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The vibration–rotation–tunneling spectrum of the polar and T-shaped-N-in isomers of $(NNO)_2$

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ABSTRACT

In this paper we report transition frequencies and line strengths computed for bright states of the NNO dimer. We use a previously reported potential obtained from explicitly correlated coupled-cluster calculations and fit using an interpolating moving least-squares method. The rovibrational Schroedinger equation is solved with a symmetry adapted Lanczos algorithm and an uncoupled product basis set. All four inter-molecular coordinates are included in the calculation. We propose two tools for associating rovibrational wavefunctions with vibrational states and use them to find polar-like and T-shaped-N-in-like rovibrational states. The first tool uses a re-expansion of the rovibrational wavefunction in terms of $J = 0$ eigenfunctions. The second uses intensities. Calculated rotational transition frequencies are in very close agreement with experiment.

1. Introduction

The spectroscopy of $(NNO)_2$ has interested experimentalists and theorists for many years [1–14]. $(NNO)_2$ is a loosely bound Van der Waals complex of the type that has interested McKellar and his co-workers [1–3,15–18]. It has important large amplitude motions of the type that have interested Bunker and his co-workers [19–27]. The deepest minimum on the $(NNO)_2$ potential energy surface (PES) corresponds to a non-polar slipped-anti-parallel structure with C_{2h} symmetry. Spectra attributed to the ν_2 and ν_3 fundamentals and to the $\nu_2 + \nu_3$ combination band (intra-molecular modes) were observed [6,7]. Also observed were combination bands involving the (inter-molecular) torsion and disrotatory coordinates [2,5,9]. Transitions among states associated with a polar isomer (or isomers) of $(NNO)_2$ have also recently been observed [1,3]. As discussed in Ref. [13] (hereafter denoted paper I) and Ref. [14] there are two polar isomers and both have a slipped-parallel structure with C_s symmetry. A microwave spectrum of the polar isomer was also recorded [4]. In this paper we use an accurate PES and compute rovibrational spectra considering the four inter-molecular coordinates. In paper I we presented the PES and energy levels associated with the global non-polar minimum. In this paper we present intensities and focus on understanding the microwave spectrum of the polar isomer. There have been several theoretical studies of $(NNO)_2$ using various levels of ab initio theory to determine structures and harmonic frequencies of the possible isomers. In particular, Berner et al. used the (CCSD/aug-cc-pVDZ) method [9]. They stress the importance of the disrotatory cycle.

The potential surface has local wells for both the polar and the T-shaped-N-in (TN) shapes. There are two equivalent wells for both the polar and the TN shapes. The questions that are the focus of this paper are: (1) Are there vibrational states that are localized in the local minima (polar and TN)? How does one identify polar-like and TN-like rovibrational states if they exist? (2) To what extent are the intensities of transitions between polar-like rovibrational states determined by the selection rules one would expect if the complex were rigid and had the shape corresponding to the bottom of a polar well? (3) Does tunneling between equivalent wells give rise to splittings that might be observable? Some of these questions were addressed in a recent paper [14]. The potential used in Ref. [14] has no or perhaps very shallow TN minima and no TN states were reported, but some of polar-like states of Ref. [14] are close to those we obtain. Ref. [14] does not present intensities or discuss how to identify $J > 0$ polar-like states.

We find polar-like states and propose two tools for identifying their associated vibrational states. Polar-like states are expected owing to the fact that microwave transitions were observed [4] and assigned to the polar isomer. The first tool uses intensities. Transitions between polar-like and TN-like rovibrational states are bright, but transitions between other rovibrational states are not. States linked by weak transitions, i.e. dark states, all have significant amplitude in the global minimum well. The second tool

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uses a re-expansion of the $J > 0$ wavefunctions in the basis of $J = 0$ eigenfunctions.

2. Potential energy surface

A four-dimensional (rigid monomer) potential energy surface was made using an interpolating moving least-squares fitting method. 1757 *ab initio* points computed at the CCSD(T)-F12b/VTZ-F12 level [28] were used to produced a surface with an estimated fitting error of less than 1.5 cm^{-1}. Details were discussed in paper I. In this section, we summarize the features related to the tunneling dynamics between the two equivalent polar wells.

The coordinates used to compute the rovibrational levels and wavefunctions were described in paper I. They are r_0, the distance between the two monomers, the standard polyspherical angles $(\theta_1, \theta_2, \phi_2)$, and the Euler angles (α, β, γ) [29–32]. The nature of the large-amplitude motion is more easily understand using the extended angles $(\tilde{\theta}_1, \tilde{\theta}_2)$ defined by extending the range of (θ_1, θ_2) from $[0, \pi]$ to $[0, 2\pi]$. They were used by Hougen and Ohashi for HF dimer [33]. The disrotatory (X) and conrotatory (Y) coordinates are easily defined in terms of the extended angles: $X = (\tilde{\theta}_1 + \tilde{\theta}_2)/2$ and $Y = (\tilde{\theta}_1 - \tilde{\theta}_2)/2$. Fig. 1 is a contour diagram of the potential. For each pair of values (θ_1, θ_2) the potential is minimized with respect to r_0 for both $\phi_2 = 180°$ and $\phi_2 = 0°$. The two polar wells are in the lower panel of Fig. 1. Starting from the polar well at $(\tilde{\theta}_1 \approx 120°, \theta_2 \approx 120°)$ one moves counterclockwise around the disrotatory cycle, from one polar structure to the other, by following the potential valley to the T shaped structure at $(\theta_1 \approx 180°,\ \theta_2 \approx 90°)$ and then moving to the upper panel, proceeding to the N-in non-polar structure, denoted NN on the plot, and moving back to the lower panel and along to the polar minimum at $(\theta_1 \approx 60°,\ \theta_2 \approx 60°)$. The same path is shown in the extended coordinates in Fig. 2. In this case it is only necessary to exit and enter once to follow the path between the two polar minima P1 and P2 (P3 and P4 are copies). The full disrotatory cycle (Fig. 3), as first shown by Berner et al. [9], goes from the global minimum (non-polar-O-in) (G1), to a T-shaped O-in (TO1) transition state, to a polar well (P1), to a T-shaped-N-in (TN1) well, to the non-polar N-in transition state (NN1), to a TN2 well, to the P2 well, through a TO2 transition state, and finally back to G1.

