-axis along the dimer axis S = R_AB, which connects the monomer centers of mass. The potential has been expanded in terms of coupled spherical harmonics (v.d. Avoird et al., 1980; Steele, 1963; Egelstaff et al., 1975) depending on the polar angles of the monomer axes, (θₐ, θₐ') and (θ₈, θ₈'). The expansion coefficients, depending on the distance R, are available from ab initio calculations (Berns and v.d. Avoird, 1980; Mulder et al., 1980). The Hamiltonian is diagonalized in the basis:

\[ \chi_n(R) \sum_{j,k} j_A^{j_B} (\theta_A, \phi_A) j_B (\theta_B, \phi_B) D_{M,k} (\alpha, \beta, 0) \]  

(1a)

with the coupled spherical harmonics:

\[ Y_{i,k} = \sum_m Y_{i, m} (\theta_A, \phi_A) Y_{j, k-m} (\theta_B, \phi_B) \]  

(1b)

where (θ, φ) are the end-over-end rotation angles (the polar angles of S, relative to a space-fixed frame) and \( \chi_n(R) \) denotes a set of Morse oscillator type functions suitable for the expansion of bound states in Van der Waals dimers (Tennyson and Sutcliffe, 1982). Although this basis, of which the angular part is also used in close-coupled scattering calculations (Curtiss, 1953; Launey, 1977) is constructed from (normalized) free rotor (Brink and Satchler, 1968) wave functions \( Y_{i, j, m} \), and \( D_{M, k} \), it has been found (Tennyson and v.d. Avoird, 1980) that the lowest ro-vibrational states
of the \((N_2)_2\) dimer are actually localized around the \(D_{2d}\) equilibrium structure dictated by the potential. Characteristic for the "floppyness" of this Van der Waals complex are the large amplitudes of the librational monomer motions, however. Also, the non-negligible probability of tunneling between the two equivalent \(D_{2d}\) structures (related by inversion) and the substantial variation of the vibrational spectrum with the nuclear spin species (ortho/para \(N_2\)) are typical for non-rigid systems (Bunker, 1979). For the higher bound states the dimer vibrations, especially the librations, become increasingly delocalized. On the other hand, the \((N_2)_2\) dimer, on the whole, is much more rigid than rare gas-\(H_2\) or \((H_2)_2\) complexes, which do not possess a localized structure at all; the \(N_2\) monomers behave almost as free internal rotors.

The solution of the secular problem over the basis of Eq. (1) has been considerably simplified and the resulting ro-vibrational states have been classified (Tennyson and v.d. Avoird, 1982) by using the permutation-inversion symmetry group of the \((N_2)_2\) complex. The symmetry also determines the nuclear-spin statistical weights of the various dimer states, composed of ortho/para \(N_2\) monomers, which will be reflected in the spectral intensities of the (allowed) transitions.

FAR-INFRARED SPECTRUM

The induced dipole function for \(N_2-N_2\) pairs which Poll and Hunt (1981) have deduced from the collision induced far infrared spectrum of gaseous \(N_2\), is expressed in terms of coupled spherical harmonics just as the potential and the wave functions in the dynamical calculations of Tennyson and Van der Avoird (1982). Poll and Hunt have used a space-fixed frame, however, but it is easy to rewrite their dipole function in body-fixed coordinates, in terms of the same angular functions used in the basis of Eq. (1):

\[
\mu_{\nu} (r_A^2, r_B^2, R) = 4\pi \sum_{\lambda_A, \lambda_B, \lambda, r} \mathcal{m}_{\lambda_A, \lambda_B, \lambda} (r_A^2, r_B^2, R) \mathcal{y}_{\lambda_A, \lambda_B} (0, \theta_A, \theta_B) \mathcal{y}_{\lambda} (0, a, b, c) \times D^{(1)*}_{\nu, \lambda} (a, b, c)
\]  

(2)

