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Quantum dynamics of the van der Waals molecule \((\text{N}_2)_2\): An \textit{ab initio} treatment

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Starting with an available \textit{ab initio} \(N_2-N_2\) potential, which favors a crossed equilibrium structure for the \((\text{N}_2)_2\) dimer with well depth \(D_e = 122 \text{ cm}^{-1}\), \(R_e = 3.46 \text{ Å}\), and barriers to internal rotations of 25 and 40 \text{ cm}^{-1}\), we calculate the bound rovibrational states of this dimer for \(J = 0, 1, 2\). This is done by solving a secular problem over the exact (rigid monomer) Hamiltonian including centrifugal distortions and Coriolis interactions, using a product basis of radial (Morse oscillator) functions and angular momentum eigenfunctions. The full permutation-inversion symmetry of the system, in relation to the nuclear spin coupling, is used in order to simplify the calculations and to derive selection rules for IR absorption. We find that the \((\text{N}_2)_2\) dimer has a large number of bound rovibrational states (92 already for \(J = 0\)). These are analyzed by correlation with rigid molecule (harmonic oscillator/rigid rotor) results, on the one hand, and with the states of two freely rotating \(N_2\) monomers, on the other, and by plotting some characteristic vibrational wave functions. In the ground state, the vibrations are nearly harmonic, with a small tunneling splitting; the dissociation energy \(D_0\) ranges from 74.9 \text{ cm}^{-1} for \(oN_2-oN_2\) to 80.5 \text{ cm}^{-1} for \(pN_2-pN_2\), the mean distances \(\langle R \rangle\) equal 3.79 and 3.76 \text{ Å}, respectively. In the lower vibrationally excited states, the monomer rotations are still locked in, but strongly anharmonic and coupled, also with the dimer stretch. With increasing energy, the internal rotations become successively delocalized in the different angles, starting with the torsion \(\phi\) about \(R\). The resulting energy level diagram is so complex that it is hard to discover regularities. The results are compared with the experimental IR spectrum.

I. \textbf{INTRODUCTION}

The study of van der Waals dimers such as \((\text{N}_2)_2\) is interesting for three related reasons. Firstly, the rovibrational spectra of such van der Waals molecules, mostly prepared in supersonic nozzle beams, contain detailed and accurate information on the anisotropic intermolecular potentials,\(^1\) especially in the physically important region of the van der Waals minimum. The knowledge of these potentials is crucial for describing all kinds of properties of molecular matter in its various phases (gas, liquid, and liquid, plastic or ordered crystal). It is practically impossible to extract the potentials directly from the measured spectra, except for atomic dimers,\(^2\) but if potentials are available from other sources, they can be very sensitively tested against the spectra of van der Waals molecules. Or, if one assumes potentials that depend on a few parameters, these parameters can be accurately determined by comparison with the experimental spectra.\(^1,3,4\) Such a comparison actually involves so-called dynamical calculations of the rovibrational states of the system, starting from the assumed potential.

Second, the study of diatom–diatom van der Waals molecules like \((\text{N}_2)_2\) is important as the (quantum) dynamical problem just mentioned can be solved very accurately (to greater accuracy than the potentials), although this is certainly not easy. The method that we apply for these calculations is based on the close-coupling scheme,\(^5\) \textit{i.e.}, the wave functions for the overall rotations and the bending vibrations (monomer rotations) are expanded in angular momentum eigenfunctions (symmetric top functions and spherical harmonics)\(^6\). However, instead of solving the coupled differential equations for the radial problem, we have used a radial basis set, in the spirit of Le Roy and Van Kranendonk\(^7\) (but not a numerical one) and solved the complete secular problem over the Hamiltonian, retaining all rovibrational coupling terms. In order to make the distinction with the usual close-coupling method and with other variational methods,\(^8\) one might call this scheme the LC-RAMP (Linear Combination of Radial and Angular Momentum Products) method. Up to now, the only "floppy" molecules that have been treated to this level of exactness are diatomics and the following triatomic systems: noble gas–\(\text{H}_2\),\(^1,3,7,9,10\) \(\text{H}_2\),\(^11\) \(\text{Ar–HCl}\),\(^12–14\) \(\text{H}_2\text{O}\),\(^13,15\) and \(\text{KCN}\).\(^10,16\) The only diatom–diatom species treated by similar methods are \((\text{H}_2)_2\)\(^17,18\) and \((\text{HF})_2\),\(^19\) but in both cases approximations have been made in order to reduce the size of the secular problem. For \((\text{H}_2)_2\) the coupling of different angular basis functions has been neglected,\(^17,18\) which is justified only for \(\text{H}_2\), and in the (HF)\(_2\) case the BOARS approximation\(^20\) has been used,\(^19\) which separates the radial from the angular coordinates.

Even for strongly bound molecules accurate dynamical calculations are difficult.\(^6\) We only know of two variational calculations on tetraatomic systems, \(\text{H}_2\text{CO}\)\(^21\) and \(\text{H}_2\text{CS}\),\(^12\) using Watson’s Hamiltonian for nonlinear molecules.\(^23\) This approach is not suitable for the floppy van der Waals molecules, however.\(^16\) For larger molecules one is obliged to use drastic approximations, such as the harmonic oscillator-rigid rotor model.

Accurate dynamical calculations imply that no information is lost when calculating the rovibrational spectrum from the assumed potential, so that any discrepancy between the observed and the calculated spectra can be ascribed to this potential. In studies of solid state properties such as phonon frequencies, which are also believed to depend sensitively on the anisotropic intermolecular potentials, the route from the potentials to the calculated crystal properties is much more com-
plex and involves various approximations. Here we refer not only to the assumption of pairwise additivity of the intermolecular potentials, but also to the approximations that occur in the lattice dynamics treatment of the solid (the use of harmonic models, sometimes with perturbational or self-consistent corrections for anharmonicity, or models based on a mean field approach). Van der Waals dimers such as \( \text{(N}_2 \text{)}_2 \), for which we present an almost exact solution of the dynamical problem, i.e., including the coupling (correlation) between the various vibrational modes (translational vibrations, librations, or hindered rotations of the monomers) and their anharmonicities, may be a good testing ground for the more approximate dynamical models used in solids.

This brings us to the third reason for studying van der Waals dimers, which may be summarized by saying that a van der Waals dimer can be considered as the smallest typical unit from a molecular solid. Although it lacks the collective properties, it can certainly show characteristic features. For example, there is the possibility of transitions from low lying vibrational states of the dimer, with localized librations of the monomers, to higher levels, where the monomers exhibit large amplitude hindered or even almost free rotations. Such transitions, when studied as a function of temperature, will reflect in some respects the orientational order–disorder phase transitions in molecular crystals. And, since we can retain in the dimer all the correlations between the monomer librations or internal rotations and the translational (dimer stretch) vibrations, this could provide useful insight into the nature of these transitions. We can also compare the results of the quantum dynamical calculations with classical Monte Carlo or molecular dynamics calculations, which can then be applied to larger molecular clusters and to solids and liquids.

The reasons given for studying van der Waals dimers apply in particular to the \( \text{(N}_2 \text{)}_2 \) species, since there is great interest in the \( \text{N}_2–\text{N}_2 \) intermolecular potential for describing gas, liquid, and solid state properties. Much experimental and theoretical work has been done especially on solid nitrogen which has three different crystal phases; the ordered \( \alpha \) and \( \gamma \) phases at low and high pressure, respectively, and temperatures below 35 K, and the plastic (orientationally disordered) \( \beta \) phase above this temperature. Several \( \text{N}_2–\text{N}_2 \) model potentials have been proposed and tested via lattice dynamics calculations and comparison of the calculated lattice structure and phonon frequencies with experimental results.

Recently a detailed anisotropic \( \text{N}_2–\text{N}_2 \) potential has been obtained from \textit{ab initio} calculations. This potential has been utilized in a calculation of the lattice structure and dynamics of \( \alpha \) and \( \gamma \) \( \text{N}_2 \) crystals; the dynamics were obtained both in the harmonic model and by the self-consistent phonon (SCP) method which corrects for anharmonic effects in the lattice modes. The calculated structure, the cohesion energy and the phonon frequencies, in particular for the translational modes, are in very good agreement with experiment.

The SCP correction for anharmonicity leads to an essential improvement of the (translational) phonon frequencies. Also the pressure dependence of these frequencies is reproduced realistically. The librational phonon frequencies are somewhat too high, even after the anharmonicity corrections by the SCP model, and the softening of these modes with increasing temperature, especially near the \( \alpha–\beta \) phase transition, is not sufficiently reproduced. However, it is primarily the dynamical (SCP) model which has to be blamed for this discrepancy.

Thus, it would be interesting to see how well this \textit{ab initio} potential predicts the properties of the \( \text{(N}_2 \text{)}_2 \) dimer. At this moment, there is only one (IR) spectrum of \( \text{(N}_2 \text{)}_2 \) available; it has been measured in the gas phase at 77 K in the region of the monomer stretch frequency at 2330 cm\(^{-1}\) with a resolution of about 1 cm\(^{-1}\). Although it has been interpreted only globally, it gave rise to interesting conclusions about the rotational mobility of the \( \text{N}_2 \) monomers. We expect that more measurements on \( \text{(N}_2 \text{)}_2 \), in molecular beams at lower temperature, will soon be made. Actually, we hope that the present study will stimulate such measurements and facilitate the interpretation of the spectra. At the same time, this study is of methodological importance since the dynamical problem for the \( \text{(N}_2 \text{)}_2 \) dimer is one of the most complex cases studied so far, and the results can throw light on the nature of the internal rotations of the \( \text{N}_2 \) monomers in the dimer, but also in the solid.

