INTERMOLECULAR POTENTIALS, INTERNAL MOTIONS AND THE SPECTRA OF VAN DER WAALS MOLECULES

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ABSTRACT. The infrared spectra of \( \text{N}_2\text{Ar} \), \( \text{O}_2\text{Ar} \), \( \text{N}_2\text{N}_2 \) and \( \text{O}_2\text{O}_2 \) seem to indicate that these Van der Waals molecules possess orientationally localized (librational) states, as well as (nearly) free internal rotor states. Using the full anisotropic potential, we have calculated the rovibrational bound states of \( \text{N}_2\text{N}_2 \) and \( \text{N}_2\text{Ar} \), and also the rotational predissociation states of the latter complex, and we have evaluated the contributions of these states to the infrared spectra. Thus the infrared spectrum of \( \text{N}_2\text{Ar} \), and in principle also the spectra of the other dimers, can be understood. The onset of the regular free internal rotor structure cannot be explained from the bound states; it is due to rather narrow (0.2 to 3 cm\(^{-1}\)) rotational resonances lying in the collision continuum. The structure in the lower frequency part of the spectra is caused by transitions between localized librational states; especially this part will be sensitive to the detailed intermolecular potential. In order to exploit this sensitivity one has to measure the infrared spectra at very low temperature.

1. INTRODUCTION

The mobility of the constituents in different Van der Waals molecules varies considerably. Considering, for instance, the series of molecule-rare gas atom dimers, we observe, as one extreme, the nearly free internal rotations of \( \text{H}_2 \) in the \( \text{H}_2\text{X} \) dimers. A theoretical description of such dimers is best given by using a basis of free rotor functions, both for expanding the potential and for the rovibrational wave functions [1]. At the other end of the series are the dimers in which the (rigid) molecule is strongly aspherical, very long or flat, with one or two of its dimensions larger than the Van der Waals distance between the molecule and the rare gas atom. Internal rotations are completely prevented in that case; at specific angles (and distances) the potential becomes even infinitely repulsive. When the molecular size is comparable with the Van der Waals distance, as in benzene-argon or tetrazine-argon [2], dynamical calculations using a free rotor basis are still possible, but they converge...
very slowly. In cases like anthracene-argon or fluorene-argon [3], this description breaks down completely and one has to use different internal coordinates and different basis functions. A more natural description of the internal motion is that of the atom moving along the molecular plane and vibrating against it [4]. The amplitude of the motion along the plane can be substantial. For instance, in benzene-argon and tetrazine-argon the root-mean-square amplitude of the Van der Waals (stretch) vibration perpendicular to the plane is 0.13 Å, whereas the amplitude parallel to the plane is about 0.40 Å, in the ground state. With two quanta of vibrational excitation the latter amplitude goes up to 1.0 Å. The probability that the atom tunnels to the other side of the molecule is still negligible, however [2].

An interesting intermediate case are the Van der Waals complexes containing N₂ or O₂ molecules. According to the first interpretations of their infrared spectra [5-8], such complexes seem to exhibit both rotational vibrations (librations) and nearly free internal rotations, depending on the degree of excitation or the temperature. The homogeneous dimers N₂-N₂ and O₂-O₂ are very important because their dynamical behaviour and spectra are determined by the same intermolecular potentials that cause the properties of bulk N₂ and bulk O₂. The infrared spectra of N₂-Ar and O₂-Ar are strikingly similar to those of the homogeneous dimers, but these systems are simpler (with just one instead of three internal angles) and therefore more accessible to detailed studies. The early interpretations of the infrared spectra of these dimers [5-8], even of the diatom-diatom complexes, are based on a one-dimensional model for the hindered internal rotation. The coupling with the Van der Waals stretch was disregarded, although the excitation energies corresponding with the higher frequency parts of the infrared spectra are larger than the Van der Waals dissociation energy.