Our expansion coefficients are related to those of Poll and Hunt as:

\[
\mathcal{m}_{\lambda_A, \lambda_B, \lambda} (r_A^2, r_B^2, R) = \sum_{L=\lambda-1}^{\lambda+1} \left( \frac{2L+1}{3} \right)^{\frac{1}{2}} (\lambda \lambda \lambda L) \frac{1}{L} (0, \theta_A, \theta_B) \times A_L (\lambda, \lambda, L, r_A^2, r_B^2, R)
\]  

(3)
with very simple Clebsch-Gordan coefficients \((A, K; L, 0|1, K)\), and they satisfy the following symmetry relations:

\[
m_{A, B, A, K}(r_A, r_B, R) = 0 \text{ if } A_A \text{ and } A_B \text{ are not both even}
\]

\[
m_{A, B, A, K}(r_A, r_B, R) = (-1)^{A + 1} m_{B, A, A, K}(r_B, r_A, R)
\]

\[
m_{A, B, A, K}(r_A, r_B, R) = (-1)^A m_{A, B, A, -K}(r_A, r_B, R)
\]

(4)

Since in the far infrared region the (decoupled) monomer stretch vibrations will not be excited, Poll and Hunt could relate the collision induced absorption intensity to coefficients \(B_i\), depending on \(R\) only, which are defined by averaging \(A_i\) over the monomer vibrational ground states, \(v_A = v_B = 0\). The \(B_i(R)\) coefficients are then obtained by fitting the experimental spectrum. We apply the same averaging procedure to our dipole expansion coefficients:

\[
M_{A, B, A, K}(R) = \langle \phi_0(r_A) \phi_0(r_B) | m_{A, B, A, K}(r_A, r_B, R) | \phi_0(r_A) \phi_0(r_B) \rangle
\]

(5)

which are then expressed in the known \(B_i(R)\) via Eq. (3). The resulting coefficients are collected in Table 1. Thus, the dipole function Eq. (2), is known in terms of the same angular basis Eq. (1), as the ro-vibrational eigenstates. In order to compute the far infrared transition strengths for the \((\text{N}_2)_2\) dimer, we have to evaluate angular matrix elements (generalized Gaunt coefficients (Brink and Satcher, 1968)), which reduce to products of one 9-\(j\) symbol and five 3-\(j\) symbols, and radial matrix elements of the \(M_{A, B, A, K}(R)\) coefficients given in Table 1 over the basis \(\chi_n(R)\), which can be evaluated by numerical integration. Very similar matrix elements have been met already in the dynamical calculations (Tennyson and v.d. Avoird, 1982).

The results for a typical series of symmetry allowed vibrational transitions from the ground state in the most abundant ortho \(\text{N}_2\)-ortho \(\text{N}_2\) species (statistical weight \(21/63 = 1/3\)) are displayed in Table 2. Only the \(J = 0 + 1\) components are given. In order to produce theoretically a complete far infrared spectrum of \((\text{N}_2)_2\), one has to generate many more of such series, starting from the higher vibrational states also, if they are sufficiently populated at the considered temperature. Moreover, one has to include the higher \(J\) states in order to simulate the rotational profiles of the vibrational bands. (The end-over-end rotational constant in the ground state equals \(B_0 = 0.08 \text{ cm}^{-1}\).)
Table 1. Contributions to the N₂-N₂ interaction induced dipole function for both monomers in the vibrational ground state.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>(\lambda_A)</th>
<th>(\lambda_B)</th>
<th>(\Lambda)</th>
<th>(K)</th>
<th>(M_{\lambda_A\lambda_B\Delta K}(R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>quadrupole induction</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>(\frac{9}{2} \alpha_A \alpha_B R^{-4})</td>
</tr>
<tr>
<td>via isotropic polarizability (\alpha)</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>(-\frac{3}{2} \alpha_A \alpha_B R^{-4})</td>
</tr>
<tr>
<td>quadrupole induction</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>(\frac{14}{105} \alpha_A \alpha_B R^{-4})</td>
</tr>
<tr>
<td>via anisotropic polarizability (\gamma)</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>(\frac{14}{105} \alpha_A \alpha_B R^{-4})</td>
</tr>
<tr>
<td>hexadecapole induction</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>(\frac{25}{7} \alpha_A \alpha_B R^{-6})</td>
</tr>
<tr>
<td>via isotropic polarizability (\alpha)</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>(-\frac{10}{7} \alpha_A \alpha_B R^{-6})</td>
</tr>
<tr>
<td>overlap</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>(-\frac{3}{2} \lambda_1 - \frac{3}{2} \lambda_2) \exp[-(R-\sigma)/\rho]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>(-\frac{3}{10} \lambda_1 - \frac{3}{10} \lambda_3) \exp[-(R-\sigma)/\rho]</td>
</tr>
</tbody>
</table>