II. \( \text{N}_2–\text{N}_2 \) POTENTIAL FROM \textit{AB INITIO} CALCULATIONS

The \textit{ab initio} calculations leading to the \( \text{N}_2–\text{N}_2 \) potential have been described in Refs. 32 and 33. The following contributions have been included: (first order) electrostatic multipole–multipole interactions, all \( R^2 \), \( R^{-1} \), and \( R^{-3} \) terms; (second order) induction, multipole-induced multipole interactions, all \( R^{-4} \) and \( R^{-10} \) terms; (second order) London dispersion interactions, all \( R^{-6} \), \( R^{-8} \), and \( R^{-10} \) terms; (first order) charge penetration and exchange effects due to overlap between the monomer wave functions. The induction terms appear to be negligibly small. The dominant anisotropic contribution to the potential in the region of the van der Waals minimum is not given by the quadrupole–quadrupole interaction, as it has often been thought, but rather by the short-range exchange repulsion.

The geometry of the \( \text{(N}_2 \text{)}_2 \) dimer is determined by the vector \( \mathbf{R} \) pointing from the center of mass of molecule A to that of molecule B and by vectors \( \mathbf{r}_A \) and \( \mathbf{r}_B \) defining the orientations of the monomer axes (their lengths, \( r_A \) and \( r_B \), fixing the monomer internuclear distances), see Fig. 1. The body fixed frame that we have chosen to formulate the dynamical equations for the dimer has its \( x \) axis lying along \( \mathbf{R} \); the orientations of \( \mathbf{r}_A \) and \( \mathbf{r}_B \) are determined relative to this frame by the polar angles \( (\theta_A, \phi_A) \) and \( (\theta_B, \phi_B) \), respectively.

The intermolecular potential between two (rigid) diatomics is expressed in the form of a spherical expansion:

\[ V(\theta_A, \phi_A, \theta_B, \phi_B) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V^{\ell}_{m} \mathbf{Y}_{\ell}^m(\theta_A, \phi_A) \mathbf{Y}_{\ell}^{-m}(\theta_B, \phi_B) \]
For the latter, the short-range coefficients have been quadrature; 36 additional points gave their distance structure (just as it leads to a T-shaped equilibrium structure

\[ \text{FIG. 1. Body-fixed coordinate system, } \phi = \phi_A - \phi_B. \]

of the short-range anisotropic potential. It appeared that for \( N_2-N_2 \) anisotropic terms up to \( L_A = L_B = 4 \) inclusive are important. Actually some higher terms were included. The expansion coefficients \( v_{LA,LB,L}(R) \) in Eq. (1) are composed of long-range and short-range contributions. The long-range contributions, which are power series in \( R^{-1} \), were directly obtained from the multipole expanded electrostatic and dispersion energies (after some recoupling for the latter). The short-range coefficients have been calculated at \( R = 3 \text{ Å} \) from the \textit{ab initio} results at 105 different angle combinations \((\theta_A, \phi_A, \phi_B)\) by numerical quadrature; 36 additional points gave their distance dependence as \( \exp(-\alpha - \beta R - \gamma R^2) \). All parameters that characterize potential (1) are given in Ref. 33.

From this potential it follows that the equilibrium structure of the \( (N_2)_2 \) dimer is a crossed one \( (\theta_A = \theta_B = 90^\circ) \) with \( R_m = 3.46 \text{ Å} \) and a well depth of 1.5 kJ/mol = 122 cm\(^{-1}\). This configuration is mainly caused by the dominant anisotropic effect of the short-range exchange repulsion which favors a "closed packed" structure (just as it leads to a T-shaped equilibrium structure for \( \text{Ar}-N_2^2 \)). The dimer will be floppy with respect to bending vibrations (monomer rotations) since the barriers to such internal rotations are low: 25 cm\(^{-1}\) for a rotation over \( \phi \) through the parallel structure \( (\theta_A = \theta_B = 90^\circ, \phi = 0^\circ, R_m = 3.6 \text{ Å}) \) and 40 cm\(^{-1}\) for a rotation over \( \theta_A \) or \( \theta_B \) through the T-shaped structure \( (\theta_A = 90^\circ, \theta_B = 0^\circ, R_m = 4.2 \text{ Å}) \). The latter bending mode especially will strongly couple with the dimer stretch mode, due to the large variation in the equilibrium distance. The solution of the dynamical problem is discussed in the following sections.

III. METHOD

The nuclear dynamics problem of the nitrogen dimer has been solved in body-fixed coordinates; \( R \) the vector connecting the centers of mass of the two \( N_2 \) monomers, being embedded along the \( z \) axis. The Euler angles \( \beta \) and \( \alpha \) which describe the overall rotations of the body-fixed frame relative to the space-fixed one, are the same as the polar angles \((\beta, \alpha)\) of \( R \) in space-fixed coordinates. Actually one needs a third Euler angle \( \gamma \) to fully "body-fix" the coordinates; this angle could be chosen as \( \gamma = \phi_B \) (cf. Ref. 10) when the internal angular coordinates would be \( \theta_A, \phi_B \) and \( \phi = \phi_A - \phi_B \). We find it convenient to retain \( \phi_A \) and \( \phi_B \) as "internal" coordinates which better reflect the symmetry of the system. One must realize, however, that the true internal coordinate is \( \phi \) and that kinetic energy terms comprising internal coordinates \( \phi_A \) and \( \phi_B \) in fact contain rotation-vibration coupling terms. If all such terms are included, however, this does not present a problem.

Following Dyke, Howard, and Klemperer, the translation-free Hamiltonian for the interaction of two diatomic molecules can be written in these coordinates as

\[ H_{BF} = \frac{1}{2\mu_R} \left[ (\mathcal{H}_s - \mathcal{G}) + (\mathcal{H}_s - \mathcal{G})^2 \right] + \frac{1}{2\mu_P} \left[ \sin \theta_A P_{\theta A} + \frac{1}{\sin^2 \theta A} \right] \]

\[ \sin \theta_B P_{\theta B} + \frac{1}{2\mu_P} \left[ \sin \theta_B P_{\theta B} \right] + \frac{1}{\sin^2 \theta_B} \left[ \sin \theta_B P_{\theta B} \right] + V, \]

where

\[ \frac{1}{\mu} = \frac{1}{m_1 + m_2} + \frac{1}{m_3 + m_4}, \]

\[ \frac{1}{\mu_A} = \frac{1}{m_1 + m_2}; \quad \frac{1}{\mu_B} = \frac{1}{m_3 + m_4}. \]

and \( V \) is the potential, \( P_\alpha \) is the momentum conjugate to \( \alpha \) and \( \mathcal{J}_s \) and \( \mathcal{J}_f \) are components of the total angular momentum relative to the body-fixed \( z \) axis and

\[ \mathcal{G}_s = -\sin \phi_A P_{\phi A} - \cos \theta_A \cos \phi_A P_{\phi A} - \sin \phi_B P_{\phi B} - \cos \theta_B \cos \phi_B P_{\phi B}, \]

\[ \mathcal{G}_f = \cos \phi_A P_{\phi A} - \cos \theta_A \sin \phi_A P_{\phi A} + \cos \phi_B P_{\phi B} - \cos \theta_B \sin \phi_B P_{\phi B}. \]

This Hamiltonian can be expressed more compactly using formal angular momentum operators

\[ \mathcal{H} = \frac{R^2}{2\mu_R} \frac{\partial^2}{\partial R^2} R - \frac{R^2}{2\mu_A \mathcal{R}_A} \frac{\partial^2}{\partial \mathcal{R}_A^2} R - \frac{R^2}{2\mu_B \mathcal{R}_B} \frac{\partial^2}{\partial \mathcal{R}_B^2} R + \frac{1}{2\mu_A \mathcal{R}_A} \frac{\partial^2}{\partial \mathcal{J}_A^2} R + \frac{1}{2\mu_B \mathcal{R}_B} \frac{\partial^2}{\partial \mathcal{J}_B^2} R + \frac{1}{2\mu_P} (\mathcal{J}_s - \mathcal{J}_f)^2 + V, \]

where

\[ \mathcal{J} = \mathcal{J}_A + \mathcal{J}_B, \]

and the operators \( \mathcal{J}_A \) and \( \mathcal{J}_B \) are associated with \((\theta_A, \phi_A)\) and \((\theta_B, \phi_B)\), respectively.

This Hamiltonian can also be derived from the Hamiltonian for two interacting diatomics in space-fixed coordinates.
\[ \hat{H}_{\text{af}} = -\frac{\hbar^2}{2\mu_X} \frac{\partial^2}{\partial x^2} + \frac{\hbar^2}{2\mu_Y} \frac{\partial^2}{\partial y^2} + \frac{\hbar^2}{2\mu_Z} \frac{\partial^2}{\partial z^2} + V, \]  
(10)

where \( \hat{J}^2 \) acts on \( (\beta, \alpha) \), the polar angles of \( \mathbf{R} \) relative to the space-fixed axis, and the diatomic Hamiltonians are

\[ \hat{H}_X = -\frac{\hbar^2}{2\mu_X} \frac{\partial^2}{\partial x^2} + \frac{\hbar^2}{2\mu_Y} \frac{\partial^2}{\partial y^2} + \frac{\hbar^2}{2\mu_Z} \frac{\partial^2}{\partial z^2} + V, \]
(11)

Following the procedure developed for atom–diatom systems, \[ \text{[Eq. (10)]} \] can be transformed into Eq. (8) using the relationship

\[ \hat{J} = \hat{J}_A - \hat{J}_B = \hat{J} - \hat{J}_0, \]
(12)

In the "body-fixed" coordinate system introduced in the first paragraph of this section, the components of the total angular momentum operator \( \hat{J} \) read:

\[ \hat{J}_x = \frac{\hbar}{i} \left[ \cot(\theta) \frac{\partial}{\partial \phi_A} + \frac{\partial}{\partial \phi_B} - \frac{1}{\sin \beta} \frac{\partial}{\partial \delta \alpha} \right], \]
(13a)

\[ \hat{J}_y = \frac{\hbar}{i} \frac{\partial}{\partial \alpha}, \]
(13b)

\[ \hat{J}_z = \frac{\hbar}{i} \left[ \frac{\partial}{\partial \phi_A} + \frac{\partial}{\partial \phi_B} \right]. \]
(13c)

This leads to anomalous commutation relations.