O₂ complexes are especially interesting because of the electronic triplet spin momentum in the ground state O₂ molecule. Mainly via spin-orbit and spin-spin interactions this triplet spin momentum couples with the rotational states of O₂. The magnetic spectrum of free O₂ corresponds (nearly) with Hund's coupling case b [9]. The drastic changes of this spectrum in O₂-Ar are completely understood [10-12]; they form a direct measure of the rotational (im)mobility of O₂. In the O₂-O₂ dimer various magnetic coupling terms are important: the intermolecular exchange coupling usually represented by the Heisenberg effective spin hamiltonian, the intramolecular spin-orbit and spin-spin couplings in each O₂ monomer and the intermolecular spin-spin (magnetic dipole-dipole) coupling. All these couplings play a role in the magnetic properties of solid O₂ [13,14]. A detailed study of their effect on the magnetic spectrum of O₂-O₂ will soon be published [15].

In the present paper we shall concentrate ourselves on the internal motions of N₂ in the N₂-N₂ and N₂-Ar dimers and their effects on the infrared spectra of these dimers.
Besides a number of empirical model potentials, two detailed anisotropic N₂-N₂ potentials are available from ab initio calculations in our institute [16,17]. Just as most of the empirical model potentials which have been parameterized by fitting solid state data, our ab initio potentials have been used to calculate various properties of solid N₂. Without any parameter fitting they yield good agreement with experiment for several solid state properties, provided that the anharmonicity in the (collective) vibrations of the N₂ molecules in the solid is correctly taken into account. It may be worth mentioning that also in the solid, at low temperatures, the librations of N₂ have fairly large amplitudes (about 16° even at 0 K), so that it was necessary to develop special lattice dynamics methods [18] in order to deal with the anharmonicity of these librations. These methods were strongly inspired by our experience with Van der Waals molecules.

Among solid state physicists, it is generally believed that especially the phonon frequencies depend sensitively on the form of the intermolecular potential. We have found, however, [17] that the two different ab initio potentials do not yield more than 9% difference in these frequencies for both the ordered (α and γ) phases of solid N₂, whereas the discrepancy with the experimental frequencies is about 8%. (This is considered to be a very good agreement; most empirical model

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potentials perform much worse, even after optimization of the parameters. Better agreement could not be expected, if only because of the neglect of many-body contributions to the potential. So it is not possible by looking at the solid state data to discriminate between these two ab initio \( \text{N}_2-\text{N}_2 \) potentials and, thus, to evaluate their quality.

In Table I we have applied the same two ab initio potentials to various geometries of the \( \text{N}_2-\text{N}_2 \) dimer and we observe striking differences. The older potential \[16\] yields a crossed \( (D_2d) \) equilibrium structure, whereas the absolute minimum for the newer potential \[17\] occurs for a shifted parallel geometry. Also the relative energies of other low lying structures are different. The changes in the well depth are not larger than 20\%, however, and the variations in the repulsive and attractive contributions which lead to these changes are even more subtle. This situation is typical for a Van der Waals molecule. It illustrates that it will be very difficult by means of ab initio calculations alone, to obtain potential surfaces that are sufficiently accurate to predict equilibrium structures and barriers to internal rotation. The differences in equilibrium structure and in the barriers to internal rotations will have their consequences for the rovibrational transitions in Van der Waals molecules, however. Making dynamical calculations based on various potentials and comparing the results with the rovibrational spectra of Van der Waals molecules is probably the most discriminating method to evaluate these potentials. With the older of the two ab initio potentials such calculations on the \( \text{N}_2-\text{N}_2 \) dimer have been made already \[19,20\].

The infrared spectrum of \( \text{N}_2-\text{N}_2 \) has been measured \[7\] with a resolution of about 1 cm\(^{-1}\) in the gas phase at 77 K as a discrete structure on top of the broad collision-induced spectrum (see Fig. 1). The spectrum has been observed in the region of the \( \text{N}_2 \) monomer stretch frequency at 2330 cm\(^{-1}\) and the Van der Waals vibrations are visible in

![Figure 1. Infrared spectrum of \( \text{N}_2-\text{N}_2 \) at 77 K from ref. [7].](image-url)
combination with the $N_2$ stretch. Apart from rotational bands due to the end-over-end rotations of the dimer, the spectrum contains one peak at 9.5 cm$^{-1}$, which has been assigned as a locked rotational vibration or libration, and a fairly regular series of peaks at higher frequencies, which have been attributed to (slightly perturbed) internal rotations.

