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The vibration-rotation-tunneling levels of $\text{N}_2\text{-H}_2\text{O}$ and $\text{N}_2\text{-D}_2\text{O}$

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In this paper, we report vibration-rotation-tunneling levels of the van der Waals clusters $\text{N}_2\text{-H}_2\text{O}$ and $\text{N}_2\text{-D}_2\text{O}$ computed from an *ab initio* potential energy surface. The only dynamical approximation is that the monomers are rigid. We use a symmetry adapted Lanczos algorithm and an uncoupled product basis set. The pattern of the cluster's levels is complicated by splittings caused by H-H exchange tunneling (larger splitting) and N-N exchange tunneling (smaller splitting). An interesting result that emerges from our calculation is that whereas in $\text{N}_2\text{-H}_2\text{O}$, the symmetric H-H tunnelling state is below the anti-symmetric H-H tunnelling state for both $K = 0$ and $K = 1$, the order is reversed in $\text{N}_2\text{-D}_2\text{O}$ for $K = 1$. The only experimental splitting measurements are the D-D exchange tunneling splittings reported by Zhu *et al.* [J. Chem. Phys. **139**, 214309 (2013)] for $\text{N}_2\text{-D}_2\text{O}$ in the $\nu_2 = 1$ region of D_2O . Due to the inverted order of the split levels, they measure the sum of the $K = 0$ and $K = 1$ tunneling splittings, which is in excellent agreement with our calculated result. Other splittings we predict, in particular those of $\text{N}_2\text{-H}_2\text{O}$, may guide future experiments. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4923339>]

I. INTRODUCTION

In recent years, there has been a sustained attempt to understand the interaction between H_2O and other small molecules.^{1–9} Knowing these interactions may help us to understand hydration of molecules. In all of these complexes, the spectra are complicated by tunneling between two wells associated with structures obtained by permuting the H atoms of H_2O . In some, there are additional wells and tunneling motions. In this paper, we study $\text{N}_2\text{-H}_2\text{O}$ in which there is both H tunneling and N tunneling. Each rotational level is therefore split into four sublevels. The minima are all planar and the tunnelling can be understood by considering only motion in the plane. In all four minima, N_2 is nearly collinear with one of the OH bonds of H_2O . $\text{N}_2\text{-H}_2\text{O}$ plays an important role in the atmosphere.¹⁰

To understand the spectrum of $\text{N}_2\text{-H}_2\text{O}$, one must take large amplitude motion into account. The well depth is about 440 cm^{-1} .¹¹ There are two H tunneling paths, one of them also exchanges the two N nuclei, both barrier heights are about 200 cm^{-1} . van der Waals complexes of this kind are often studied computationally by assuming that the monomers are rigid.^{12–17} This reduces the number of vibrational coordinates to 5. It is necessary to use a large basis whose functions have amplitude in all of the wells. Normal coordinates are a poor choice for such problems. Because the required basis is large (about 10^6), it is necessary to compute eigenvalues and eigenvectors of the Hamiltonian matrix with an iterative eigensolver.^{18–30}

We report rovibrational energy levels of both $\text{N}_2\text{-H}_2\text{O}$ and $\text{N}_2\text{-D}_2\text{O}$. For $\text{N}_2\text{-H}_2\text{O}$, a $K = 0$ microwave (MW) spectrum was observed by Leung *et al.*³¹ Zhu *et al.* measured an infrared (IR) spectrum of $\text{N}_2\text{-D}_2\text{O}$ in the $\nu_2 = 1$ bend region of D_2O ,

probing for the first time $K = 1$ levels.³² Both experiments provide only a partial picture. As expected, the H-H and D-D exchange tunneling splittings are much larger than the N-N exchange tunneling splittings. They cannot be measured due to selection rules. The sum or difference of the H-H and D-D splittings for different K can be measured. The difference can be measured if the symmetric tunneling state is below the anti-symmetric state for both K values. The sum can be measured if the order is inverted for one K value. Zhu *et al.* determine the sum of the $K = 0$ and $K = 1$ D-D exchange tunneling splittings for $\text{N}_2\text{-D}_2\text{O}$ from the difference between two transitions because the order of the symmetric and antisymmetric levels is different in $K = 0$ and $K = 1$. We compute relevant rovibrational levels and obtain all the tunneling splittings directly. We report the splittings themselves and show that the $K = 1$ tunneling splitting is significantly less than the $K = 0$ splitting; Zhu *et al.* assumed that they were equal. We also deduce the $K = 0$ and $K = 1$ tunneling splittings in the $\nu_2 = 1$ bend region from our computed $\nu_2 = 0$ splittings and the IR experimental data of Zhu *et al.*

It is not possible to compute a rovibrational spectrum without a potential energy surface (PES). For $\text{N}_2\text{-H}_2\text{O}$, there is a number of *ab initio* PESs.^{11,33,34} In this paper, we work with the *ab initio* PES made by Tulegenov *et al.*,¹¹ called TWHH hereafter, who used the systematic inter-molecular potential extrapolation routine procedure and extrapolated to the complete basis set (CBS) limit. Very recently Ellington and Tschumper characterized six $\text{N}_2\text{-H}_2\text{O}$ stationary points using the probably more accurate explicitly correlated CCSD(T)-F12 (coupled cluster singles and doubles with triples included perturbatively) method at the CBS limit.³⁵ In Ref. 36, Sandler *et al.* proposed another PES, and using it and the diffusion quantum Monte Carlo method, they computed the ground state energy and wavefunction and ground state rotational constants.