Empirical parameters:

- Quadrupole moment \(Q\) = \(-1.09 \text{ a.u.}^2\)
- Hexadecapole moment \(\Phi\) = \(-10.4 \text{ a.u.}^4\)
- Isotropic polarizability \((\alpha_0 + 2\alpha_3)/3 = \alpha = 11.92 \text{ a.u.}^3\)
- Polarizability anisotropy \(\alpha_\parallel - \alpha_\perp = \gamma = 4.76 \text{ a.u.}^3\)
- Overlap parameters:
  - \(\sigma\) = \(3.68 \text{ Å}\)
  - \(\rho\) = \(0.11 \sigma\)
  - \(\lambda_1 = \pm 1 \times 10^{-3} \text{ a.u.}^3\)
  - \(\lambda_3 = 1 \times 10^{-3} \text{ a.u.}^3\)
Table 2. Transition strengths $|<\psi|\chi>|^2$ in $10^{-6} e^{2}a_{0}^{2}$ for $A_{1}^{+} (J=0) \rightarrow B_{1}^{-}(J=1)$ transitions\(^a\) from the ground $A_{1}^{+}$ state in ortho $N_2$ – ortho $N_2$ dimers.

<table>
<thead>
<tr>
<th>$\Pi_{1}$ level number</th>
<th>$Q_{2}^{\text{b)}$</th>
<th>$\epsilon_{2}^{\text{b)}}$</th>
<th>$(\lambda_{1},\lambda_{2})^{2}^{\text{b),c)}$</th>
<th>$2Q_{4}^{\text{b)}$</th>
<th>$2(\lambda_{1},\lambda_{2})Q^{\text{c)}$</th>
<th>$2(\lambda_{1},\lambda_{2})\epsilon^{\text{b),c)}$</th>
<th>total without overlap</th>
<th>total(^c)</th>
<th>frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.2</td>
<td>0.8</td>
<td>0.0</td>
<td>0.7</td>
<td>-10.2</td>
<td>-0.61</td>
<td>-0.1</td>
<td>1.5</td>
<td>22.8</td>
</tr>
<tr>
<td>2</td>
<td>5.85</td>
<td>0.25</td>
<td>0.13</td>
<td>0.0</td>
<td>-2.43</td>
<td>-1.78</td>
<td>0.16</td>
<td>0.37</td>
<td>-0.03</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>0.626</td>
<td>0.320</td>
</tr>
<tr>
<td>4</td>
<td>8.37</td>
<td>0.94</td>
<td>0.0</td>
<td>0.38</td>
<td>-5.51</td>
<td>0.17</td>
<td>-0.06</td>
<td>1.19</td>
<td>3.70</td>
</tr>
<tr>
<td>5</td>
<td>5.46</td>
<td>1.47</td>
<td>0.16</td>
<td>0.0</td>
<td>-5.67</td>
<td>-1.88</td>
<td>0.29</td>
<td>0.98</td>
<td>0.15</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>
</tr>
<tr>
<td>7</td>
<td>0.115</td>
<td>0.0</td>
<td>0.0</td>
<td>0.009</td>
<td>-0.004</td>
<td>0.004/-0.063</td>
<td>0.0</td>
<td>0.001</td>
<td>0.111</td>
</tr>
</tbody>
</table>

\(^a\) the symmetry labeling of the $\Pi_{1,2}$ dimer states refers to the permutation-inversion group $S_{4}$ of $C_{1}$, see (Tennyson and v.d. Avoird, 1982)