In the calculations [19,20] the rovibrational states of $N_2-N_2$ have been expanded in a basis of free rotor functions, expressed in a dimer-fixed coordinate frame, multiplied by a basis of Laguerre functions for the Van der Waals stretch. The dimer Hamiltonian with the anisotropic $N_2-N_2$ potential that was available from ab initio calculations [16] has been diagonalized in this basis. All bound states

![Near IR T=2K](image1)

Figure 2. Calculated infrared spectrum of $N_2-N_2$ at 2 K from ref. [20].

![Near IR T=25K](image2)

Figure 3. Calculated infrared spectrum of $N_2-N_2$ at 25 K from ref. [20], using all bound states.
of the $N_2$-$N_2$ dimer have thus been calculated. Using an empirical
dipole function obtained from the collision-induced infrared spectrum
[21], we have also calculated the strengths of all the allowed
bound-bound dipole transitions and thus generated the complete infrared
spectra, both in the far- and near-infrared regions. The spectrum in
the region of the $N_2$ stretch frequency is shown in Fig. 2, at very low
temperature (2 K) and in Fig. 3 at somewhat higher temperature (25 K).

Figure 4. Cuts through ro-vibrational wave functions with $R$ and $\phi$
fixed at the values specified below. The states are labelled $\Gamma(k,n)$,
where $\Gamma$ is the PII(16) symmetry label, $k$ the angular momentum around
the intermolecular axis $R$ and $n$ a sequence number for the levels
belonging to the same $\Gamma$ and $k$. Shown are the ground state $A'^+_1(0,1)$
($R=7.0$ $a_0$, $\phi=90^\circ$) and the excited levels for which transitions from
the ground state are strongest; near-infrared: shifted parallel
($R=7.4$ $a_0$, $\phi=0^\circ$) structure $A'^+_2(1,1)$; far-infrared: T-structure
($R=7.4$ $a_0$, $\phi=0^\circ$) $B'^+_1(0,1)$ and $\delta$-excited state ($R=7.4$ $a_0$, $\phi=90^\circ$) $B'^+_1(1,1)$. 
In the low temperature spectrum specific transitions from the vibrational ground state to some low lying excited states are clearly distinguishable. These states are more or less localized, see Fig. 4, around the different local minima in the potential. Already at 25 K many states are populated, the energy differences between them do not show a regular pattern as in harmonic vibrations or free rotations, and so the structure in the spectrum is rather blurred. So we think that the lower frequency part of the experimental infrared spectrum [7] at 77 K can certainly not be ascribed to a single librational transition. It will be due to many different transitions which could only be resolved at much lower temperature.

A surprising feature in the calculated spectra, Figs. 2 and 3, is the complete absence of the series of bands at higher frequency which have been assigned [7] to (nearly) free internal rotations. Although all the bound states up to the dissociation limit have been included in the generation of the infrared spectrum, no regular pattern of free internal rotor transitions is visible still. We believed that such a pattern, which has been observed experimentally, might actually be due to rotational (predissociation) states lying in the continuum, i.e. to rotational resonances. Both the fairly high temperature (77 K) of the experiment and the observation that the structure in the spectrum continues beyond the dissociation energy support this assumption. In order to study this possibility we have started calculations on the N$_2$-Ar dimer, which is simpler than N$_2$-N$_2$, but has a very similar infrared spectrum [8], see Fig. 5. The results of these studies are reported in the sequel of this paper.