The fundamental stretching frequency of \( \text{N}_2 \) is 2330 cm\(^{-1}\). \( \text{[48]} \) This is well separated from the dimer modes which can be expected to lie below 100 cm\(^{-1}\). This suggests that a separation between high and low energy vibrational coordinates can be made. This approximation has often been used\(^{49-51,7,9-20}\) and has recently been shown to hold very well for atom–diatom vander Waals systems.\(^{49}\) Accordingly, we have treated the two diatoms as rigid; this has consequences for the symmetry which we will return to.

For rigid homonuclear diatomics with \( r_A = r_B = r_0 \) and \( \mu_A = \mu_B = \mu_H \), the body-fixed Hamiltonian (8) reduces to

\[ \hat{H} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{2\mu} \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \right) + V(R, \theta_A, \theta_B, \phi). \]
(14)

This Hamiltonian represents a collision complex formed by two diatomics. In this work we are interested in the bound states of such a complex.

Suitable basic functions for Eq. (14) are

\[ R^{-1} \chi_n(R) Y_{lA}^{\lambda \mu} \left( \theta_A, \phi_A \right) Y_{lB}^{\lambda \mu} \left( \theta_B, \phi_B \right) D_{\delta \alpha}^{\kappa \lambda \mu} \left( \alpha, \beta, 0 \right), \]
(15)

with

\[ Y_{lA}^{\lambda \mu} = \sum_{m} Y_{lA,m} \left( \theta_A, \phi_A \right) Y_{lB,m} \left( \theta_B, \phi_B \right) \times \left( j_A, m; j_B, k - m \mid j, k \right). \]
(16)

The rotation functions \( D_{\delta \alpha}^{\kappa \lambda \mu} \) and Clebsch–Gordan coefficients are conventional.\(^{51}\)

With the potential in the form of Eqs. (1) and (2), the angular integration over basis functions (16) can be performed analytically:

\[ \langle Y_{lA}^{\lambda \mu} | V(R, \theta_A, \theta_B, \phi) | Y_{lB}^{\lambda \mu} \rangle \delta_{\delta \alpha} \delta_{\kappa \lambda \mu} \delta_{lA,lB} = \delta_{\delta \alpha} \sum_{lA,lB,L} \frac{1}{2} H_{lA,lB,L} (R) \delta_{lA,lB,L} \langle j_A, j_B | j'_A, j'_B, j; j, j \rangle, \]
(17)

where

\[ H_{lA,lB,L} (R) = \begin{pmatrix} j'_A, j_B | j_A, j_B, j; j, j \end{pmatrix} \]

and

\[ \beta = \omega_\alpha \left( \frac{\mu}{2D_\alpha} \right)^{1/2}. \]
(24)

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and $a$ is the integer closest to $A$. In Eqs. (22)–(24), $R_e$ is the equilibrium separation, $\omega_0$ the fundamental vibrational frequency, and $D_0$ the dissociation energy of the diatomic. In practice these parameters are optimized variationally to give the best basis set for a particular problem.

In order to obtain the complete matrix elements, it is also necessary to integrate over the radial coordinate $R$. This is done following Tennyson and Sutcliffe. 10 Overlap and kinetic energy integrals are evaluated analytically and those over $\tilde{v}_{L',L,R}(R)$ and $R^{-2}$ are calculated numerically using Gauss–Laguerre integration. For this we used a scheme based on the zeros of $L^2_n$, which is sufficient to evaluate integrals between radial basis functions with $n<12$. Further details can be found in Ref. 10.

It is convenient to talk in terms of the vibrational and rotational levels of the molecule. Vibrational levels can, for a nonlinear molecule, be identified as those arising when one solves the secular problem with $J = 0$. As we neglect any hyperfine coupling to nuclear spins and we are dealing with closed shell singlet monomers, $J$ is a good quantum number. Rotational transitions are obtained by comparing solutions of secular problems with different $J$'s.

The projection of $J$ onto the body-fixed axis $k$ has often been treated as a good quantum number, 4,10,13,16 This approximation is equivalent to neglecting the matrix elements off-diagonal in $k$. Since these terms couple vibrational and rotational motions, they are often called "Coriolis" interactions, 10,16 although they are not the same as the Coriolis terms arising from the conventional vibration-rotation Hamiltonian due to WatsonS4,47 which arise when the Eckart conditions are used for embedding.

For the Hamiltonian of Dyke et al., 33 [Eq. (3)], these Coriolis interactions are complicated in form. However, when the Hamiltonian is represented using angular momentum operators, the only term that couples functions which differ in $k$ is $\hat{J} \cdot \hat{J}$. The matrix elements of this operator are given by Eq. (20).

The dimension of the full secular matrix is approximately proportional to $2J + 1$. For $J = 0$ the diagonalization is already expensive and for some cases with $J = 1$ it is prohibitive. In Sec. V we therefore investigate the effect of neglecting these off-diagonal Coriolis interactions and thus reduce the dimension of the secular matrix that needs to be diagonalized for rotationally excited states.

Even for the rotational ground state ($J = 0$), however, the secular matrix can become unmanageable. In the following section we show how, by the use of permutation and inversion symmetry, the problem can be made tractable.

IV. SYMMETRY IN (N2)2

In addition to the invariance under uniform translations, rotations and inversion, the symmetry that characterizes the nuclear dynamical problem for the (N2)2 dimer is represented by the elements of the permutation group $S_4$ operating on the nuclear coordinates (i.e., if we assume that all the constituent nuclei are identical). Except for the translations which have been separated off, all this symmetry is also present in the full Born–Oppenheimer nuclear Hamiltonian (3) or (8), although it is not obvious from the form in which this Hamiltonians is expressed. The rotational symmetry leads to the total angular momentum $J$ and its space-fixed component $M$ being good quantum numbers and we only have to deal explicitly with the permutation-inversion group $S_4 \times C_4$. 48

In model Hamiltonians this symmetry is usually lowered. 45 For instance, if we assume the N2 monomers to be rigid, which leads to the "collision complex" Hamiltonian (14), not all permutations are feasible (in the sense of Longuet–Higgins). 50 The feasible permutations form a subgroup of $S_4$ of order 8 which we designate $S'_4$; its elements are listed in Table I with the nuclei numbered as in Fig. 1. In the harmonic oscillator/ rigid rotor limit of the dimer one can use the $D_{2h}$ point group (which is isomorphic with $S'_4$) symmetry of the nuclear framework in its crossed equilibrium structure.

In the present section we treat the different symmetry aspects, the relation between the models and the correspondence with the nuclear spin states. It is shown how the symmetry adaptation of the basis functions (15) leads to a considerable simplification of the dynamical problem and to a classification of the rovibrational states of the dimer. Selection rules for infrared absorption are discussed in Sec. VII.

A. Permutation-inversion symmetry

The $S'_4 \times C_4$ symmetry of (N2)2 in the collision complex model with two rigid (strongly bound) monomers is reflected in the first place by the potential: only terms with even $L_A$, $L_B$, and $L$ occur in the spherical expansion (1) and, moreover, the coefficients satisfy the relation $v_{L_A,L_B,L}(R) = v_{L_A,L_B,L}(R)$. The symmetry aspects of $A_2$–$A_2$ collision complexes have been treated extensively by Metropolis51 using a space-fixed coordinate system. Since we express our basis functions in body-fixed coordinates and, moreover, we use coupled spherical harmonics [Eq. (16)] rather than simple products, we have to revise his analysis but we can follow the outlines of his paper. 51 The action of the permutation-inversion group $S'_4 \times C_4$ on the external and internal body-fixed coordinates is shown in Table I. Using the properties of spherical harmonics and rotation functions the transformation properties of the basis (15) are easily derived: Table II. One can adapt the basis to the group $S'_4 \times C_1$ in the following manner (where the radial factors are left unaltered since they are totally symmetric). First, the generalized spherical harmonics $Y^{L,\Lambda}_{j_A,j_B}$ are symmetric with respect to the interchange of $j_A$ and $j_B$, by forming combinations for $j_A + j_B$ even:

$$Y^{L,\Lambda}_{j_A,j_B} = \begin{cases} \frac{1}{\sqrt{2}} [Y^{L,\Lambda}_{j_A,j_B} + (-1)^i Y^{L,\Lambda}_{j_A,j_B}^*] & \text{for } j_A \neq j_B \quad (i = 0 \text{ or } 1), \\ Y^{L,\Lambda}_{j_A,j_B} & \text{for } j_A = j_B \quad (i = 0), \end{cases}$$

(25a)


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TABLE I. Transformation of the \((N_2)_2\) body fixed coordinates under \(S_z \otimes C_4\).

<table>
<thead>
<tr>
<th>(E)</th>
<th>(\beta)</th>
<th>(\alpha)</th>
<th>(\theta_A)</th>
<th>(\phi_A)</th>
<th>(\theta_B)</th>
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</thead>
<tbody>
<tr>
<td>(P_{12})</td>
<td>(\beta)</td>
<td>(\alpha)</td>
<td>(\pi - \theta_A)</td>
<td>(\pi + \phi_A)</td>
<td>(\pi - \theta_B)</td>
<td>(\pi + \phi_B)</td>
</tr>
<tr>
<td>(P_{13})</td>
<td>(\beta)</td>
<td>(\alpha)</td>
<td>(\theta_A)</td>
<td>(\phi_A)</td>
<td>(\pi - \theta_B)</td>
<td>(\pi + \phi_B)</td>
</tr>
<tr>
<td>(P_{14})</td>
<td>(\beta)</td>
<td>(\alpha)</td>
<td>(\pi - \theta_A)</td>
<td>(\pi + \phi_A)</td>
<td>(\pi - \theta_B)</td>
<td>(\pi + \phi_B)</td>
</tr>
<tr>
<td>(P_{15})</td>
<td>(\beta)</td>
<td>(\alpha)</td>
<td>(\theta_A)</td>
<td>(\phi_A)</td>
<td>(\pi - \theta_B)</td>
<td>(\pi + \phi_B)</td>
</tr>
<tr>
<td>(P_{16})</td>
<td>(\beta)</td>
<td>(\alpha)</td>
<td>(\theta_A)</td>
<td>(\phi_A)</td>
<td>(\pi - \theta_B)</td>
<td>(\pi + \phi_B)</td>
</tr>
</tbody>
</table>

Next we take the inversion symmetry into account (for \(k \neq 0\)):

\[
Y^{j_A, k}_{1-1, 1} = \frac{1}{\sqrt{2}} \left[ Y^{j_A, k}_{1, 1} D'^{j_A, k}_{1, 1} + (-1)^k Y^{j_A, k}_{1, -1} D'^{j_A, k}_{1, -1} \right],
\]

with \(\kappa = 0\) or 1, while the functions with \(k = 0\) need not be symmetrized; they transform as the symmetric \((\kappa = 0)\) combinations. These symmetry adapted basis functions \(\psi\) span the irreducible representations of the full permutation-inversion group \(S_z \otimes C_4\), see Table III, and if we use this angular basis in the LC-RAMP scheme (Sec. III) and transform the Hamiltonian matrix accordingly, the secular problem separates into 12 blocks. Diagonalization of these blocks yields the rovibrational states of the \((N_2)_2\) dimer, classified with respect to \(S_z \otimes C_4\) (see Table III).