\(b\) contributions from: pure quadrupole induction ($Q_{2}^{2}$)

pure hexadecapole induction ($\epsilon_{2}^{2}$)

pure overlap terms $(\lambda_{1},\lambda_{2})^{2}$

quadrupole-hexadecapole interference terms $2Q_{4}^{\text{b)}$

quadrupole-overlap interference terms $2(\lambda_{1},\lambda_{2})Q$

hexadecapole-overlap interference terms $2(\lambda_{1},\lambda_{2})\epsilon$

\(^c\) results for $\lambda_{1} = -1. \times 10^{-3} a_{0}$ and $\lambda_{1} = 1. \times 10^{-3} a_{0}$, respectively. (The sign of $\lambda_{1}$ was undetermined (Poll and Hunt, 1981))
Pure end-over-end rotational transitions are forbidden in ortho-ortho and para-para dimers; they occur only in mixed ortho-para dimers (symmetry E\(^{-}\); statistical weight 18/63 = 2/7) with transition strengths (for individual \(J = 0 \rightarrow 1\) transitions) up to 65 \(\times 10^{-16}\) e\(\text{a}^{-1}\). The ground state rotational constant \(B_0\) equals 0.08 cm\(^{-1}\) = 2400 MHz, also for ortho-para dimers, the distortion constant \(D_0\) equals 18 kHz.

Even before finishing the formidable task of generating theoretically a complete far infrared spectrum of \((\text{N}_2)_2\) dimers (Brocks and v.d. Avoird, 1984), one can draw some interesting conclusions already from results as those listed in Table 2. The first observation is that several (also higher) transitions from the ground state obtain comparable intensities. This is in contrast with more rigid molecules with nearly harmonic vibrations, where practically all intensity goes into the fundamental bands, and it is another manifestation of the non-rigid nature of the Van der Waals molecule \((\text{N}_2)_2\) (cf. the previous section).

The second observation is that the intensities of most transitions are substantially affected by the overlap contributions to the induced dipole moment, particularly via the interference with the long range \(R^-\) and \(R^+\) contributions. For comparison we quote the conclusion of Poll and Hunt (1981) that the long range terms cause about 90% of the total intensity in the collision induced nitrogen gas spectrum (85% originates from quadrupolar induction and only 5% from hexadecapolar induction), while the remaining 10% is largely due to the interference between the \(\lambda_3\) overlap term and the quadrupole terms. Such interference terms in general are much more important in the dimer spectrum and they occur also between dipole contributions with different \(\lambda_3, \lambda_2, \lambda_1, L\) because the \(\text{N}_2\) molecules in the dimer are truly interacting via the anisotropic potential. Therefore, it should be possible by looking at the intensities of specific dimer transitions to determine the various induced dipole contributions in more detail, as Dunker and Gordon (1978) have done for some \(\text{H}_2\)-rare gas complexes. In particular, one can try to establish the sign of \(\lambda_3\): for positive \(\lambda_3\), the \(\Delta k = 1\) transitions are most affected by the overlap terms, for negative \(\lambda_3\), the \(\Delta k = 0\) transitions are changed mostly (compare the left/right columns of Table 2; the approximate quantum number \(k\) denotes the projection of the overall angular momentum \(J\) on the dimer axis \(R\)). We close this section by concluding that, in spite of the preceding remarks about the overlap terms being relatively more important than in the continuum spectrum, the transition strengths in the \((\text{N}_2)_2\) dimer can still be calculated to within a factor of two from the long range contributions alone.

NEAR INFRARED SPECTRUM

The structured part of this spectrum due to the discrete tran-
sitions in \( N_2 \) dimers has actually been measured (Long et al., 1973) in the region of the monomer stretch frequency, 2330 cm\(^{-1}\). In order to calculate the infrared absorption intensities in this range, in principle one should know the dependence of the induced dipole expansion coefficients, Eq. (2), on the monomer bond lengths, \( r_A \) and \( r_B \). In practice, however, the monomer vibrations can be de-coupled from the dimer modes and one can make the assumption that the potential between ground state monomers, \( v_{A,v=0}, v_{B,v=0} \), practically does not change when one monomer is excited: \( v_{A,v=1}, v_{B,v=0} \) or \( v_{A,v=0}, v_{B,v=1} \). The latter assumption is expected to hold well for \( N_2 \) molecules as these are very strongly bound and the average bond length hardly changes with (low) vibrational excitations (Herzberg, 1950). For \( H_2 \) the changes are more appreciable (LeRoy and v. Kranendonk, 1974; LeRoy and Carley, 1980).