Figure 5. Infrared spectrum of N$_2$-Ar at 87 K from ref. [8].
3. BOUND AND ROTATIONAL RESONANCE STATES AND THE INFRARED SPECTRUM OF N$_2$Ar

3.1. Theory

The Hamiltonian which describes the nuclear motions in a dimer that consists of two rigid molecules, has been discussed by Brocks et al. [22]. The special case of an atom-diatom system has been subject to extensive studies [1]. Bound states of this Hamiltonian are usually calculated by an expansion in a basis set which consists of products of free rotor angular functions and radial basis functions. The angles describe the orientations of the molecules and of the complex as a whole, and the radius is the distance between the centers of mass of the molecules. The expansion parameters are then variationally optimized; this method has been called SE [1] or LC RAMP [19]. The details of the calculation and possible approximations depend on the particular coordinate reference frame which is chosen [1,22]. However, as our calculations are exact within the finite space spanned by our basis, these details are irrelevant here.

The resulting pattern of energy levels is very dependent on the interaction potential, especially on its anisotropy, and on the rotational constants of the molecules. For atom-diatom systems, notable extreme cases are H$_2$Ar, which behaves like a (an)harmonic oscillator/rigid rotor molecule [23], and N$_2$Ar, where H$_2$ behaves as a free internal rotor [1]. Approximate labeling schemes for the states, which are based on the anisotropy of the interaction potential versus the rotational constant of the diatom, have been discussed by Ewing [24]. In case of a strongly anisotropic potential and/or a small rotational constant, the labels of the harmonic oscillator/rigid rotor model can be used. For N$_2$Ar, which has a triangular equilibrium structure, this amounts to $v_3$, the stretch quantum number describing the motion in the radial direction, $v_4$, the bend quantum number describing the orientational motion of the diatom in the complex, and $k$, the symmetric top rotational quantum number. (If the atom is relatively heavy compared to the diatom, and the atom-diatom distance is larger than the diatom bond length, the asymmetry splitting is small. The complex is then a near prolate symmetric top.) In case of a nearly isotropic potential and/or a large rotational constant, the diatom can be treated as a free internal rotor. The labels of this model are $j$, the angular momentum quantum number associated with the rotation of the diatom, and $\ell$, the angular momentum quantum number associated with the rotation of the vector which connects the center of mass of the diatom with the atom. In both models, the states are labelled additionally with the overall rotational quantum number $J$ and with the parity, which are exact quantum numbers. A correlation diagram for the two models has been given by Henderson and Ewing [8]. This diagram is complicated, but can be simplified, if one disregards for the moment the rotational fine structure caused by $J$ and $\ell$. The correlation between the two models is then simply:

$$v_3 + k \leftrightarrow j$$  \hspace{1cm} (1)
In the next section we will try to assign labels to the calculated states of \( \text{N}_2\text{Ar} \) and to determine their positions in the correlation diagram.

At the temperatures of bulk gas experiments, such as in refs. [5–8], continuum states are strongly occupied. Most of these contribute to the infrared spectrum as a broad structureless band, the so-called collision induced absorption [21]. Some continuum states, however, give rise to additional structure. A state, in which the diatom is excited as an internal rotor, can have a finite life time \( \tau \), before the diatom rotational energy is transformed into translational energy (between atom and diatom) and the complex dissociates. In the spectrum, a transition to such a state results in a homogeneously broadened line having a width \( \Gamma \sim 1/\tau \). Such a state is called a rotational resonance.

The calculation of continuum states is costly, especially by numerical close coupling calculations. In order to establish the possible role of rotational resonances in the infrared spectrum of \( \text{N}_2\text{Ar} \) we therefore adopt two procedures. In the first, more approximate procedure, we consider rotational resonances as if they were bound states, i.e., we exclude all dissociation channels. This allows a relatively cheap calculation of the approximate position of a large number of resonances. Moreover, these (quasi) bound states can be classified along the same lines as the truly bound states. The second procedure involves more computational effort as the calculations are repeated while adding the dissociation channels. The coupling with these channels results in a level shift of the quasi bound states, and in a broadening, which is characterized by a certain width. The latter calculations are performed for a subset of resonance states, from which we hope to draw conclusions related to all these states. If the coupling to the dissociation continuum is strong, both width and level shift are large. Such a state is thus not separately observable in the spectrum. For a weak coupling the state can be observed due to its small width. But then the level shift is also small, and the quasi bound level determined in the first procedure is a good approximation of the position of the resonance. So, as a result of the first procedure, the pattern of energy levels for the resonance states and its impact on the structure of the spectrum can be discussed. As a result of the second procedure, it can be determined which of the resonances are actually observable.