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II. COMPUTATIONAL METHOD

The angular coordinates we use are $\alpha, \beta, \alpha_A, \beta_A, \gamma_A$, and α_B, β_B . See Fig. 1. α and β are the polar angles of $\mathbf{r}_0$ in a space-fixed (SF) frame. $\mathbf{r}_0$ is the vector from the center of mass of H₂O to the center of mass of N₂. The axis system whose orientation is specified by α, β is denoted the dimer-fixed (DF) frame. The remaining angles specify the orientation of axis systems attached to the monomers (which we call monomer-fixed (MF) frames) with respect to the DF frame. The MF frame for H₂O (monomer A) is obtained by rotating the DF frame by three standard Euler angles ($\alpha_A, \beta_A, \gamma_A$). The MF frame for N₂ (monomer B) is obtained by rotating the DF frame by two standard Euler angles (α_B, β_B). In the H₂O MF frame, the z -axis is along the C₂ axis with the O atom having a positive z coordinate and the x -axis in the H₂O plane with the H₁ atom having a positive x coordinate. The MF frame is attached to N₂ such that its z -axis is along the N₄–N₅ vector. Note that $\alpha_A - \alpha_B$ is a vibrational coordinate and that there are only 5 vibrational coordinates. The monomers are assumed to be rigid. As first discussed by Brocks *et al.*,³⁷ the kinetic energy operator (KEO) in these coordinates can be written in compact form,

$$T = T^A + T^B - \frac{1}{2\mu_0 r_0^2} \frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + T_{int}, \quad (1)$$

$$T^A = B_x^{(A)} (j_x^{\text{MF},A})^2 + B_y^{(A)} (j_y^{\text{MF},A})^2 + B_z^{(A)} (j_z^{\text{MF},A})^2, \\ T^B = B^{(B)} (j^{\text{MF},B})^2, \quad (2)$$

$$T_{int} = \frac{1}{2\mu_0 r_0^2} \left[J^2 - \cot \beta \frac{\partial}{\partial \beta} + j^2 - 2\mathbf{j} \cdot \mathbf{J} \right].$$

Components of *all* the angular momentum operators in T_{int} are in the DF frame with $\mathbf{J}$ the total angular momentum and $\mathbf{j} = \mathbf{j}^A + \mathbf{j}^B$ the sum of angular momenta of monomers A and B. In contrast, the components of angular momentum operators in

T^A and T^B are in the MF frames. It is because the total angular momentum is projected onto the DF frame that we call the 8 coordinates ($\alpha, \beta, \alpha_A, \beta_A, \gamma_A, \alpha_B, \beta_B, r_0$) used in Eq. (1) DF coordinates.

Alternatively, one could use another set of angles.³⁸ Three of them, $\alpha^{\text{MF}}, \beta^{\text{MF}}, \gamma^{\text{MF}}$, specify a MF frame for H₂O with respect to the SF frame. The orientation of $\mathbf{r}_0$ and $\mathbf{r}_{\text{NN}}$, with respect to this MF frame, is given by the polar angles (θ, ϕ) and (θ', ϕ') . It is because the total angular momentum is projected onto the H₂O MF frame that we call these 8 coordinates ($\alpha^{\text{MF}}, \beta^{\text{MF}}, \gamma^{\text{MF}}, \theta, \phi, \theta', \phi', r_0$) MF coordinates. The five MF vibrational coordinates ($r_0, \theta, \phi, \theta', \phi'$) are often used to represent the inter-monomer PES because they are intuitive.^{11,39,40} In our previous paper on H₂O–H₂, we did rovibrational calculations using MF coordinates to check results obtained with DF coordinates. In that paper, we point out that the vibrational (and Coriolis) coupling is proportional to $B_0 = 1/(2\mu_0 r_0^2)$ in the DF coordinates and to the rotational constants of H₂O in the MF coordinates. For both H₂O–H₂ and H₂O–N₂, the coupling is much smaller in the DF coordinates because B_0 is very small. Thus, in this paper, the DF coordinates are chosen to calculate rovibrational levels and wavefunctions.

We use a large basis whose functions are products of functions of a single coordinate. The basis has the virtue that it is simple. The basis size is not a problem if the Lanczos algorithm is used. The angular basis functions, $|j_A k_A m_A; j_B(m_B); J K M\rangle$, apart from a normalization factor, are the (uncoupled) product functions,^{13,14}

$$D_{m_A, k_A}^{j_A*}(\alpha_A, \beta_A, \gamma_A) D_{m_B, 0}^{j_B*}(\alpha_B, \beta_B, 0) D_{M, K}^{J*}(\alpha, \beta, 0), \quad (3)$$

with the constraint $K \equiv m_A + m_B$. Due to the constraint, possible values of j_B depend on m_A . The matrix elements of the KEO of Eq. (1) in this basis are analytic and the KEO matrix is sparse. See Ref. 14 for details. To take advantage of the inversion symmetry, the basis is parity adapted (M is set to zero and not indicated),

$$u_{j_A k_A m_A; j_B(m_B); K}^{JP} = N_{k_A m_A K} \frac{1}{\sqrt{2}} \left[|j_A k_A m_A; j_B(m_B); J K\rangle + (-1)^{J+k_A+P} |j_A \bar{k}_A \bar{m}_A; j_B(\bar{m}_B); J \bar{K}\rangle \right], \quad (4)$$

with $N_{k_A m_A K} = (1 + \delta_{k_A, 0} \delta_{m_A, 0} \delta_{K, 0})^{-1/2}$ and $\bar{K} = -K$, etc. $P = 0$ and 1 correspond to even parity and odd parity, respectively. In the parity-adapted basis, the restrictions on the quantum numbers are (i) $K \geq 0$, (ii) $m_A \geq 0$ if $K = 0$, and (iii) $k_A \geq 0$ if $m_A = K = 0$. We label levels with their so-called spectroscopic parities e and f . e and f correspond to $(-1)^{J+P} = 1$ and -1 , respectively. They are also labelled by K , the projection of total angular momentum on the z -axis of the DF frame, which is almost a good quantum number. It is assigned by analyzing the calculated wavefunctions.¹⁴ The final basis functions are products of the parity adapted angular functions and discrete variable representation (DVR) functions^{41–43} for the inter-monomer distance.