B. Symmetry in the harmonic oscillator/rigid rotor limit

In order to gain a better understanding of the internal motions in the \((N_2)_2\) dimer, it is useful to compare the solutions of the full dynamical problem (Sec. III) with the harmonic oscillator/rigid rotor limit. In this limit, the dimer looks as a prolate symmetric top rigid rotor with the crossed equilibrium structure \((\theta_A = \theta_B = \phi = 90^\circ)\). Its vibrations are given by (linearized) displacements of the nuclei from their equilibrium positions with the force constants obtained as the second derivatives of the potential at the equilibrium geometry. The internal displacement coordinates have to satisfy the Eckart conditions \(^{35}\) and they can be adapted to the \(D_{2d}\) point group symmetry of the equilibrium structure. Since they span only different irreducible representations of \(D_{2d}\), if we consider the monomer stretch modes \(\Delta \nu_A\) and \(\Delta \gamma_B\) to be decoupled from the dimer vibrations, they are simultaneously the normal coordinates of the harmonic problem (see Table IV).

The Wilson \(G\) matrix in terms of these coordinates can be derived by the usual techniques \(^{32}\); alternatively, one can start from the kinetic energy terms in Hamiltonian (3), neglect the rovibrational coupling terms and introduce the equilibrium values for the coordinates. The force constants (the elements of the \(F\) matrix \(^{32}\)) are obtained from the spherically expanded potential (1) by using differentiation formulas for spherical harmonics. \(^{33}\) The fundamental frequencies obtained by diagonalizing \(F \cdot G\) are presented in Sec. V.

The total wave functions in the harmonic oscillator/rigid rotor model (with the monomer stretches decoupled) can be written as follows:

\[
\psi^{j_A, j_B, \nu}_{\nu_1, \nu_2, \nu_3, \nu_4} D'^{j_A, k}_{j_B, k'} = \int_0^1 D_3 \left( \begin{array}{c} \psi_B \cr \psi_A \end{array} \right) D_3 \left( \begin{array}{c} \nu_1 \cr \nu_2 \cr \nu_3 \cr \nu_4 \end{array} \right),
\]

where \(n_1, n_2, n_3,\) and \(n_4\) count the vibrational quanta in the different normal modes and \(D'_{ji, k}\) are the symmetric top rigid rotor functions. \(^{6}\) Because of the degeneracy in the \((\Delta \theta_A, \Delta \theta_B)\) mode we still have to symmetrize this basis, by taking combinations for \(n_2 = n_3\) even:

\[
\psi^{j_A, j_B, \nu}_{\nu_1, \nu_2, \nu_3, \nu_4} = \frac{1}{\sqrt{2}} \left[ \psi^{j_A, j_B, \nu}_{\nu_1, \nu_2, \nu_3, \nu_4} + (-1)^{\nu} \psi^{j_A, j_B, \nu}_{\nu_1, \nu_2, \nu_3, \nu_4} \right], \quad \nu = 0 \text{ or } 1,
\]

TABLE II. Transformation of angular basis functions (15) under \(S_z \otimes C_4\).

<table>
<thead>
<tr>
<th>(E)</th>
<th>(Y^{j_A}_{1, 1})</th>
<th>(D'^{j_A}_{1, 1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{12})</td>
<td>((-1)^j A)</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
<tr>
<td>(P_{13})</td>
<td>((-1)^j B)</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
<tr>
<td>(P_{14})</td>
<td>((-1)^{j + j'} B)</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
<tr>
<td>(P_{15})</td>
<td>((-1)^{j + j'} A)</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
<tr>
<td>(P_{16})</td>
<td>((-1)^j B)</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
<tr>
<td>(E^*)</td>
<td>((-1)^{j + j' + j'^*})</td>
<td>(Y^{j_A}_{1, 1})</td>
</tr>
</tbody>
</table>

TABLE III. Classification of symmetry adapted basis (26) according to the irreducible representations of $S^2 \otimes C_i$ and $N_2$ nuclear spin (ortho-para). The e/o labels denote even/odd values of $j_A$, $j_B$, $i$, $j$, and $k + J$. (The latter two quantum numbers are combined since the symmetry depends only on the parity of their sum; the quantum number $k$ enters only via $k$.)

<table>
<thead>
<tr>
<th>$j_A + j_B$</th>
<th>$j_B$</th>
<th>$i$</th>
<th>$j$</th>
<th>$k + J$</th>
<th>$N_2$ nuclear spin</th>
<th>$S'_1 \otimes C_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>o/e</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td>basis:</td>
<td>e</td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>ortho-ortho</td>
<td>$B_2$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$B_2$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$B_2$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$B_2$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$B_2$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-ortho</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>e</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>e</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>e</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>o</td>
<td>e</td>
<td>e</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>o</td>
<td>e</td>
<td>o</td>
<td>ortho-para</td>
<td>$E$</td>
</tr>
</tbody>
</table>

and two-vectors for $n_0 + n_1$ odd:

$$\psi_{1a,1b}^{11} = \psi_{1a,1b}^{11} \otimes \psi_{1m,1n}^{21}.$$ (28b)

Thus, the vibrational basis functions are adapted to $D_{2d}$ and the total wave functions to $D_{2d} \otimes SO(3)$.

We can further extend the connection with the (symmetrized) solution of the full dynamical problem (Sec. IV A) if we also invoke the inversion operation [since the space in which the dynamical problem is solved is invariant under the rotation-inversion group $O(3)$, rather than just the rotation group $SO(3)$]. In the harmonic oscillator/rigid rotor model the inversion carries the $(N_2)_2$ dimer from one crossed equilibrium structure with $\theta = 90^\circ$ into another, equivalent one with $\phi = 270^\circ$.

Around each of these two structures we have vibrational solutions of the type (28) which we label $\psi_{1a,1b}^{10}$ and $\psi_{1a,1b}^{210}$. By taking combinations:

$$\psi_{1a,1b}^{10} = \frac{1}{\sqrt{2}} \left[ \psi_{1a,1b}^{10} + (-1)^\tau \psi_{1a,1b}^{210} \right]$$ with $\tau = 0 \; \text{or} \; 1$, (29)

the basis becomes adapted to $D_{2d} \otimes O(3) = D_{2d} \otimes C_i \otimes SO(3)$. The classification of its vibrational part with respect to $D_{2d} \otimes C_i$ (Table IV) is shown in Table V. Since the group $D_{2d}$ is isomorphic with the permutation-inversion group $S_4 \otimes C_i$, the irreducible representations are labeled differently in Tables III and V, in order to avoid confusion.

In the harmonic oscillator model the combinations with $\tau = 0$ and $\tau = 1$ are degenerate. By using the basis (29) with the full potential (1) in a variational or perturbational treatment these combinations will be split in energy due to tunneling through the barriers at $\phi = 0^\circ$ and $180^\circ$. This tunneling splitting is also found in the full dynamical treatment.

We proceed by looking at the local symmetry of the full dynamical wave functions about the equilibrium structure (or, actually, about the two equivalent equilibrium structures). This is performed by writing the

$$\Delta R = -(\Delta z_1 + \Delta z_2 - \Delta z_3 - \Delta z_4),$$
$$\Delta \phi = -(\Delta z_1 - \Delta z_2 - \Delta z_3 + \Delta z_4)/2R, \quad \Delta \phi = (\Delta z_1 + \Delta z_2 + \Delta z_3 - \Delta z_4)/2R, \quad \Delta \phi = (\Delta z_1 - \Delta z_2 + \Delta z_3 + \Delta z_4)/2R.$$
TABLE V. Classification of the harmonic oscillator functions (29), combined for the two equivalent equilibrium structures (φ = 90° and 270°), with respect to $D_{2d} \otimes C_1 (\Omega_{\text{eq}})$. Local symmetry of the RAMP basis (26) for $J = 0$ about these equilibrium structures.