The calculation of the resonance position and width in the second procedure is based on an expansion in the same basis set as was used for the bound states. The states resulting from the variational calculation which have a positive energy then represent the continuum in the way explained in ref. [25]. These states can be used to calculate an approximate resonance phase shift:

\[
\delta^E_i (\epsilon_n + \epsilon_{n+1}) = \sum_{m=1}^{n} | \langle i | m \rangle |^2
\]

Here \( \epsilon_n \) is the \( n \)th positive eigenvalue of the variational calculation and \( |m\rangle \) the associated eigenstate. The state \( |i\rangle \) is the closed channel part of the resonance, i.e., the result of the calculation.
where the dissociation channels are excluded. As outlined in ref. [25],
this approximate phase shift can be used to obtain the resonance
parameters. The true phase shift is a continuous function of the
energy \( E \), and a resonance is characterized by a sharp rise of this
function around the energy \( E_i \), which is called the position of the
resonance. For the discrete function of Eq. (2), the situation
where \( E_i \approx \epsilon_n \) would mean that:

\[
|<i|n>|^2 > |<i|m>|^2 , \quad m \neq n
\]  

(3)

In general, a basis set contains one or more intrinsic parameters;
changing these parameters results in a shift of the eigenvalues \( \epsilon_n \)
of the variational calculation. If the discrete approximation of Eq. (2)
resembles the true phase shift, and the differences between the
eigenvalues do not vary too drastically in changing the basis set
parameters, then the quantity \( |<i|n>|^2 \) has its maximum in the
situation where \( E_i = \epsilon_n \). Reversing the argument, the position of the
resonance \( E_i \) can be found by maximizing \( |<i|n>|^2 \), while varying the
intrinsic basis set parameters. The width of the resonance can in
principle be found by assuming a Breit-Wigner line shape [26] between
the points \( \{\epsilon_n + \epsilon_{n-1}\} \) and \( \{\epsilon_n + \epsilon_{n+1}\} \). The complications which arise
if \( \epsilon_{n-1} \) and/or \( \epsilon_{n+1} \) represent a neighbouring resonance, lead to a
somewhat modified procedure. This has been discussed in ref. [25].
From a different starting point Grabenstetter and LeRoy have developed
a similar procedure [27].

The calculations will only yield meaningful results when the
resonances are isolated, i.e. non-overlapping. Accurate close coupling
calculations on ArHCl by Ashton et al. [28] indicate the validity
of that assumption for narrow resonances. Those are also the most
interesting ones in our case. Our procedure was tested on rotational
resonances of \(^3\)HeAr [25] and the results were compared to accurate
close coupled values [29]. The calculated resonance positions were
in excellent agreement; the widths were 25% too high, but their
ratios were again in excellent agreement. Considering that these
calculations are relatively cheap for resonances at not too high
energies, these results are satisfactory.

3.2. Results

For the calculations we have used the semi-empirical potential of
Candori et al. [30], which has been constructed using a fair amount
of experimental data. It is most convenient if this interaction
potential is expressed as a series expansion in Legendre
polynomials. For that purpose, the potential has been numerically
transformed into such a form. Truncation of the series at the
Legendre polynomial of order 8 had an effect of less than 0.005 cm\(^{-1}\) on
the bound state eigenvalues. With the basis we have used, these
eigenvalues were converged within 0.05 cm\(^{-1}\).