To facilitate plotting the wavefunction, the parity-adapted basis of Eq. (4) is further manipulated and we find

$$u_{j_A k_A m_A; j_B(m_B); K}^{J0} = N_{k_A m_A K} (2\pi)^{-3/2} \sqrt{2} \\ \times \cos(m_A \alpha_A + m_B \alpha_B + k_A \gamma_A) \\ \times \bar{d}_{m_A k_A}^{j_A}(\beta_A) \bar{d}_{m_B 0}^{j_B}(\beta_B) \bar{d}_{0K}^J(\beta), \quad (5)$$

$$u_{j_A k_A m_A; j_B(m_B); K}^{J1} = i(2\pi)^{-3/2} \sqrt{2} \\ \times \sin(m_A \alpha_A + m_B \alpha_B + k_A \gamma_A) \\ \times \bar{d}_{m_A k_A}^{j_A}(\beta_A) \bar{d}_{m_B 0}^{j_B}(\beta_B) \bar{d}_{0K}^J(\beta) \quad (6)$$

for even parity and odd parity, respectively. The i factor can be dropped. Thus, a wavefunction expanded in either basis is real and can be easily plotted. In Sec. VI, wavefunction plots are used to help understand the tunneling dynamics.

FIG. 1. The dimer-fixed coordinates used to compute rovibrational levels of $\text{N}_2\text{-H}_2\text{O}$. The dimer-fixed (DF) frame (in red) is obtained by rotating a space-fixed frame by two successive Euler angles (α , β) so that the z -axis is aligned with vector $\mathbf{r}_0$. The N_2 MF frame (in blue) is obtained by rotating the DF frame first about z -axis by α_B (leading to the red dashed frame) and then about the y -axis by β_B . The H_2O monomer-fixed (MF) frame (in blue) is obtained by rotating the DF frame by three successive Euler angles (α_A , β_A , γ_A) following the z - y - z convention.⁶⁹

The full permutation inversion group of $\text{N}_2\text{-H}_2\text{O}$, G_8 , is used to do the calculation. Because the dipole moment is of A_1^- symmetry, the transition selection rule is $A_1^+ \leftrightarrow A_1^-$, $A_2^+ \leftrightarrow A_2^-$, $B_1^+ \leftrightarrow B_1^-$, and $B_2^+ \leftrightarrow B_2^-$. Here, $A(B)$ indicate that a state is symmetric (anti-symmetric) with respect to permutation of the two H; 1(2) indicate that a state is symmetric (anti-symmetric) with respect to permutation of the two N. Within each parity block, we use the symmetry adapted Lanczos (SAL) algorithm.⁴⁴⁻⁴⁶ Transformation properties of the basis functions in G_8 are given in Ref. 14. They are used to make projection operators. The SAL enables one to obtain all levels from one set of matrix-vector products. The matrix-vector products required to use the SAL are evaluated by doing sums sequentially.^{43,47,48}

III. POTENTIAL ENERGY SURFACE

We have done calculations on the TWHH PES¹¹ which is fitted to a function of the five MF vibrational coordinates (r_0 , θ , ϕ , θ' , ϕ'). A small difference between these MF coordinates and the MF coordinates described in Sec. II is that the MF frame origin is fixed on the O atom rather than the center of mass of H_2O . The geometries of both monomers are determined from experimental rotational constants.¹¹ Because the DF coordinates are used in the rovibrational calculation, it is necessary

to transform the DF coordinates of each quadrature point to the MF coordinates used by Tulegenov *et al.* in order to evaluate the potential. The geometry of the global minimum (C_s symmetry) with the energy -440.9 cm^{-1} is shown in Fig. 2 and the structure parameters are in Table 1 of the supplementary material.⁴⁹ N-N is almost aligned with OH bond and acts as a proton acceptor. There is a second equivalent global minimum where N-N is bonded to the second OH bond. There are two planar C_{2v} saddle points. The first one has N_2 on the H side of H_2O (shown in Fig. 2 and called $C_{2v}(\text{H})$ in this work and structure II in Ref. 35). Its barrier height is 214.2 cm^{-1} . The second one has N_2 on the O side of H_2O (called $C_{2v}(\text{O})$ in this work and structure IV in Ref. 35). Its barrier height is 192.2 cm^{-1} . The two barrier heights compare favorably with the benchmark values of 196 and 178 cm^{-1} of Ref. 35, respectively. In principle, the system can tunnel between global minima with the N_2 molecule bound to different H nuclei through both C_{2v} saddle points. This tunneling is related to H-H exchange and hence is called H-H exchange tunneling in this paper. Tunneling through the $C_{2v}(\text{H})$ saddle point (solid line in Fig. 3) does not permute the N nuclei and is expected to be more important than tunneling through one of the $C_{2v}(\text{O})$ saddle points (dashed lines in Fig. 3), which do permute the N nuclei, despite the fact that it is higher in energy, because the tunneling path is shorter. There is a second tunneling process corresponding to N-N exchange. It has much smaller splittings. A potential contour plot for planar configurations is shown in Fig. 3. The potential contours are plotted in extended angles based on the DF coordinates (and defined in Sec. VI) which have the advantage that all planar configurations are reached by continuously changing the coordinates. In the DF coordinates (also called dynamical coordinates in this article), planar geometries have $\alpha_A = \alpha_B$ and γ_A equal to 0 or π . In Fig. 3, there are four global minima because there are four non-equivalent versions⁵⁰ connected by permutation of the two H and the two N nuclei. We shall discuss tunnelling paths and wavefunctions in Sec. VI.