<table>
<thead>
<tr>
<th>$n_1 + n_2$ even,</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
<th>$\nu$</th>
<th>$\tau$</th>
<th>$D_{2d} \otimes C_1$</th>
<th>$j_A$</th>
<th>$j_B$</th>
<th>$i$</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o o o o e e</td>
<td>$A_{1u}$</td>
<td>e e e e o j$_A + j_B$ even,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o o o o e e</td>
<td>$A_{1u}$</td>
<td>e e e e o basis:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e e e e e e</td>
<td>$B_{1u}$</td>
<td>e e o o e $\Psi_{J_A = j_B}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$n_1 + n_2$ odd,</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
<th>$\nu$</th>
<th>$\tau$</th>
<th>$D_{2d} \otimes C_1$</th>
<th>$j_A$</th>
<th>$j_B$</th>
<th>$i$</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>e/o o/e o e</td>
<td>$E_u$</td>
<td>e/o o/e $\cdots$</td>
<td>e j$_A + j_B$ odd,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e/o o/e o o</td>
<td>$E_u$</td>
<td>e/o o/e $\cdots$</td>
<td>e j$_A + j_B$ odd,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e/o o/e o e</td>
<td>$E_u$</td>
<td>e/o o/e $\cdots$</td>
<td>e $\Psi_{J_A = j_B}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Internal angular coordinates in the basis (15) are: $\theta_A = \theta_{A, H} + \Delta \theta_A$, $\theta_B = \theta_{B, H} + \Delta \theta_B$, $\phi = \phi_{\text{eq}} + \Delta \phi$ and replacing the curvilinear displacement coordinates $\Delta \theta_A$, $\Delta \theta_B$, and $\Delta \phi$ by rectilinear ones. Since the latter carry the irreducible representations of $D_{2d}$ (see Table IV) we can define the action of the point group operations on the angular displacements and also on the angular basis functions (15) close to equilibrium. Again, using the transformation properties of spherical harmonics, we can classify the local $D_{2d}$ symmetry of the symmetrized basis (26) about the equilibrium structure(s). This is done for $J = k = 0$ states in Table V, which then shows the (local) symmetry correlation under $D_{2d} \otimes C_1$ with the harmonic oscillator states including tunneling [Eq. (29)]. This correlation is used for interpreting the low lying vibrational states in $(N_2)_2$ in Sec. V (see Fig. 2).

C. Nuclear spin multiplicity of the rovibrational states

$^{14}$N atoms have nuclear spin $I = 1$. Even though we do not consider the nuclear spin terms explicitly, for instance by looking at the hyperfine spectrum, we are still interested in the nuclear spin coupling in $(N_2)_2$ since this coupling is connected to the rovibrational states of the dimer via their permutation symmetry. Knowledge of this connection is important since the nuclear spin multiplicities of the rovibrational states weight the intensities of the transitions between them.

So, for instance, the symmetric $A_1$ states in ortho-$N_2$ monomers (with even $J$) have $I = 0$ and $I = 2$ (total multiplicity 6); the antisymmetric $A_2$ states in para-$N_2$ (odd $J$) correspond with $I = 1$ (multiplicity 3). This leads to a weight factor of 2 for the intensities in o-$N_2$ compared with p-$N_2$.

For the $(N_2)_2$ dimer composed of two strongly bound $N_2$ monomers we also have to couple the monomer spin moments $I_A$ and $I_B$ (each having the values 0, 1, or 2) and find out how the resultant spin states, $I = 0$, 1, 2, 3, and 4, are distributed over the rovibrational states. The total rovibrational and nuclear spin wavefunction must be symmetric with respect to interchange of the $^{14}$N nuclei, which are bosons. This means that rovibrational wavefunctions which carry a given irreducible representation of $S_4$ must be multiplied by nuclear spinfunctions that carry the same representation (in the case of degenerate representations one must also sum over
the components). The rovibrational wave functions have been adapted to $S'_4$ already (see Table III). By looking at the adaptation of the nuclear spin functions to the chain $S_2 \otimes S_2 \subset S'_2 \subset S_4$, we have derived the nuclear spin multiplicity of these states and their relation with the monomer nuclear spins (see Table VI).

V. CALCULATIONS WITH J = 0

All our calculations used a fixed $N_2$ bondlength of 1.094 Å, the experimental value and the one used for deriving the potential surface. This value gives a rotational constant for $^{14}N_2$ of 2.013 cm$^{-1}$. As our calculations are variational, we first optimized the radial basis and checked the convergence properties of the basis set as a whole. For this it was assumed that the radial and angular basis sets can be treated as independent.

The radial functions were optimized for the dimer ground state (symmetry $A_1^g$) using a basis set which contained all radial functions with $n \leq 3$ (4 functions) and angular functions with $j_A$, $j_B \leq 4$ (14 $A_1^g$ functions). As an initial guess the parameters were given values suggested by the potential: $D_E = 122$ cm$^{-1}$, $R_s = 3.48$ Å, and $\omega_s = 40.0$ cm$^{-1}$. Again, the energy proved to be relatively insensitive to $D_E$ and $R_s$ was found to be the critical parameter. Optimal values were $D_E = 125$ cm$^{-1}$, $R_s = 3.94$ Å, and $\omega_s = 29.6$ cm$^{-1}$. This leads to an $\alpha$ value of 17.

Table VII shows the convergence of the basis set. The ground state is well represented by a basis set with $j_A$, $j_B \leq 8$ (only even values contribute by symmetry) and $n \leq 3$. We thus chose to work with a basis comprising all angular functions given by $j_A$, $j_B \leq 9$ and the five radial functions with $n \leq 4$. For $J = 0$ this basis consists of 3350 functions. However, use of the symmetrized basis functions (26) means that the largest $J = 0$ secular matrix, for the $E^*$ block, was of dimension 475.

Table VIII shows the energies of all the 92 bound states we found with $J = 0$, labeled by the irreducible representations of the permutation-inversion group. They are our calculated vibrational levels for the nitrogen dimer. The spectrum is irregular, surprisingly dense (several atom–diatom van der Waals complexes have only one bound $J = 0$ state) and has several features of interest.

There are two models which can be used to analyze the spectrum. First, the dimer can be considered as a rotational constant for $^{14}N_2$ of 2.013 cm$^{-1}$.

### Table VII. Convergence of the angular and optimized radial basis sets.

<table>
<thead>
<tr>
<th>$j_A$</th>
<th>$j_B$</th>
<th>$n_{\text{max}}$</th>
<th>Energy/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>-47.346</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>-69.731</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>-74.408</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>-74.937</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>-74.945</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>-69.542</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-73.451</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-74.367</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>-74.405</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>-74.111</td>
<td></td>
</tr>
</tbody>
</table>

### Table VIII. Vibrational energies (in cm$^{-1}$) of the $J = 0$ bound states relative to two ortho–$N_2$ monomers. $o$ and $p$ refer to whether the complex derives from ortho or para monomers.

<table>
<thead>
<tr>
<th>$j_A$</th>
<th>$j_B$</th>
<th>$n$</th>
<th>Energy/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-74.945</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-58.138</td>
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<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-53.045</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>-41.748</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-35.027</td>
</tr>
<tr>
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<tr>
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<td>0</td>
<td>1</td>
<td>-6.880</td>
</tr>
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</table>

J. Chern. Phys., Vol. 77, No. 11, 1 December 1982
anharmonicity in the potential causes the harmonic oscillator model to overestimate the fundamental frequencies by up to 40%. The zero point energy, however, is well represented suggesting that the ground state is fairly harmonic in character.

Figure 2 gives the correlation between localized (harmonic oscillator) and completely delocalized (free rotor) states. For example, the E* states appear as doublets (one E* and one E") in the localized (harmonic oscillator) model. These correlate with free rotor states on the right of the figure with different groupings, the lowest states being a singlet (E") and then a triplet (E* and two E"). The lowest E* state thus changes its partner across the diagram. The calculated state distribution for the low-lying vibrational states (the central levels in Fig. 2) is found to be intermediate between the harmonic oscillator and free rotor models.

Further insight into the (de)localized nature of the vibrational states is given by taking suitable two-dimensional cuts through the full four-dimensional wave function. Figures 3 and 5 give some illustrative cuts. Figures 3 and 4 present cuts through the ground state showing that it is indeed localized in the region of the equilibrium structure ($\mathbf{R}_m = 3.46 \text{ Å}, \theta_A = \theta_B = 90^\circ, \phi = 90^\circ, \text{ or } 270^\circ$). We attribute the small negative amplitudes at $\phi = 0^\circ, 180^\circ$, and $360^\circ$ to the effects of a truncated basis set.

Figure 3 also plots the degenerate ($\theta_A, \theta_B$) bending fundamental. This state already shows signs of delocalization, there is significant amplitude at the barrier which lies at $0^\circ$ or $180^\circ$ in the ($\theta_A, \theta_B$) coordinate. Strong coupling to R is also shown.

Figure 4 shows the effect of increasing excitation in the $\phi$ coordinate. The lowest $\mathbf{B}_1$ and first excited $\mathbf{A}_1$ states correspond to the $\phi$ fundamental and first overtone, respectively. The role played by tunneling in the $\phi$ coordinate will be discussed later.

Symmetry considerations alone are not sufficient to unambiguously determine which level corresponds to the fundamental stretch. The situation is complicated by the low-lying overtones in both $\phi$ and ($\theta_A, \theta_B$) coordinates with the same $\mathbf{A}_1$ symmetry. Thus, the first excited $\mathbf{A}_1$ state is clearly a $\phi$ fundamental and first overtone. It is shown in Figure 5 that the second excited $\mathbf{A}_1$ state which we identify with the stretching fundamental, although there is clearly mixing (Fermi resonance) with both bending overtones.

The harmonic oscillator levels in Fig. 2 are combinations of the three fundamental energies obtained by considering the curvature of the potential minimum. Recent calculations use the local $D_{4h}$ symmetry about the equilibrium (see Table V) to determine the fundamental vibrational frequencies predicted by the harmonic oscillator model with the full dynamical results. The

![Figure 2](image-url)

**TABLE IX.** Comparison of "fundamental" vibrational energies for the harmonic oscillator model and full secular matrix calculations.

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>$D_{4h}$</th>
<th>$S_4$ @ $C_1$</th>
<th>Energy (cm$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>$\Delta \mathbf{R}$</td>
<td>$\mathbf{A}_1$</td>
<td>$\mathbf{A}_1^*$</td>
<td>39.2, 33.2</td>
</tr>
<tr>
<td>$\Delta \theta_A, \Delta \theta_B$</td>
<td>$\mathbf{E}$</td>
<td>$\mathbf{E}^*$</td>
<td>22.1, 14.2</td>
</tr>
<tr>
<td>$\Delta \phi$</td>
<td>$\mathbf{B}_1$</td>
<td>$\mathbf{B}_1^*$</td>
<td>13.9, 8.1</td>
</tr>
<tr>
<td>Zero-point energy</td>
<td></td>
<td></td>
<td>48.7, 47.1</td>
</tr>
</tbody>
</table>


Downloaded 08 May 2012 to 128.40.5.150. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions
Another way of analyzing the wave function is to look at its probability distribution. Figure 6 shows the density of the lowest four $A_i^1$ states in the radial coordinate after integration over the angular variables. The node in the curve corresponding to the third excited $A_i^1$ state reinforces our assignment that this is the stretching fundamental. An interesting feature of Fig. 6 is the progressive movement of the density in the radial coordinate.