After these assumptions, one can use the same wave functions calculated by Tennyson and Van der Avoird (1982) for the \( N_2 \) dimer vibrations and rotations, multiplied by the following monomer vibration functions, adapted to the overall permutation-inversion symmetry:

\[
\phi_0(r_A) \phi_0(r_B) \quad \text{for the ground state, } v_{A,v=0} = v_{B,v=0} = 0
\]

\[
2^{-\frac{1}{2}}[\phi_1(r_A) \phi_0(r_B) + \phi_0(r_A) \phi_1(r_B)] \quad \text{for the excited states lying around 2330 cm}^{-1}
\]

Moreover, the monomer stretch functions \( \phi_0(r) \) and \( \phi_1(r) \) to a very good approximation may be replaced by harmonic oscillator functions (Svendsen and Oddershede, 1979). Expanding the dipole functions as Taylor series in \( \Delta r_A = r_A - r_{A,eq} \) and \( \Delta r_B = r_B - r_{B,eq} \), what one needs to know then are the first derivatives of the dipole expansion coefficients \( m_{\lambda_A,\lambda_B,L,K}(r_A, r_B, R) \) with respect to \( r_A \) or \( r_B \), taken at the equilibrium bonds lengths, \( r_{A,eq} \) and \( r_{B,eq} \). In general, these derivatives are not known, but we invoke the last conclusion of the previous section, that the long range induced dipole contributions alone are sufficient to compute the infrared intensities to within a factor of two, and restrict ourselves to those contributions, then they can be calculated. What is required are the first derivatives of the \( N_2 \) quadrupole (Q) and hexadecapole (P) moments and the anisotropic polarizability (\( \alpha, \gamma \)) with respect to the bond length \( r \). These data are available from accurate ab initio calculations (Svendsen and Oddershede, 1979; Amos, 1980; Langhoff et al., 1983); the polarizability derivatives have been compared with Raman intensities. The final factors

\[ N_{\lambda_A,\lambda_B,L,K}(R) \]
Table 3. Contributions to the $N_2-N_2$ 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>$\kappa$</th>
<th>$N_{\lambda_A \lambda_B \Lambda \kappa}(R)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>quadrupole induction via isotropic polarizability $a$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>(9/10) $\frac{d\sigma_B}{dr_B} \pm \frac{d\sigma_B}{dr_A} R^{-4} \langle \Delta r \rangle_{01}$</td>
</tr>
<tr>
<td>quadrupole induction via anisotropic polarizability $\gamma$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>(3/10) $\frac{d\gamma_B}{dr_B} \pm \frac{d\gamma_B}{dr_A} R^{-4} \langle \Delta r \rangle_{01}$</td>
</tr>
<tr>
<td>hexadecapole induction via isotropic polarizability $a$</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>(25/18) $\frac{d\phi_B}{dr_B} \pm \frac{d\phi_B}{dr_A} R^{-6} \langle \Delta r \rangle_{01}$</td>
</tr>
</tbody>
</table>

The $N_2$ 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 $(\frac{1}{2\mu_i}) \langle \kappa_i \rangle$, with reduced mass $\mu=7$ amu and fundamental frequency $\nu=2330$ cm$^{-1}$

Ab initio parameters (Amos, 1980)

\[
\frac{d\sigma}{dr}_{\text{eq}} = 1.15 \text{ esu} \\
\frac{d\sigma}{dr}_{\text{eq}} = -2.53 \text{ esu}^3 \\
\frac{d\phi}{dr}_{\text{eq}} = 5.8 \text{ esu}^2 \\
\frac{d\phi}{dr}_{\text{eq}} = 6.5 \text{ esu}^2
\]
Table 4. Transition strengths in $10^{-9} \text{e}^2 \text{a}^{-2}$ for $A_4^+(J=0) + B_5^-(J=1)$ transitions\(^a\) from the lowest $A_4^+$ state in ortho $N_2$ (v=1) - ortho $N_2$ (v=0) dimers