We find that the TWHH PES has small symmetry errors (up to 0.17 cm^{-1}) for large r_0 values. These errors are removed by averaging the four points linked by the H-H and N-N

FIG. 2. C_s global minimum (a) and $C_{2v}(\text{H})$ saddle point of $\text{N}_2\text{-H}_2\text{O}$. There is tunneling between the two versions of the global minima. See also Fig. 3.

FIG. 3. Contour plot of the PES (in cm^{-1}) for planar configurations. The extended DF angles are used. r_0 is optimized to find the energy minimum. The red contour interval is 50 cm^{-1} . The four blue contours between -440 and -410 cm^{-1} show the minimum region. The three green contours at -245 , -235 , and -225 cm^{-1} reveal details near the two saddle points: $C_{2v}(\text{H})$ and $C_{2v}(\text{O})$. All four versions of the global minimum are shown with 1 to 4 labels in a square box. A cyclic path connecting the minimum is indicated by the solid and dashed curves that connect versions $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$. The solid black lines mark the regions in which H-H exchange tunneling is important.

permutation operations, denoted by σ_{HH} and σ_{NN} . Without averaging, the eigenvalues of the tridiagonal matrix built by the SAL are not copied as its size increases. To do the averaging, one needs to know how the inversion and the H-H and N-N permutation operations affect the DF coordinates. This is given in Table X of Ref. 14. The averaging is complicated by the fact that only half of the quadrature grid is stored, due to inversion symmetry. Some of the symmetry partners obtained by straightforwardly applying the permutation operations in Table X of Ref. 14 are not on the stored portion of the grid. For example, if the stored set is defined by halving the range of γ_A to $[0, \pi]$, applying σ_{HH} to a point changes $\gamma_A \rightarrow \gamma_A + \pi$, and the new point is not in the stored set. In this case, to avoid this problem, instead of σ_{HH} we use σ_{HH}^* , which changes $\gamma_A \rightarrow \pi - \gamma_A$ and transforms a stored point into a stored point. The three symmetry partners are obtained from the following three symmetry operations: σ_{HH}^* , σ_{NN} , and $\sigma_{\text{HH}}^* \sigma_{\text{NN}}$.

IV. CALCULATIONAL DETAILS

We have done calculations with different basis sizes to test convergence. The final bend basis set has $j_{\text{max}} = 14$ for both H_2O and N_2 and the potential integrals are computed with $N_\theta = 15$ Gauss-Legendre quadrature points for β_A and β_B and $N_\phi = 30$ evenly spaced quadrature points in $[0, 2\pi]$, with the first point at zero for γ_A and $\alpha_A - \alpha_B$. For the stretch basis, we use the tri-diagonal Morse (TDM) DVR basis, proposed by Wei and Carrington (WC).⁵¹ We use the WC TDM basis, rather than a sine DVR basis as we did in Ref. 14, because the TDM basis

required to achieve the same accuracy is smaller. For $\text{H}_2\text{O}-\text{N}_2$, the TDM DVR basis is preferable because the potential well is deeper. However, we do use a large sine DVR basis to compute benchmark levels to test the final TDM basis. The sine basis, although larger than the TDM, has the advantage that the only parameters, the minimum and maximum values of the coordinate, are easy to choose in such a way that one can be certain that results are not biased by the choice. A TDM basis was first used in a variational calculation by Tennyson and Sutcliffe (TS).⁵² The basis has four parameters, D_e , ω_e , R_e , and α .⁵² The first three parameters are the dissociation energy, harmonic frequency, and equilibrium distance for the Morse potential. The basis functions involve an associated Laguerre polynomial, L_n^α , which depends on the fourth parameter, α . α must be larger than -1 but is otherwise arbitrary. In principle, one could variationally optimize all four parameters by minimizing 5D vibrational levels. In practice, we fix $D_e = 440.9 \text{ cm}^{-1}$ to the dissociation energy of $\text{N}_2-\text{H}_2\text{O}$. As noted in Ref. 52, levels are not very sensitive to D_e . The two parameters ω_e and R_e are systematically varied to minimize a few $5D A_1^+$ vibrational levels computed with 20 TDM basis functions and the aforementioned bend basis.

For the final parameter, α , we considered two options. TS⁵² set $\alpha = [A]$, the integer part of $A = 4D_e/\omega_e$. WC,⁵¹ on the other hand, set $\alpha = A - 2[A/2]$, because with this choice all the $[A/2]$ bound levels of the Morse Hamiltonian are exactly reproduced by the TDM basis.⁵³ Knapp and Diestler⁵³ show that with $\alpha = A - 2M$, the M by M top left corner of the matrix representing the Morse Hamiltonian is uncoupled to the rest of the matrix and its eigenvalues are exactly the first M Morse levels ($M \leq [A/2]$). If N_{r_0} , the number of TDM basis functions, is less than $[A/2]$, α should be $A - 2N_{r_0}$ so that the first N_{r_0} Morse levels are exactly reproduced. For $\text{N}_2-\text{H}_2\text{O}$, $[A/2]$ is 17 and always smaller than N_{r_0} .) The TS and WC values of α are quite different: TS's α is a large integer and WC's α is between 0 and 1 and non-integer. TS's choice leads to (i) a narrower point range and (ii) many points in the region of the repulsive wall of the Morse potential. To resolve these problems, Tennyson and co-workers often choose a value of R_e larger than the true value. This shifts the point range so that it includes the dynamically important region. Our tests show that WC's choice is more efficient and it is adopted. Fig. 1 of the supplementary material plots the TDM basis for the two choices.⁴⁹ The final parameters are $\omega_e = 57 \text{ cm}^{-1}$, $R_e = 7.2a_0$ (the corresponding Morse potential has $[A/2] = 15$ bound levels), and $\alpha = 0.94$. In comparison, the potential for r_0 with all other angles minimized has 17 bound states and $\omega_e = 57.6 \text{ cm}^{-1}$. Therefore, the optimized TDM parameters are close to the parameters for the minimized potential. Finally, 30 TDM basis functions are chosen. This leads to 637 000 basis function for the $J = 0$ even parity calculation. Convergence tests show that all A_1^+ vibrational energy levels up to 125 cm^{-1} , computed with the basis defined above, differ by less than 0.0001 cm^{-1} from levels obtained using a large benchmark basis with $N_{r_0} = 120$ sine DVR functions in the range $[5.0 a_0, 26.0 a_0]$, $j_{\text{max}} = 19$, $N_\theta = 20$, and $N_\phi = 40$, which has 8×10^6 functions for $J = 0$.