**FIG. 3.** Cuts through the lowest $J=0$, $A_i^1$ and $E'$ vibrational wave functions with $\theta_B$ and $\phi$ fixed at 90°. The contours enclose regions with 8%, 16%, 32%, and 64% of the maximum amplitude. Solid curves correspond to positive amplitude and dashed curves to negative amplitude.

**FIG. 4.** Cuts through the $J=0$ wave functions of the lowest $A_i^1$, $B_i^1$, $B_i^2$ and first excited $A_i^1$ states with $\theta_A$ and $\theta_B$ fixed at 90°. Contours as in Fig. 3.

**FIG. 5.** Cuts through the $J=0$ wave function of the third excited $A_i^1$ state. The upper plot is for $\theta_B$ and $\phi$ fixed at 90° and the lower plot for $\theta_A$ and $\theta_B$ fixed at 90°. Contours as in Fig. 3.

**FIG. 6.** Normalized probability distribution in the stretching coordinate of the four lowest $J=0$ states of $A_i^1$ symmetry. The curves were obtained by integrating over all angular coordinates. For comparison the equilibrium separation ($R_m$) and the minimum of the isotropic potential ($R_m^{(4)}$) are marked.
TABLE X. Comparison of $J=0 \rightarrow 1$ transition frequencies within the $A^1_I$ and $B^1_J$ blocks for a full calculation and one neglecting Coriolis interactions. Energies are relative to the correlating $A^1_I J=0$ state, for which the vibrationally averaged value of $R$ and the rotational constant $B$ are shown. $J=1$ states labeled, $\kappa=0$ and $1'$ are of $B^1_J$ symmetry, and those labeled $\kappa=1'$ are $A^1_I$.

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>$\langle R \rangle$ (Å)</th>
<th>$2B$ (cm$^{-1}$)</th>
<th>$\kappa$</th>
<th>No Coriolis</th>
<th>Full</th>
</tr>
</thead>
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<tr>
<td>$-74.945$</td>
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<td>$16.794^a$</td>
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<td>$1^*$</td>
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<td>$13.958$</td>
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<tr>
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<td></td>
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<td>$1^*$</td>
<td>$13.350$</td>
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<tr>
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<td>$0$</td>
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<tr>
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<td>$1^*$</td>
<td>$12.174$</td>
<td>$12.141^b$</td>
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<td>$0$</td>
<td>$0.152$</td>
<td>$0.216^b$</td>
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<td></td>
<td></td>
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<td>$11.769$</td>
<td>$11.764$</td>
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$^a,b$These states are strongly mixed.

ordinate with excitation. The lower states are peaked about the equilibrium geometry ($R=3.46$ Å) suggesting they are localized in nature; the higher ones are peaked about the minimum in the isotropic potential ($R^{1\text{st}}=4.17$ Å) showing that they behave more like free internal rotors. Table X gives vibrationally averaged values of $R$ and the rotational constants for these states. Below these vibrationally excited levels, there is one other state (symmetry $B^1_J$) which is only $2.4$ cm$^{-1}$ above the ground state. This state (see Fig. 4) is due to the splitting of the ground state by tunneling through the low barrier, $25$ cm$^{-1}$, in the $\phi$ coordinate which separates the equivalent equilibrium structures at $\phi=90^\circ$ and $270^\circ$. A one-dimensional model$^{16}$ (with $\theta_A$ and $\theta_B$ fixed at $90^\circ$ and the optimum $R$ for each $\phi$), results, after solving Mathieu’s equation, in a tunneling splitting of only $0.8$ cm$^{-1}$ for the same barrier height.$^{16}$ This difference is due to several effects. First, the $\phi$ coordinate couples with the other coordinates: this results in a lowering of the effective moment of inertia, especially through coupling with $(\theta_A, \theta_B)$ and a lowering of the effective barrier due to the effects of vibrational averaging over $R$. At $R=3.79$ Å, which is the average distance for the ground state dimer, the barrier is $14$ cm$^{-1}$ rather than $25$ cm$^{-1}$. Furthermore, there are higher barriers $40$ cm$^{-1}$ in the degenerate $(\theta_A, \theta_B)$ coordinate which separate the same equilibrium structures; tunneling through these can also contribute to the splitting.

Figure 4 illustrates the effect of tunneling in the $\phi$ coordinate. The $A^1_I$ and $B^1_J$ states lie well below the barrier and hence are localized in the region of the potential minimum. The vibrational fundamental ($B^1_J$ state) is also still “localized” in the $\phi$ coordinate (well below the barrier in energy) but shows significant tunneling through the barrier. One would expect higher excitations, such as the first excited $A^1_I$ state shown in Fig. 4, to become increasingly delocalized, although experience$^{16}$ has shown that the onset of delocalization (or the point where tunneling becomes rotation) is difficult to determine.

VI. ROTATIONALLY EXCITED STATES

As discussed in Sec. III, the exact calculation of rotationally excited states within our formalism rapidly becomes prohibitively expensive. Already for $J=1$, it would be necessary to solve secular problems of dimension 1300 and 1175 for the two $E$ blocks which is
impractical even if iterative diagonalization techniques\textsuperscript{59,60} are employed. Indeed we were unable to converge the cyclic diagonalization for the $E^-$ block even when its dimension was reduced by treating $k$ as a good quantum number.

Such difficulties make an approximation, such as the neglect of Coriolis interactions, which further decouples the problem, very attractive. Table X compares results obtained for a full calculation and for one in which Coriolis interactions have been neglected. This approximation means that the terms off-diagonal in $k$ [Eq. (21)] have been omitted.

It can be seen that the approximation is indeed very good, with the levels being shifted by less than 0.1 cm\textsuperscript{-1}, with the exception of the case where near degeneracy causes strong mixing and makes the labeling of the energy levels by $k$ arbitrary. This accuracy might not be acceptable if judged by the experimental errors in determining rotational spectra of conventional molecules, but is certainly comparable to the accuracy of vibrational spectra and better than can be expected of the potential energy surface.

We have thus performed calculations for all states with $J = 1$ and $J = 2$ assuming $k$ to be a good quantum number. Tables XI, XII, and XIII summarize the results for $k = 0$, 1, and 2, respectively.

Table XI shows results for $k = 0$, which can be regarded as pure rotational transitions ($\Delta k = 0$) that are well represented by (see Table X):

$$ \Delta E_{j'j} = [J'(J' + 1) - J(J + 1)] \langle R^2 \rangle / 2 \mu, $$

where the rotational constant $B$ is obtained by vibrationally averaging $R^2$ for the relevant $J = 0$ vibrational state. For these transitions the effect of the centrifugal barrier in the potential is indetectable. The transitions from $J = 1$ to $J' = 2$ with $\Delta k = 0$ shown in Table XII can be interpreted similarly.

All the $k = 1$ states given in Table XII are degenerate with $k = -1$ states. This is because the energies are independent of the sign of $k$ [or the parity of $\kappa$, Eq. (28)]. Thus there is a degeneracy between symmetry blocks whose angular functions only differ by the value of $\kappa$. This degeneracy will, of course, be lifted by the inclusion of the Coriolis terms. However, Table X demonstrates that a near degeneracy still remains.

The differences between $k = 0$ ($J = 0$ or 1) and $k = 1$ ($J = 1$) levels are too large for pure rotational transitions and they are not always positive. As $j \geq k$, use of $k = 1$ eliminates all basis functions with $j = 0$. The lowest $A_1^-$ is $0 (J = 0$ or 1) states are dominated by basis func-

### TABLE XI. Five lowest pure rotational transition ($\Delta k = 0$) frequencies (in cm\textsuperscript{-1}), calculated neglecting Coriolis interactions. Upper rows are for $J = 0$, $k = 0$. Lower rows are for $J = 1, k = 0$. The symmetry labels refer to the final rotational states. The corresponding states with $J = 0$ are given in Table VIII.

<table>
<thead>
<tr>
<th>$A^+_1$, $B^+_1$</th>
<th>0.170</th>
<th>0.158</th>
<th>0.161</th>
<th>0.153</th>
<th>0.147</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^+_1$</td>
<td>0.338</td>
<td>0.314</td>
<td>0.324</td>
<td>0.306</td>
<td>0.294</td>
</tr>
<tr>
<td>$B^+_1$</td>
<td>0.145</td>
<td>0.139</td>
<td>0.146</td>
<td>0.146</td>
<td>0.146</td>
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<td>$A^+_1$</td>
<td>0.290</td>
<td>0.280</td>
<td>0.296</td>
<td>0.296</td>
<td>0.296</td>
</tr>
<tr>
<td>$A^+_1$</td>
<td>0.166</td>
<td>0.151</td>
<td>0.148</td>
<td>0.169</td>
<td>0.153</td>
</tr>
<tr>
<td>$B^+_1$</td>
<td>0.322</td>
<td>0.302</td>
<td>0.287</td>
<td>0.338</td>
<td>0.306</td>
</tr>
<tr>
<td>$A^+_1$</td>
<td>0.141</td>
<td>0.151</td>
<td>0.150</td>
<td>0.138</td>
<td>0.139</td>
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<tr>
<td>$B^+_1$</td>
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<td>0.277</td>
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<tr>
<td>$E^+$</td>
<td>0.153</td>
<td>0.150</td>
<td>0.152</td>
<td>0.149</td>
<td>0.152</td>
</tr>
<tr>
<td>$E^+$</td>
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<td>0.300</td>
<td>0.304</td>
<td>0.300</td>
<td>0.303</td>
</tr>
<tr>
<td>$A^+_1$</td>
<td>0.148</td>
<td>0.149</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
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<tr>
<td>$A^+_1$</td>
<td>0.295</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
</tr>
<tr>
<td>$B^+_1$</td>
<td>0.169</td>
<td>0.151</td>
<td>0.154</td>
<td>0.151</td>
<td>0.151</td>
</tr>
<tr>
<td>$A^+_1$</td>
<td>0.341</td>
<td>0.301</td>
<td>0.307</td>
<td>0.302</td>
<td>0.302</td>
</tr>
<tr>
<td>$A^+_1$</td>
<td>0.150</td>
<td>0.140</td>
<td>0.150</td>
<td>0.140</td>
<td>0.140</td>
</tr>
<tr>
<td>$B^+_1$</td>
<td>0.300</td>
<td>0.280</td>
<td>0.280</td>
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</tr>
<tr>
<td>$A^+_1$</td>
<td>0.172</td>
<td>0.157</td>
<td>0.170</td>
<td>0.153</td>
<td>0.152</td>
</tr>
<tr>
<td>$B^+_1$</td>
<td>0.343</td>
<td>0.316</td>
<td>0.340</td>
<td>0.306</td>
<td>0.305</td>
</tr>
<tr>
<td>$E^+$</td>
<td>0.157</td>
<td>0.157</td>
<td>0.153</td>
<td>0.144</td>
<td>0.149</td>
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<tr>
<td>$E^+$</td>
<td>0.314</td>
<td>0.312</td>
<td>0.307</td>
<td>0.290</td>
<td>0.299</td>
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</tbody>
</table>
tions with \( j = 0 \); their removal from the basis set causes the lowest \( A'_1 \), \( J = 1 \), \( k = 1 \) state to be close in energy to the first excited \( A'_1 \), \( J = 0 \) (and \( J = 1 \), \( k = 0 \) state. This is the cause of the near degeneracy noted in Table X. Similar, but less marked, behavior can be seen from the other states.