Three tunneling paths connect the two polar wells. Two of them follow the disrotatory cycle, one in a clockwise sense and one in an anticlockwise sense. The first path (called disrotatory path I) is P1 → TO1 → G1 → TO2 → P2. The second path (called disrotatory path II) is P1 → TN1 → NN1 → TN2 → P2. These two paths are marked by dashed arrows in Fig. 3. The third path is conrotatory (Fig. 4). It is P1 → RT → P3. When the path is defined by finding values of X and r_0 that minimize the potential for each value of Y the RT transition state is approximately rectangle-shaped. Its coordinates are $\theta_1 = 91.9°$, $\theta_2 = 88.1°$, and $r_0 = 6.996$ bohr. The blue contours of Fig. 1 reveal RT. The RT shape is not an exact rectangle and therefore its point group symmetry is not C_{2v} but rather C_s, the same as other points along this path. The energetics of the various stationary points are given in Table 1. Geometries of all the stationary points except RT are also given in Table 5 of paper I. The barrier height for disrotatory path I is 105 cm^{-1} (TO). The barrier height for disrotatory path II is 142 cm^{-1} (NN). The barrier height for the conrotatory path is 400 cm^{-1} (RT). The width of the conrotatory barrier is much less than the width of the barrier of disrotatory path II. Disrotatory path I has two barriers.

It is not clear that only one of the three paths is important and therefore the tunneling dynamics could be quite complicated. This may be contrasted with the tunneling in HF dimer where one disrotatory path is the dominant path. Mills [34] and also Hougen and Ohashi concluded [33] that if one tunneling path is dominant the symmetry of a vibration–rotation–tunneling level is a product of the symmetry of a rotational factor, determined assuming a rigid shape with the symmetry of the point group of the transition state shape, and the symmetry of a vibrational/tunneling factor. According to our calculation the tunneling splittings are very small, primarily because the mass of the monomer is relatively large. Even if it were possible to identify one or more paths as being more important, doing so would have no consequences for understanding the spectrum.

3. Calculating energy levels and wavefunctions

The polyspherical coordinates defined in the previous section are used to compute the energy levels. Details were given in Paper I. Euler angles specify the orientation of a body-fixed frame attached such that the z-axis is along $\mathbf{r}_0$ and the x-axis is along the vector $\mathbf{r}_0 \times \mathbf{r}_1 \times \mathbf{r}_0$. $\mathbf{r}_0$ is the inter-monomer vector and $\mathbf{r}_1$is the vector along monomer 1, pointing from the external N atom to O atom. The kinetic energy operator in these coordinates is well known [35]. For the stretch coordinates we use potential optimized discrete variable representation (PODVR) functions [36–41] and for the bend and rotational coordinates we use parity-adapted rovibrational functions [30,31]. In our calculations the angular quantum numbers (see paper I) l_1, l_2, and m_2 all have the same maximum value. Even and odd parity levels are calculated separately.

Within each parity block, we use a symmetry adapted variant [42–44] of the Cullum and Willoughby Lanczos method [45] to compute the energy levels. Eigenvalues are obtained by computing matrix–vector products. Potential matrix–vector products are evaluated by using quadrature and doing sums sequentially [37,44,46–48]. Kinetic energy matrix-elements are given in Ref. [35]. The wavefunctions are obtained from eigenvectors of the Hamiltonian matrix that are computed as described previously [30,49]. Similar techniques have been used to compute energy levels of many molecules [37,50–53]. The full permutation–inversion (PI) symmetry group for the Hamiltonian we use is G_4, composed of operations $\{E, \sigma_{ex}\} \otimes \{E, E^*\}$ where σ_{ex} permutes monomer 1 with monomer 2 [19]. A/B label symmetric and anti-symmetric irreducible representations (irreps) with respect to σ_{ex} and ± label even and odd parities. There are four PI irreps: $(A+, B+, A-, B-)$. Transformation properties of parity-adapted rovibrational basis functions under G_4 operators are given in Ref. [54]. The dipole moment of the complex has $A-$ symmetry. Allowed transitions are therefore $A+ \leftrightarrow A-$ and $B+ \leftrightarrow B-$. For the results presented in Section 6 we use the basis, quadrature points, masses and NNO rotational constant used in paper I.

4. Identifying rovibrational states associated with polar-like or TN-like vibrational states

When coupling between vibration and rotation is not too strong, each rovibrational wavefunction can be approximated as a product of a vibrational wavefunction and a rotational function. The vibrational wavefunction associated with a rovibrational state can be determined on the basis of the energy level pattern, if all vibrational levels are widely-spaced. Energy levels are calculated separately for each J and for each J one can identify groups of 1, 3, 5,… rotational levels. This simple procedure fails when rotational and vibrational energy levels are similar, i.e. when the density of vibrational states is large. Note that although the density of vibrational states may make it impossible to determine the vibrational wavefunction associated with a rovibrational state, it does not necessarily invalidate the product approximation. The simple procedure also fails whenever there are groups of nearly degener-