To specify the KEO of Eq. (1), one needs masses and rotational constants. The masses are taken from Ref. 54. For

the rigid rotor monomer Hamiltonians, experimental rotational constants are used, neglecting the higher order centrifugal corrections which are very small, but larger for H₂.¹⁴ We use the following experimental rotational constants: $A = 27.8807\text{ cm}^{-1}$, $B = 14.5215\text{ cm}^{-1}$, and $C = 9.2778\text{ cm}^{-1}$ for the $v_2 = 0$ state of H₂O;⁵⁵ $A = 15.4200\text{ cm}^{-1}$, $B = 4.8453\text{ cm}^{-1}$, and $C = 7.2730\text{ cm}^{-1}$ for the $v_2 = 0$ state of D₂O;⁵⁶ $A = 16.6339\text{ cm}^{-1}$, $B = 7.3388\text{ cm}^{-1}$, and $C = 4.7895\text{ cm}^{-1}$ for the $v_2 = 1$ state of D₂O;⁵⁷ and $B = 1.989\,50\text{ cm}^{-1}$ for the $v = 0$ state of N₂.⁵⁸

V. RESULTS

The calculated A_1^+ and A_1^- rovibrational levels of N₂-H₂O are given in Table I and the B_1^+ and B_1^- levels are in Table II. The A_2^+ and A_2^- levels are in Table II of the supplementary material,⁴⁹ and the B_2^+ and B_2^- levels are in Table III of the supplementary material.⁴⁹ The quantum number K is assigned as in Ref. 14 and is unambiguous in all cases except for a few which are marked with a star. The same tables for N₂-D₂O are given in Tables III and IV and Tables IV and V of the supplementary material.⁴⁹ In these tables, levels are sorted first by e/f label and then in order of increasing energy. The A_2^+/A_2^- and B_2^+/B_2^- tables are in the supplementary material⁴⁹ because the N-N exchange tunneling is small.

A. N₂-H₂O levels and the MW experiment

The $K = 0$ MW spectra of N₂-H₂O and many of its isotopologues were recorded by Leung *et al.*³¹ Due to the low temperature (1K) of the jet, they did not record $K = 1$ spectra because the $K = 1$ levels are too high, owing to the large A rotational constants ($\sim 12\text{ cm}^{-1}$). They saw transitions between levels, which we label as A_1^+/A_1^- , A_2^+/A_2^- , B_1^+/B_1^- , and

TABLE II. B_1^+ and B_1^- rovibrational levels of the $v_2 = 0$ state of N₂-H₂O.

Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
$\Sigma(K = 0)$					
e	2.8008	2.9955	3.3849	3.9690	4.7475
e	37.5731	37.7846	38.2074	38.8414	37.2616
e	59.2120	59.4152	59.8215	60.4309	61.2435
e	67.5723	67.7579	68.1292	68.6870	69.4326
f	53.5273	53.7251	54.1206	54.7139	55.5048
$\Pi(K = 1)$					
e		19.1501	19.5456	20.1387	20.9293
e		35.4694 ^a	35.8679	36.4653	37.2616
e		51.3696 ^a	51.8389	52.5423	53.4791
f		19.1510	19.5483	20.1440	20.9382
f		35.4703 ^a	35.8703	36.4702	37.2696
f		51.3698 ^a	51.8395	52.5435	53.4813
$\Delta(K = 2)$					
e			44.0542	44.6820	45.5188
e			61.5151	62.1308	62.9549
f			44.0542	44.6819	45.5187
f			61.5145	62.1281	62.9472

^aDue to coupling, all the B levels in this line are below the corresponding A levels. This also occurs for B levels in Table III of the supplementary material.⁴⁹

B_2^+/B_2^- and which are split by H-H exchange tunneling and N-N exchange tunneling. Selection rules only allow transitions within each of these four groups. Fig. 2 of the supplementary material shows four such MW $R(0)$ transitions.⁴⁹ The experimental MW transitions are compared with our calculations in Table V. The agreement is very good with differences not more than 10^{-3} cm^{-1} , reflecting the accuracy of the TWHH PES and the accuracy of the rigid monomer approximation. The differences increase with increasing J . Our calculation shows that the H-H exchange tunneling splitting, 2.8 cm^{-1} , is much bigger than the N-N exchange tunneling splitting,

TABLE I. A_1^+ and A_1^- rovibrational levels of the $v_2 = 0$ state of N₂-H₂O, relative to a zero-point energy (ZPE) at $-195.059\,83\text{ cm}^{-1}$.

Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
$\Sigma(K = 0)$					
e	0.0000	0.1944	0.5832	1.1663	1.9436
e	33.7822	34.0001	34.4356	35.0881	35.9567
e	47.1059	47.3181	47.7428	48.3806	49.2335
e	62.1185	62.3090	62.6901	63.2620	64.0249
f	58.9438	59.1410	59.5353	60.1268	60.9154
$\Pi(K = 1)$					
e		18.5052	18.9023	19.4979	20.2919
e		38.2726	38.6688	39.2631	40.0556
e		51.7629	52.2039	52.8679	53.7571
f		18.5070	18.9077	19.5086	20.3097
f		38.2746	38.6745	39.2743	40.0737
f		51.7420	52.1421	52.7468	53.5601
$\Delta(K = 2)$					
e			41.7086	42.3579	43.2226
e			54.6171	55.3817	56.3952
f			41.7086	42.3580	43.2227
f			54.6164	55.3791	56.3887

TABLE III. A_1^+ and A_1^- rovibrational levels of the $v_2 = 0$ state of N₂-D₂O, relative to a ZPE at -231.9453 cm^{-1} .

Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
$\Sigma(K = 0)$					
e	0.0000	0.1851	0.5553	1.1106	1.8509
e	34.6332	34.8591	35.2507	35.8379	36.6204
e	55.3417	54.5458	55.9537	56.5651	57.3792
e	64.4795	64.6616	65.0256	65.5711	66.2973
f	45.9976	46.1850	46.5598	47.1220	47.8715
$\Pi(K = 1)$					
e		11.6397	12.0101	12.5657	13.3064
e		32.4864	32.8626	33.4270	34.1793
e		54.6649	55.0636	55.6617	56.4593
f		11.6409	12.0139	12.5732	13.3189
f		32.4889	32.8702	33.4420	34.2043
f		54.6702	55.0791	55.6923	56.5096
$\Delta(K = 2)$					
e			38.3184	38.8952	39.6641
e			52.1406	52.7067	53.4613
f			38.3184	38.8952	39.6641
f			52.1406	52.7067	53.4613

TABLE IV. B_1^+ and B_1^- rovibrational levels of the $v_2=0$ state of N_2-D_2O .

Parity	$J=0$	$J=1$	$J=2$	$J=3$	$J=4$
$\Sigma(K=0)$					
e	0.2202	0.4052	0.7752	1.3302	2.0700
e	35.1142	35.3092	35.6992	36.2841	37.0636
e	56.6751	56.8748	57.2742	57.8730	58.6710
e	65.1519	65.3304	65.6875	66.2230	66.9368
f	45.3957	45.5837	45.9598	46.5237	47.2756
$\Pi(K=1)$					
e		11.5392	11.9099	12.4658	13.2070
e		32.1126	32.4910	33.0584	33.8149
e		54.5803	54.9854	55.5927	56.4021
f		11.5402	11.9129	12.4718	13.2169
f		32.1140	32.4950	33.0665	33.8283
f		54.5835	54.9949	55.6118	56.4338
$\Delta(K=2)$					
e			38.3353	38.9117	39.6800
e			52.2730	52.8405	53.5970
f			38.3353	38.9117	39.6800
f			52.2730	52.8405	53.5970

0.0017 cm^{-1} , see Fig. 2 of the supplementary material⁴⁹ and Fig. 4. The NN splitting is ignored in IR studies of N_2-D_2O and 1/2 subscripts in the symmetry labels are dropped. Our calculation also shows that both H–H and N–N splittings depend very little on J .

The order of the symmetry labels of the four split levels is interesting. Whereas for the larger H–H exchange splitting A is below B state, as expected, we find that the 2 level may be below the 1 level. This is due to the fact that the 1 and 2 levels are close enough that coupling influences their order. For example, B_2 may be lower in energy than B_1 . Whether or not 1 is lower than 2 will depend on the potential. Coupling also determines the order of the four A states and the four B states with $K=1$, as discussed below. Our calculation shows that the B_1 level is above the B_2 level for all J when $K=0$. One cannot determine the order from the MW experiment of Leung *et al.* For both $K=0$ and 1, the $J=1$ splitting pattern is obtained from that for $J=0$ by multiplying with a factor whose symmetry is A_1^- , as seen in Figs. 2 and 3 of the supplementary material.⁴⁹ This could be explained by determining how the symmetry of D_{MK}^J changes with J .

N_2-H_2O and N_2-D_2O are asymmetric tops that are nearly symmetric tops because $B-C$ is very small. For example, $B-C$ is about 0.001 cm^{-1} for N_2-D_2O . Therefore, the two $K=1$ levels, correlated with the $+/-$ (parity) label, have very similar energies. The near degeneracy of two levels with the same K is sometimes called the asymmetric rotor K -type

doubling.⁵⁹ This effect is also seen in water dimer.⁶⁰ The K -type doubling is as small as the N–N exchange tunneling splitting. Therefore, the 8 $K=1$ levels are separated into two clusters of 4 levels by the large H–H exchange tunneling splitting. Coudert and Hougen^{61,62} developed an effective Hamiltonian theory to explain the splitting pattern of water dimer in terms of effective parameters. The pattern here is similar to that in H_2O-DOD where H–H exchange tunneling splitting is also the largest (see Table IX of Ref. 62 and Fig. 8 of Ref. 60). The $K=1$ levels for $J=1$ and $J=2$ of N_2-H_2O are shown in Fig. 3 of the supplementary material where allowed A_2 transitions are indicated.⁴⁹ See also Fig. 4. The $K=1, 2, \dots$ levels in Tables I and II and Tables II and III of the supplementary material should assist experimentalists looking for transitions among these levels in N_2-H_2O .⁴⁹ The K -doublet splitting decreases with K and is only significant for $K=1$. For $K=2$, the K -doublet becomes almost degenerate for both molecules.