<table>
<thead>
<tr>
<th>$B_1$ level number</th>
<th>$Q^2$(^b)</th>
<th>$\phi^2$(^b)</th>
<th>$2Q \phi$(^b)</th>
<th>total</th>
<th>$\Delta k$</th>
<th>$\nu (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.4</td>
<td>0.8</td>
<td>5.4</td>
<td>15.6</td>
<td>1</td>
<td>22.1</td>
</tr>
<tr>
<td>2</td>
<td>3.97</td>
<td>0.25</td>
<td>1.99</td>
<td>6.21</td>
<td>0</td>
<td>25.1</td>
</tr>
<tr>
<td>3</td>
<td>1.10</td>
<td>0.0</td>
<td>-0.02</td>
<td>1.08</td>
<td>1</td>
<td>33.1</td>
</tr>
<tr>
<td>4</td>
<td>2.38</td>
<td>0.92</td>
<td>2.97</td>
<td>6.27</td>
<td>1</td>
<td>42.0</td>
</tr>
<tr>
<td>5</td>
<td>3.77</td>
<td>1.45</td>
<td>4.67</td>
<td>9.89</td>
<td>0</td>
<td>46.5</td>
</tr>
<tr>
<td>6</td>
<td>0.240</td>
<td>0.061</td>
<td>0.241</td>
<td>0.542</td>
<td>1</td>
<td>47.5</td>
</tr>
<tr>
<td>7</td>
<td>0.0526</td>
<td>0.0</td>
<td>0.0026</td>
<td>0.0552</td>
<td>1</td>
<td>53.9</td>
</tr>
</tbody>
</table>

\(^a\) symmetry labeling as in Table 2

\(^b\) contributions from:
- pure quadrupole induction ($Q^2$)
- pure hexadecapole induction ($\phi^2$)
- quadrupole-hexadecapole interference terms $2Q \phi$

\(^c\) absolute frequency = 2329.7 ± $\nu$
applied in calculating the near infrared intensities in the \((N_2)_2\) dimer, which replace the

\[ M_{A_iA_j} \cdot A_k(R) \]

factors (Table 1) used for the far infrared transitions, are given in Table 3.

Looking at the same series of dimer transitions \(A_i^+(J=0) \rightarrow B_i^-(J=2)\) in ortho \(N_2-\)ortho \(N_2\) as in Section 3, we find the results presented in Table 4.

These transitions now occur as side-bands to the monomer transition at 2330 cm\(^{-1}\), which is practically not shifted (0.1 cm\(^{-1}\)) in the dimer. These \(A_i^+ \rightarrow B_i^-\) transitions are allowed when the excited state monomer wave function (6) has the plus sign; this plus sign reappears in the coefficients of Table 3 which are used to calculate intensities. In addition to these transitions, other dimer transitions from the \(A_i^+\) ground state become allowed: \(A_i^+(J=0) \rightarrow A_i^+(J=1)\), \(A_i^+(J=1) \rightarrow A_i^+(J=2)\), \(A_i^+(J=2) \rightarrow A_i^+(J=3)\), etc. Such transitions correspond with the minus signs in Eq. (6) and Table 3, and they are forbidden in the far infrared region. Their intensities are listed in Table 5.