A number of calculations for various overall rotational states \( J \)
(remember that \( J \) is the only exact quantum number) have been performed.
Approximate labels, as discussed in the previous section, have been
assigned to the resulting states on the basis of energy level separations and the coefficients of the dominant basis functions. If these states are sorted on their radial stretch quantum number $v_8$, for each $v_g$ a correlation diagram can be made with the levels of the harmonic oscillator/rigid rotor model on one side and the free internal rotor model on the other side. Such a diagram is given in Fig. 6 for the levels with $v_g=0$, $v_8$, $k$ from 0 to 3 and $J=k$. In the lower energy range one observes many crossings in the correlation between the $N_2Ar$ levels and the free internal rotor levels and few crossings between the $N_2Ar$ levels and the harmonic oscillator/rigid rotor levels. Especially in the vibrational ground state $N_2Ar$ has a rigid rotor like spectrum. Already at the second bending overtone, the rigid rotor character is diminished, as indicated by the relatively large splitting of the rotational excitations. A transition range starts here, where the $N_2Ar$ levels cannot be assigned to either one of the limiting models. In this range also the $v_8$ and $v_9$ modes are strongly coupled and part of the assignment becomes rather arbitrary. At higher energy the number of crossings between the $N_2Ar$ levels and the free internal rotor levels decreases. With some imagination a $j=5$ multiplet can be recognized just below the dissociation limit. For other $v_8$ states, the conclusions are more or less similar; we will come back to this point later. A general conclusion is that at temperatures where only bound states are sufficiently populated, a free internal rotor character is practically absent. Only at very low temperatures, the rigid rotor character may be observed; increasing the temperature involves the levels in the transition region and the resulting spectrum becomes very complicated. These conclusions are consistent with the $(N_2)_2$ results.

The experimental spectrum of Henderson and Ewing [8] was obtained for a temperature of 87 K, at which continuum states are strongly populated. Most of this spectrum was interpreted in terms of a one-dimensional hindered internal rotor model. Our calculated bound states cannot explain the observed structure in the spectrum. So, unless the potential of Candori et al. [30] is substantially wrong, the explanation must invoke the rotational resonance states. If the latter are treated as bound states (see previous section), the assignment of approximate labels is similar. Fig. 7 gives the results for the $v_g=0$ rotational resonances. These states clearly show a free internal rotor character. Figs. 6 and 7 then give a complete characterisation of the $v_g=0$ states of $N_2Ar$. A distinct free internal rotor pattern is not observed until the resonance states are reached, i.e. for $j=6$. Results for other $v_8$ states are similar. By excitation in the radial stretch mode, the average distance between atom and diatom increases. The interaction potential becomes less anisotropic at larger distances. Therefore, for these radially excited states, a free rotor pattern is observed for lower $v_8$ and $k$ than for the $v_g=0$ states. However, the radial excitation energy compensates for this earlier onset of free internal rotor character. So on the whole, the free internal rotor pattern is observed only for resonance states.

The onset of free internal-rotor character can be estimated from diagrams like Figs. 6 and 7 and it is given in Table II as a function of the radial (stretch) excitation. In a one-dimensional model [8]
Figure 6. Bound states of $\text{N}_2\text{Ar}$ with stretch quantum number $v_s=0$ and overall rotational quantum number $J=k$, correlated with the levels of the harmonic oscillator/rigid rotor model and those of the free internal rotor model. The states are labeled with bend quantum number $v_b$ and symmetric top quantum number $k$ or diatom rotational quantum number $j$. 
Figure 7. Rotational resonances with \( v_s = 0 \), \( J = k \), labeling see Figure 6.
Radial stretch excited states \((v_3=0, k=0)\), vibrationally averaged atom-diatom distances and potential values at the T-shaped and linear geometries of \(N_2Ar\). The onset of the internal rotor character is estimated from diagrams like Figs. 6 and 7.

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it can be related to the rotational barrier which is by definition the difference in potential energy between the T-shaped and the linear structure. In the multi-dimensional case, this definition of the rotational barrier has little meaning, as is shown in Table II, where the values of the potential for the vibrationally averaged distances are given. Instead, one should consider the topology of the potential surface in all coordinates.