The states of \( E^+ \) and \( E^- \) symmetry are lower in energy for the \( k = 1 \) (\( J = 1 \)) calculation than in the \( k = 0 \) (\( J = 0 \) or 1) case. Arguing in space-fixed coordinates, using the "vector model",\(^{18}\) the coupling of angular momenta can be represented by

\[
I_a + I_b + l = J + l = J,
\]

(30)

where \( l \) is associated with the rotations of the vector \( R \) (angles \( \alpha, \beta \)). Equation (30) is the vector coupling equivalent of the operator relationship in Eq. (12).

Within the vector model (or if the interaction potential is isotropic) \( l \) is a good quantum number and the energies are ordered by increasing \( l \) (not by increasing \( J \)). For the lowest ortho-para interaction \( (I_a = 0; I_b = 1) \) \( j \) is necessarily odd and hence couples to \( J = 1 \) for the ortho-para ground \( (l = 0) \) state. Thus \( J = 0 \) corresponds to an ortho-para excited \( (l = 1) \) state. Conversely, ortho-ortho and para-para complexes can always have \( j \) even and hence can couple to \( J = 0 \) with \( l = 0 \). This argument is harder to reproduce in body-fixed coordinates, but of course the physics is unaltered.

Table XIII shows the behavior of \( k = 2 \) (\( J = 2 \)) states. States which had major contributions from functions with \( j = 1 \) in the \( k = 1 \) (\( J = 1 \) or 2) calculation are now raised in energy. For the para-para system there is also a low lying \( J = 2 \) (\( k = 2 \)) state which can be thought to originate from \( j = 2 \), \( l = 0 \) coupling in the vector model. It is clear, however, from the substantial number of bound states found at this level that stable dimers will be formed with high \( J \) and \( k \). In the subsequent section we discuss the \((N_2)_2\) dimer spectrum.

**VII. IR SPECTRUM**

Mainly on the basis of the similarity of the \((N_2)_2\) infrared spectrum\(^{28}\) with that of \(Ar-N_2\) and model calculations for the latter system,\(^{36}\) Long et al. have drawn the following conclusions. The \((N_2)_2\) dimer has a \( T \)-shaped equilibrium structure with \( R_e = 3.7 \) Å. The first vibrational excitation of the dimer is interpreted as a librational transition, with frequency 9.5 cm\(^{-1}\), so they believe that in the first excited state the internal rotations of the monomers are still locked-in. Higher excitations which have frequencies that are similar to the \( N_2 \) rotational frequencies (although somewhat shifted), are thought to be transitions to (slightly) hindered internal rotor states. The barrier to internal rotations deduced from the spectrum\(^{16}\) is \( 15-30 \) cm\(^{-1}\).

It should not be forgotten, however, that \((N_2)_3\) with its three internal angles is considerably more complicated than \(Ar-N_2\) which has only one bending coordinate. So, for instance, the closest packed structure, which is actually calculated\(^{27}\) to be the equilibrium structure, is not a \( T \)-shaped one as in \(Ar-N_2\) but a crossed one. However, the \( R_e \) value of 3.5 Å is close to that of Long et al. (whereas the \( R_e \) value found for the \( T \)-shaped complex is much larger: \( 4.2 \) Å). For the different bending coordinates different barriers to internal rotations are calculated: 25 and 40 cm\(^{-1}\) (see Sec. II).

**A. Selection rules**

Before making some remarks about the interpretation of the \((N_2)_2\) spectrum\(^{16}\) on the basis of our dynamical calculations, we first look at the selection rules for IR absorption. In free \( N_2 \) all vibrational and rotational transitions are IR forbidden. In the dimer they become weakly allowed by the \( N_2-N_2 \) interactions. The intensities are determined by the dipole operator which can be written in spherical form (in the body fixed frame of Sec. III, Fig. 1) as:

\[
\mu_a(R, \theta_A, \phi_A, \phi_B; \alpha, \beta) = \sum_{L,A,L_B,K} m_{L,A,L_B,K}(R) \times Y_{L,A,L_B,K}^{\pm \phi_A \phi_B \alpha \beta}(\theta_A, \phi_A, \phi_B) D_{L,K}^{I}(\alpha, \beta, 0),
\]

(31)

with the generalized spherical harmonics \( Y_{L,A,L_B,K}^{\pm} \), defined as in Eq. (16), describing its dependence on the internal angular coordinates and \( D_{L,K}^{I} \) with \( \nu = 0 \) or \( -1 \) depending on the "external" rotation angles \( \alpha \) and \( \beta \). The expansion coefficients \( m_{L,A,L_B,K} \) depend on \( R \) and also on \( r_A \) and \( r_B \) if we include the monomer stretching motions. This expression shows immediately that, in order to obtain transition moments between basis states (15), one must have \( \Delta \beta = 0 \) or \( \pm 1 \), \( \Delta k = 0 \) or \( \pm 1 \) and \( \Delta M = \nu \). Additional selection rules follow from the permutation-inversion symmetry (Sec. IV A) which leads to the

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**TABLE XIII. Energies (in cm\(^{-1}\)) of the (ten lowest) bound states with \( J = 2 \), \( k = 2 \) calculated neglecting Coriolis interactions.**

| \( A'_1, B'_1 \) | \( o \) | \( o \) | -61.971 | -44.758 | -35.201 | -31.425 | -28.427 |
| \( -22.821 \) | -3.131 |
| \( -13.208 \) | -10.816 |
| \( B'_1, A'_1 \) | \( p \) | \( p \) | -70.056 | -51.191 | -46.716 | -34.275 | -26.670 |
| \( -24.690 \) | -19.611 |
| \( B'_2, A'_1 \) | \( o \) | \( o \) | -67.877 | -46.507 | -33.813 | -28.647 | -22.865 |
| \( -20.642 \) | -15.269 |
| \( E^+, E^- \) | \( o \) | \( p \) | -54.158 | -49.318 | -42.596 | -35.485 | -33.870 |
| \( -30.892 \) | -26.114 | -22.934 |

---

\( J \) and \( \phi \) correspond to the rotation of the \( A \) monomer, \( R \) being the axis of rotation. \( l \) is the angular momentum operator associated with \( R \). \( m_{L,A,L_B,K} \) is the expansion coefficient of Eq. (31).
conditions that:

$$m_{L_A, L_B, K} \neq 0,$$

only for \(L_A \) and \(L_B \) even,

$$m_{L_A, L_B, K} = (-1)^K m_{L_B, L_A, K},$$

$$m_{L_A, L_B, K} = (-1)^K m_{L_B, L_A, K_1, K_2}.$$  \(32\)

These conditions imply that \(\mu_d \) is totally symmetric \((A_i)\) under the permutation group \(S_4\) and antisymmetric under inversion; it carries the representation \(B_1\) of \(S_4 \otimes C_1\).

Using the classification of the rovibrational states under this group the following transitions are allowed:

$$A_1^+ \rightarrow B_1^+,$$

$$A_2^+ \rightarrow B_2^+,$$

$$E^+ \rightarrow E^-.$$  \(33\)

All the specific selection rules imposed by the symmetry: \(A_j \) even, \(A_j \) even, and restrictions on \(A_i, A_e, A_s, \) and \(A_J\) are implicit in this list \(33\) and Table III.