Due to selection rules, the MW (and IR) experiments cannot directly measure the H–H exchange tunneling and the N–N exchange tunneling splittings. However, the difference of the tunneling splittings, e.g., $\Delta_{J+1}(K) - \Delta_J(K)$, for two different J can be deduced from the difference of two MW transitions. For example, the difference of the A_1 and A_2 $R(0)$ lines in Fig. 2 of the supplementary material⁴⁹ is $2 \times 10^{-5} \text{cm}^{-1}$ (from both experiment and the calculation of Table V) and this difference is equal to $\Delta_1^N(K) - \Delta_0^N(K)$ (N superscript indicates it is for N–N exchange tunneling). This shows both that the tunneling splitting depends only weakly on J and that the theoretical prediction of the variation of the tunneling splitting with J is very accurate, a quantity as small as a few 10^{-5}cm^{-1} .

B. N_2-D_2O levels and the IR experiment

Zhu *et al.*³² measured the IR spectra of N_2-D_2O in the $v_2=1$ bend region of D_2O in a supersonic jet expansion, using a rapid-scan tunable diode laser spectrometer. Three subbands were measured: $K=1 \leftarrow 0$, $K=0 \leftarrow 1$, and $K=0 \leftarrow 0$. This was the first time that transitions to $K=1$ levels were observed. Their results therefore provide valuable information about tunneling splittings of both $K=0$ and $K=1$ levels. We can test the intermolecular PES and our calculation by comparing their experimental and our theoretical results. We therefore computed levels of N_2-D_2O . The small N–N exchange tunneling splitting is even smaller in N_2-D_2O than in N_2-H_2O and is not considered in the analysis in this section (it was also ignored in the IR experimental study).

As expected, because of the heavier mass of D_2O , all the tunneling splittings of N_2-D_2O are smaller. More interestingly, the order of split levels, see Figs. 4 and 5, in N_2-H_2O and

TABLE V. Microwave $K=0$ transitions (in cm^{-1}) of N_2-H_2O . The experimental data are from Leung *et al.*³¹

	A_1			A_2			B_1			B_2		
	Observed	Calculated	o-c	Observed	Calculated	o-c	Observed	Calculated	o-c	Observed	Calculated	o-c
R(0)	0.193 92	0.194 41	−0.000 49	0.193 89	0.194 39	−0.000 50	0.194 41	0.194 72	−0.000 32	0.194 41	0.194 72	−0.000 31
R(1)	0.387 81	0.388 79	−0.000 98	0.387 74	0.388 74	−0.001 00	0.388 78	0.389 41	−0.000 63	0.388 79	0.389 42	−0.000 63
R(2)	0.581 63	0.583 11	−0.001 47	0.581 52	0.583 04	−0.001 52

FIG. 4. Schematic diagram of the energy levels of $K=0$ and 1 states of N₂-H₂O. Calculated energies in cm⁻¹ for each level are given. The difference of the two indicated $R(0)$ transitions is equal to the difference of the $J=0$ and $J=1$ tunneling splittings.

N₂-D₂O is different. The most notable difference is the order of the $K=1$ A and B levels: for N₂-H₂O, the A levels are lower than the B levels by 0.65 cm⁻¹, whereas for N₂-D₂O, the A levels are higher than the B levels by 0.10 cm⁻¹. The A/B order reversal of $K=1$ levels has significant consequences. For example, for N₂-H₂O, the difference between the two $R(0)$ $K=1 \leftarrow 0$ transitions is equal to the difference $|\Delta_1(1) - \Delta_0(0)|$, whereas for N₂-D₂O, the difference between the same two transitions is equal to the sum $\Delta_1(1) + \Delta_0(0)$. This is clearly demonstrated in Figs. 4 and 5. The order of the smaller splittings, between 1 and 2 and between + and -, is also not the same in N₂-H₂O and N₂-D₂O, but of course their effect on the spectrum is less important. We do not attempt to explain the order of the levels as it is due to potential coupling.

In the discussion below, the A/B tunneling splitting for each (J, K) is denoted by $\Delta_J(K)$. The same tunneling splitting for the water $v_2 = 1$ excited state is denoted by $\tilde{\Delta}_J(K)$. When $K > 0$, there are two $\Delta_J(K)$, one for + symmetry and one for - symmetry. They differ by at most 0.001 cm⁻¹ and the +/- label is therefore not added to the $\Delta_J(K)$ symbol. $\Delta_J(K)$ is almost independent of J (the largest difference is less than 0.001 cm⁻¹) and we shall therefore drop the J subscript from $\Delta_J(K)$ when it is not needed to understand the discussion.

Zhu *et al.*,³² following a suggestion in Ref. 63, assumed $\Delta_0(0)$ and $\Delta_1(1)$ were equal. They further assumed that the

H-H tunneling splitting is equal to half the difference of the A rotational constants in the A and B states (the A constants are obtained by fitting an asymmetric top Hamiltonian to the A and B levels separately). They find a tunneling splitting of 0.163 59(28) cm⁻¹. This number is actually the average of $K=0$ and $K=1$ tunneling splittings.