At this stage it is useful to consider whether the calculated levels can lead to the interpretation of the experimental spectrum \([8]\), if only qualitatively. For this purpose, a crude procedure for the construction of a spectrum is chosen. We disregard the overall rotational fine structure associated with different \(J\) values. The set of levels from Figs. 6 and 7 is taken, together with the equivalent levels for the stretch excited states. Each level is weighted with the appropriate Boltzmann factor and with its spin statistical weight. Allowed transitions are determined by a set of selection rules and it is assumed that they all have equal strengths. For harmonic oscillator like states the selection rules are

\[(a) \ \Delta v_3=0 \ ; \ \Delta v_3=0, \pm 1 \ ; \ \Delta k=0, \pm 1\]

\[(b) \ \Delta v_3=\pm 1 \ ; \ \Delta v_3=0 \ ; \ \Delta k=0, \pm 1\]

If the transition dipole moment is mainly determined by the \(N_2\) quadrupole induced dipole on Ar (and possibly by low order exchange terms), the selection rules for a free internal rotor are
For each \( v_s \), a threshold is set, below which the harmonic oscillator selection rules apply, and above which the free rotor selection rules are valid. These thresholds are given in Table II. The transition lines that are thus computed are artificially broadened by applying a Lorentz profile of uniform width (2.5 cm\(^{-1}\)). Thus a simulated spectrum is constructed, which is given in Fig. 8 for the experimental temperature. Fortunately, the gross structure of the spectrum does not depend sensitively on the thresholds or the Lorentz width. The experimental spectrum was measured near the \( N_2 \) monomer stretch frequency of 2330 cm\(^{-1}\); in order to compare the experimental values with Fig. 8 one should thus subtract this value. Qualitatively the agreement is good, especially in the higher energy region, where the characteristic structure of a free internal rotor spectrum is observed. This is direct evidence for our assertion that the regular structure of the experimental spectrum is mainly due to rotational resonance states, and not to the bound states. The peaks in the simulated spectrum are even closer to free internal rotor transitions than the experimental peaks. However, one should be careful to draw quantitative conclusions on the basis of such a crude calculated spectrum. In reality, the transition strengths should be calculated with the use of a reasonable interaction dipole surface; furthermore the overall rotational bands will have to be included. This will also yield a definite assignment of the structure in the lower frequency part of the spectrum, which contains contributions from transitions between localized bending states and from stretch transitions. As calculations on \((N_2)_2\) have shown, however, the required computational effort is substantial [20].

![Simulated spectrum](image)

Figure 8. Simulated spectrum of \( N_2 \)Ar at \( T=87 \) K, from simplified model (see text). The vertical lines indicate the positions of the ortho/para \( N_2 \) free rotor transitions with their spin statistical weights.
TABLE III

Rotational resonance parameters and assignments for the J = 0 resonances.

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(a) these states are mixed

The widths of the J=0 resonances were obtained by using the procedure outlined in the previous section. The properties of the rotational resonances are intimately connected with the free internal rotor character. Therefore we have changed the labeling of states somewhat, as compared to Figs. 6 and 7. In Table III the states are labeled with the stretch quantum number v_s and the diatom angular momentum j. For j<4, this labeling is obvious, apart from some occasional mixing of nearby resonances. For j=3 and especially j=2 the states are strongly mixed and the labeling is highly approximate. The position of the resonances is shifted, as compared to the quasi bound state calculations. In most cases, however, the shifts are smaller than the widths of the resonances, which confirms the validity of the quasi bound calculations. The only exceptions are the j=2 resonances, but these have a large width and are probably overlapping, so the model breaks down anyway.