Actually, the measured \(36\) IR spectrum of \((N_2)_2\) involves the vibrational excitation of one of the monomers. Still using the picture that the monomer stretch vibrations are decoupled from the dimer vibrations, this means that, after absorption of an IR photon, the system moves on the intermolecular potential surface associated with one ground state \((u = 0)\) \(N_2\) monomer and the other \(N_2\) monomer in its first vibrationally excited \((u = 1)\) state. Our dynamical calculations have been performed with the ground state \(N_2-N_2\) potential surface. We think, however, that the excited state potential, and also the rovibrational wave functions of the dimer, are very similar to the ground state results, since the average internuclear distance in \(N_2\) changes only very slightly by the first vibrational excitation. \(50\)

On the other hand, the monomer excitation also affects the selection rules. If one monomer is excited, the dimer rovibrational wave functions must be multiplied by \(x_i(r_A) x_j(r_B)\) or \(x_i(r_A) x_k(r_B)\) rather than by \(x_0(r_A) x_0(r_B)\). Simultaneously with the symmetrization of the basis in \((j_A, j_B)\) \(32\) under the permutation group \(S_4\), one must symmetrize in \((i_A, i_B)\) too; the resulting selection rules are different. If one does not wish to include the monomer vibrations explicitly, the selection rules for ground state-excited state transitions can be taken into account effectively by assuming that the two \(N_2\) monomers are no longer identical. This leads to the permutation-inversion group \(S_4 \otimes C_1\). In terms of the original rovibrational states adapted to \(S_4 \otimes C_1\), the following transitions become allowed, in addition to those indicated above \(33\):

$$A_1^+ \rightarrow A_1^+,$$

$$B_1^+ \rightarrow B_1^+.$$  \(34\)

Finally, it is worth comparing the selection rules that are usually applied to normal molecules. Actually, these hold only if the harmonic oscillator/rigid rotor limit is valid. The vibrational and tunneling wave functions can then be classified with respect to \(D_{2h} \otimes C_1\) \(32\). Although this group is isomorphic with the permutation-inversion group \(S_4 \otimes C_1\), the selection rules are completely different. This is because the dipole operator \(\mu_d\), which is invariant \((A_i)\) under permutations of the nuclei, carries the representations \(B_1\) \((\mu_0 = \mu_d)\) and \(E\) \((\mu_{xx} + \mu_x y)\) of the point group \(D_{2h}\) and the representations \(A_{2g}\) and \(E_u\) of \(D_{2h} \otimes C_1\). Using the classification in Table \(V\) one easily derives these selection rules. It must be emphasized, however, that they need no longer be obeyed when the amplitudes of the vibrations become large, so that, at best, they are indicative for the intensities of the transitions between the lowest (localized) vibrational states of the \((N_2)_2\) dimer.

### B. Comparison with experiment

As the IR transitions leave the nuclear spins unaffected we shall distinguish our results for different \((N_2)_2\) dimers according to the nature of their constituents: ortho \(N_2\) and para \(N_2\). For ortho-ortho dimers the \(A_1^+\), \(J = 0\) ground state lies at \(-74.9 \text{ cm}^{-1}\) relative to the separated ortho \((j_A = j_B = 0)\) monomers, so the dissociation energy is \(D_0 = 74.9 \text{ cm}^{-1}\). For the ortho-para complex the lowest state has \(E^+\) symmetry and \(J = 1\) and it lies at \(-72.8 \text{ cm}^{-1}\); the dissociation energy is \(D_0 = 76.8 \text{ cm}^{-1}\) relative to ortho \((j_A = 0)\) and para \(N_2\) \((j_B = 1)\). The para-para dimer has its lowest energy at \(-72.5 \text{ cm}^{-1}\), in the \(B_2^+\) state for \(J = 0\): \(D_0 = 80.5 \text{ cm}^{-1}\) relative to two para monomers \((j_A = j_B = 1)\), while another para-para \((B_2^+\), \(A_1^+)\) state close to the ground state occurs for \(J = 2\) at \(-70.1 \text{ cm}^{-1}\): \(D = 78.1 \text{ cm}^{-1}\). Thus, the strongest van der Waals bond actually occurs between two para \(N_2\) monomers \((j_A = j_B = 1)\). \(17\) For \(N_2\) the binding is much stronger, however, and the number of bound states is much larger. The energy distributions of these states are similar for ortho and para \(N_2\) compounds, in contrast with \((H_2)_2\) which has two para-para, four para-ortho, and ten ortho-ortho bound states. \(11\) This is caused by the stronger anisotropy in the \(N_2-N_2\) potential and the smaller rotational constant: \(B_{2g} = 2.0 \text{ cm}^{-1}\) \((B_{2g} = 65 \text{ cm}^{-1})\), which makes the monomer rotational quantum numbers \(j_A\) and \(j_B\) much less good than they are for \(H_2\). Indeed, we observe in the rovibrational wave functions calculated for \((N_2)_2\) that strong mixing occurs between basis functions with different (even/odd) \(j_A\) and \(j_B\).

Not far above the lowest states just mentioned we find many vibrationally and rotationally excited states for each type of dimer. Therefore, at the temperature for which the IR spectrum has been measured: \(77 \text{ K} = 54 \text{ cm}^{-1}\), many of these states will be populated and it is difficult to find a direct relation between the calculated levels and transition frequencies and the experimental spectrum.

Probably the simplest to interpret are the pure endover-end rotational \(\Delta J = 1\) transitions. In Sec. VI it has been shown that the frequencies of these transitions, at least for \(J \lesssim 2\), can be accurately evaluated, in general, from the vibrationally averaged value \((\text{for } J = 0)\) of the end-over-end rotational constant: \(B = (I_2\mu^2)^{-1}\). This \(B\) value decreases slightly with vibrational excitation (see Tables X and XI); its ground state values are...
of about 8 cm\(^{-1}\). The effective barrier is lower, how­

ever, due to averaging over the other internal coordi-

nates; for \(\langle R \rangle = 3.79 \, \text{Å}\) the barrier is only 14 cm\(^{-1}\). The

first excited state is this direction is already strongly

anharmonic, fundamental frequency 8.1 cm\(^{-1}\) (harmonic

value 13.9 cm\(^{-1}\)), and the higher states are certainly de­

localized in \(\phi\). They are still localized in the other

bending directions \(\theta_A^0\) and \(\theta_B^0\), however, and it is only

at higher energies that the monomers can rotate more

freely in all directions. Completely free internal rota­

tions are especially hindered by the strong repulsion in

the linear structure \((\theta_A^0 = \theta_B^0 = \phi = 0^\circ)\). The combination

of partly free internal rotations and bending vibrations,

with strong coupling also to the dimer stretch vibrations,

leads to an complicated energy level scheme over a large

range of bound states, in which it is hard to observe

regularities. We note here that such regularities in the

IR spectrum could only be interpreted for Ar–N\(_2\) [which

is less complicated than (N\(_2\))\(_2\) since there is just one

barrier to internal rotation] by combining groups of in­

dividual transitions.\(^{36}\) Before one can make a similar

analysis for (N\(_2\))\(_2\), it will be necessary to perform cal­

culations for higher \(J\) and \(k\) values, and maybe to include

basis functions with higher \(j_A\) and \(j_B\) as well for the

bound states near to the dissociation limit, and to make

assumptions about the intensities. On the other hand

what our calculations suggest is that part of the mono­

mer rotational structure in the (N\(_2\))\(_2\) dimer spectrum

is due to resonances or metastable states in the dis­

sociation continuum. If such resonances are long lived,

due to a low rotation-predissociation rate for (N\(_2\))\(_2\), one

would expect sharp N\(_2\) rotational bands.

VIII. CONCLUSIONS

After analyzing the results of our full quantum dy­

namical calculations on (N\(_2\))\(_2\) and comparing them with the

experimental IR spectrum, we can draw the follow­
ging general conclusions. The (N\(_2\))\(_2\) dimer is a typical

dimer molecule which is intermediate between normal

rigid molecules and special van der Waals bound sys­
tems with free internal rotations, such as (H\(_2\))\(_2\) and

noble gas-H\(_2\) dimers. It shows characteristics of both

these extremes. The ground state is localized and near­

ly harmonic, although split by tunneling. The (N\(_2\))\(_2\)

dimer has a large number of bound vibrational (and ro­
national) states. On the other hand, the stability of the

ground state is different for ortho–ortho, ortho–para,

and para–para complexes, just as for (H\(_2\))\(_2\), although the

states with different monomer rotation quantum numbers

\(j_A\) and \(j_B\) are strongly mixed (in contrast with (H\(_2\))\(_2\)

where \(j_A\) and \(j_B\) are still very good quantum numbers).

As we increase the vibrational energy, the (N\(_2\))\(_2\)
dimer changes its character: the bending modes which, for

the low lying vibrational states, are anharmonic and

strongly coupled to each other and to the dimer stretch

mode, go over into hindered rotations for higher states.

There is a range of intermediate states, however, where

the monomer rotations are almost free in some directions

and still localized in others. The energy level pattern for

these states is complicated and it is hard to retrieve the

regularities observed in the experi­

mental IR spectrum\(^{36}\) by looking at the individual

transitions. A complete analysis of this spectrum also

requires the states with higher \(J\) and \(k\) values than we

have calculated and, furthermore, it will be necessary
to make assumptions about the intensities and to combine groups of transitions, as it has been done for Ar–N₂ in a much simpler model. 39

On the other hand, we want to encourage new measurements of the IR spectrum of (N₂)₂ or measurements of its Raman or hyperfine spectrum, with the higher resolution and lower temperatures that can now be reached in nozzle beams. We expect that, both in the range between 5 and 25 cm⁻¹, where Long et al. 36 only found one vibrational peak, and in the region above 25 cm⁻¹, where they only identified monomer rotational envelopes, more detailed structure will actually be present. By comparison of this structure with dynamical calculations like ours, much can be learned about the accuracy of such calculations and, in particular, of the potential on which they are based.

Finally, we conclude that the results are also of interest for understanding the dynamics of solid N₂, especially the transition from the orientationally ordered α phase, with librations that become more and more anharmonic with increasing temperature, to the orientationally disordered β phase, where one expects the internal N₂ rotations to become delocalized. A similar transition occurs in the (N₂)₂ dimer when its internal energy is increased. It would be very useful to make a thermodynamic study of this dimer as a function of temperature. Knowledge of the full dynamical solutions of (N₂)₂ is also useful for comparison with more approximate models (classical Monte Carlo or Molecular Dynamics, mean field, libron models, etc.) that have been applied to solid N₂ and other molecular crystals and liquids. Work along these lines is in progress.

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2See Refs. 23–36 in the review (Ref. 1) of Le Roy and Carley.
14J. A. Vliegenhart (private communication).
22P. Botaschwin (private communication).
41J. H. van Vleck, Phys. Rev. 33, 467 (1929).
45P. M. Morse, Phys. Rev. 34, 57 (1929).
53A. Varshalovich, A. N. Moskaliev, and W. K. Cherson-


56E. B. Wilson, Chem. Rev. 27, 31 (1940).


58A. van der Avoird (unpublished work).