Comparing the results of Table 4 and Table 5 with those in Table 2 we can draw the following conclusions. Generally, the near infrared transition strengths are about 1000 times smaller than the far infrared values. This is mainly determined by the size of the monomer transition strength \(\frac{|\langle \phi_2 | \Delta \phi | \phi_1 \rangle|^2}{\epsilon} = 0.00185 \, \text{cm}^{-1}\). The variations in the individual ratios for corresponding \(A_i^+ \rightarrow B_i^-\) transitions in the far and near infrared are much smaller, but still significant. This can be understood if one realizes that the first term in Tables 1 and 3 yields the dominant contribution to the far and near infrared line strength, respectively; the contributions from the other long range terms are not negligible, however, and those terms have opposite signs in Tables 1 and 3. The intensities of \(A_i^+ \rightarrow A_i^+\) transitions which are forbidden in the far infrared, are even larger than those of the \(A_i^+ \rightarrow B_i^-\) transitions. The first term from Table 3 is clearly dominant here. The first \(A_i^+ \rightarrow A_i^+\) transition is a pure end-over-end rotational (\(J = 0 \rightarrow 1\)) transition. This transition is stronger than the vibrational ones, just as we have found for the ground state (previous section); it forms part of the P and R branches observed by Long et al., (1973). In the ground state such rotational transitions are allowed only for mixed ortho-para dimers, however, whereas here they occur also in the homogeneous, ortho-ortho and para-para, complexes.

CONCLUSIONS

The present calculations have shown that the structure in the collision induced far and near infrared spectra which is due to dimer contributions contains detailed information, not only on the inter-
Table 5. Transition strengths in $10^{-9} e^2 a_0^2$ for $A_1^+(J=0) + A_2^-(J=1)$ transitions a) from the lowest $A_1^+$ state in ortho $N_2 (v=1)$ - ortho $N_2 (v=0)$ dimers

<table>
<thead>
<tr>
<th>$A_2$ level number</th>
<th>$Q_{2b)}$</th>
<th>$\delta_{2b)}$</th>
<th>$2Q_{2b)}$</th>
<th>total</th>
<th>$\Delta k$</th>
<th>$\nu (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0</td>
<td>-20</td>
<td>505</td>
<td>0</td>
<td>0.165</td>
</tr>
<tr>
<td>2</td>
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<td>0</td>
<td>-14</td>
<td>214</td>
<td>1</td>
<td>16.8</td>
</tr>
<tr>
<td>3</td>
<td>1.30</td>
<td>0</td>
<td>0.09</td>
<td>1.39</td>
<td>0</td>
<td>17.1</td>
</tr>
<tr>
<td>4</td>
<td>18.7</td>
<td>0</td>
<td>-1.1</td>
<td>17.6</td>
<td>0</td>
<td>22.1</td>
</tr>
<tr>
<td>5</td>
<td>4.64</td>
<td>0.02</td>
<td>-0.55</td>
<td>4.10</td>
<td>1</td>
<td>30.1</td>
</tr>
<tr>
<td>6</td>
<td>5.53</td>
<td>0.03</td>
<td>-0.81</td>
<td>4.75</td>
<td>0</td>
<td>33.3</td>
</tr>
<tr>
<td>7</td>
<td>28.5</td>
<td>0.1</td>
<td>-3.4</td>
<td>25.1</td>
<td>1</td>
<td>35.9</td>
</tr>
</tbody>
</table>

a) symmetry labeling as in Table 2
b) contributions as in Table 4
c) absolute frequency = 2329.7 ± V
molecular potential, but also on the interaction induced dipole function. In order to extract this information from the spectra and, in particular, to evaluate the importance of different contributions to the induced dipole, one first has to interpret the dimer spectra. This task is very difficult indeed, because Van der Waals complexes such as the \( (N_2)_2 \) dimer are too "floppy" to apply the more or less standard models for the dynamics of rigid molecules, on the one hand, while, on the other hand, they are substantially more rigid than \( (N_2)_2 \) dimers, where the infrared spectrum becomes relatively simple again due to the nearly free internal \( H_2 \) rotations. Calculations as the present one can be very helpful with this interpretation. Further work in trying to generate a complete infrared spectrum of the \( (N_2)_2 \) dimer including all the bound-to-bound vibrational transitions with their rotational profiles, is in progress (Brocks and v.d. Avoird, 1984). We think that it would be profitable also if one could (re)measure the near and far infrared spectra of \( (N_2)_2 \), with higher resolution and/or sensitivity (at lower temperatures, possibly in molecular beams), because we expect that actually more transitions should be visible than those found by Long et al. in 1973.

REFERENCES

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Schäfer, J., and Meyer, W., 1984, this volume.

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