Despite the strong anisotropy of the potential, the resonances are
INTERMOLECULAR POTENTIALS, INTERNAL MOTIONS AND THE SPECTRA

surprisingly narrow. The calculated widths are in the range of 0.18 to 3.5 cm$^{-1}$. For $\text{N}_2\text{Ar}$, our method overestimated the widths [25], so they might even be smaller. The main reason for this sharpness seems the exclusion of the \( j \rightarrow j - 1 \) dissociation route for symmetry reasons. The states with even and odd \( j \) belong to ortho and para nitrogen, respectively, and transitions between these two species are excluded. The variation of the widths with the stretch quantum number \( \nu_s \) within the same \( j \) series follows the same pattern that has been observed by Ashton et al. in $\text{ArHCl}$ [28]. At first the width increases slightly with increasing \( \nu_s \), but then it drops sharply as the energy reaches the threshold for the dissociation channel, associated with that particular \( j \) value. The reason for this behaviour is probably the large increase of the average distance \( R \) with stretch excitation, see Table II, whereby the anisotropy of the potential decreases. This anisotropy is the driving factor for the conversion of the internal rotational energy to the translational energy, which leads to the dissociation of the complex. Therefore, it determines the resonance line widths. Exceptions to this pattern (besides the \( j=2 \) resonances already mentioned) are the \( j \) resonances, which are even below the \( j-2 \) thresholds, e.g. \((\nu_s, j) = (0,6) \) and \((0,7)\). Because of the additional exclusion of the \( j \rightarrow j - 2 \) and \( j \rightarrow j - 3 \) dissociation routes and the energy or momentum gap law [31,32], these resonances are relatively narrow.

Resonances for other \( J \) states are expected to behave similarly to the \( J=0 \) resonances. Resonances having a width of about 1 cm$^{-1}$ or less can probably be observed in the experimental spectra [5-8]. The states which are more excited in the stretch mode have a smaller width and thus give rise to a sharper structure in the spectrum. As these states have a relatively strong free internal rotor character, as compared to the states that are less excited in the stretch mode, this gives the spectrum an extra free internal rotor accent.

4. CONCLUSIONS

Using an expansion in a finite basis set, we have been able to calculate both bound and rotational resonance states of $\text{N}_2\text{Ar}$. These states have been used to interpret the infrared spectrum of this Van der Waals molecule. At low temperature, the spectrum appears to be determined by transitions in the low frequency range between bound states which represent localized vibrations around a distinct local minimum. At higher temperature, the structure in this spectrum is blurred and it is extended to somewhat higher frequencies. Major contributions then result from transitions between bound states which are not well localized. Moreover, these states show appreciable mixing of Van der Waals stretch and hindered rotation modes. The majority of the states up to the dissociation limit have this character. A similar analysis of this frequency range has been made for the infrared spectrum of $\text{N}_2$-$\text{N}_2$.

At higher frequencies, the experimental spectrum shows the characteristic structure of a nearly free internal rotor. This structure appears to be caused by transitions involving states with energies
above the dissociation limit, which are called rotational resonances or predissociation states. During the lifetime of such a state, a collision complex is formed. Given a rotational state, the lifetime of the complex is longer the more it is excited in the radial stretch mode (as long as the radial excitation energy itself does not exceed the dissociation energy, of course). This can be understood by noting that the average distance increases with stretch excitation and the effective interaction potential becomes more nearly isotropic. A long lifetime means a small line width and a sharp contribution to the spectrum.

The infrared spectrum of $^3$Ar is thus understood. For $^3$N$_2$, $^3$O$_2$, and $^3$O$_2$ the infrared spectra in the higher frequency range are very similar to that of $^3$Ar; these can be interpreted along the same lines. According to the reasoning of the previous paragraph, the states which cause the internal rotor structure in the spectrum, do not depend sensitively on the anisotropy of the potential. This part of the spectrum is therefore not liable to yield a detailed test on the accuracy of the potential. Moreover, the effort which is needed to calculate all the resonances is substantial. The lower frequency part of the spectrum contains information which is more suitable for this purpose. It corresponds with transitions between states which are localized around different local minima. These states are thus very sensitive to the topology of the potential surface. In order to access this information, experiments should be performed at low temperatures, presumably using molecular beams, with a reasonably high resolution.

Finally, we note that, although the present paper refers to the infrared spectra of Van der Waals dimers, the same considerations apply to their Raman spectra.

5. REFERENCES

4. G. Brocks and D. van Koeven, to be published.
15. G. Brocks and A. van der Avoird, to be published.