Our calculation shows that the tunneling splittings of $K=0$ and $K=1$ are not equal and that the splitting of $K=1$ is about twice that of $K=0$ (see below). Using ground state combination differences (GSCDs), we have derived the sum of the experimental tunneling splittings, $\Delta_0(0) + \Delta_1(1)$, from the transition data in the supplementary material of Zhu *et al.*,³² as illustrated in Table VI and Fig. 6. First, the ground state ($v_2 = 0$) difference between two A levels, 11.589 cm⁻¹, is derived from two IR transitions using GSCD, see the first line of Table VI and the black dashed line of Fig. 6. Second, the ground state difference between two B levels, 11.263 cm⁻¹, is derived from two IR transitions using GSCD, see the second line of Table VI and the blue dashed line of Fig. 6. Using experimental data, the difference of these two differences is $\Delta_0(0) + \Delta_1(1) = 0.327$ cm⁻¹. This is indeed about twice that splitting obtained by Zhu *et al.*,³² from the difference of the A rotational constants. They assume that $\Delta_0(0) + \Delta_1(1)$ is the difference of the A rotational constants in the A and B states. $\Delta_0(0) + \Delta_1(1)$ is actually nearly the difference between

FIG. 5. Schematic diagram of the energy levels of $K=0$ and 1 states of $\text{N}_2\text{-D}_2\text{O}$. Calculated energies in cm^{-1} for each level are given. The difference of the two indicated $R(0)$ transitions is equal to the sum of the $J=0$ and $J=1$ tunneling splittings.

$A + (B + C)/2$ for the A and B states, where the symmetric top energy level equation is used and the average of B and C is used as the effective B constant. From the asymmetric top fitting constants of Zhu *et al.*, it is clear that $(B + C)/2$ is about an order of magnitude smaller than A and that the difference of $(B + C)/2$ in the A symmetry and B symmetry states is even smaller. This explains why they use only the A rotational constants. Our derivation of $\Delta_0(0) + \Delta_1(1) = 0.327 \text{ cm}^{-1}$ from experimental lines does not require determining rotational constants for which one needs higher- J levels. It also enables a direct comparison of theory and experiment. The $\Delta_0(0) + \Delta_1(1)$ derived from our variational calculation is 0.321 cm^{-1} , agreeing nicely with the experimental data, with an error of 0.006 cm^{-1} . See Table VI. Note that this error is an order of magnitude smaller than the error in the energy differences between $K=0$ and $K=1$ levels listed on the first two lines of Table VI. The calculation gives in addition the tunneling splitting for each K : $\Delta(0) = 0.220 \text{ cm}^{-1}$ and $\Delta(1) = 0.101$. In the second half of Table VI, we repeat the above analysis using experimental transitions between $J=2$ and $J=1$ levels and find that $\Delta_2(0) + \Delta_1(1)$ is identical to $\Delta_0(0) + \Delta_1(1)$, confirming the weak dependence of the tunneling splitting on J .

As reported, the $K=1$ tunneling splitting is about half the $K=0$ tunneling splitting. This can be understood by thinking in terms of an effective K dependent tunneling barrier. The

$K=1$ tunneling splitting is smaller because rotation about the a -axis (inter-monomer axis) pushes the minima of the effective PES apart. This reduces $|\langle \Psi_L | H | \Psi_R \rangle|^2$, where $|\Psi_R\rangle$ and $|\Psi_L\rangle$ are basis functions for a two-state model that are localized in the two wells. $2|\langle \Psi_L | H | \Psi_R \rangle|^2$ is the tunneling splitting in a

TABLE VI. $K=0$ and $K=1$ H-H exchange tunneling splittings $\Delta_J(0)$ and $\Delta_J(1)$, for the $v_2=0$ state of $\text{N}_2\text{-D}_2\text{O}$, determined from the ground state combination differences (GSCDs) using the two experimental transitions indicated in column one. Each line is denoted ${}^{\Delta K}J_K(J)$, where $\Delta K = p, q, r$ and $\Delta J = P, Q, R$. The energy of a level is denoted $E(J, K, \Gamma)$.

Two lines	Ground state difference	Observed	Calculated	o - c
${}^qR_0(0), {}^pQ_1(1)$	$E(1, 1, A^+) - E(0, 0, A^+)$	11.589	11.641	-0.052
${}^qR_0(0), {}^pQ_1(1)$	$E(1, 1, B^+) - E(0, 0, B^+)$	11.263	11.320	-0.057
Splittings				
	$\Delta_0(0) + \Delta_1(1)$	0.327	0.321	0.006
	$\Delta_0(0)$		0.220	
	$\Delta_1(1)$		0.101	
${}^qP_0(2), {}^pQ_1(1)$	$E(1, 1, A^+) - E(2, 0, A^+)$	11.034	11.086	-0.051
${}^qP_0(2), {}^pQ_1(1)$	$E(1, 1, B^+) - E(2, 0, B^+)$	10.708	10.765	-0.057
Splittings				
	$\Delta_2(0) + \Delta_1(1)$	0.327	0.321	0.006
	$\Delta_2(0)$		0.220	
	$\Delta_1(1)$		0.101

FIG. 6. Deduce the ground state tunneling splittings from the IR bands of $\text{N}_2\text{-D}_2\text{O}$. Levels above the dashed-dotted line are for the $v_2=1$ excited state. The gap between a $K=0$ and a $K=1$ level (linked by the dashed line) can be deduced from the experiment. The difference between the two gaps gives the sum of the ground state $K=0$ and $K=1$ tunneling splittings. The difference between the A and B ${}^PQ_1(1)$ lines gives the sum of the excited state $K=0$ and ground state $K=1$ tunneling splittings. The difference between the A and B ${}^QR_0(0)$ lines gives the difference of the excited state $K=0$ and ground state $K=1$ tunneling splittings.

two-state model. The same ideas were applied to HF dimer, but in that case, the $K_a=1$ rotation of HF dimer pushes the system away from the linear geometry and *towards* the tunneling region.⁶⁴

It is also important to calculate the tunneling splitting in the $v_2=1$ vibrational state. This can be done by using a pair of experimental IR A and B transitions and the variationally calculated tunneling splitting in the $v_2=0$ vibrational state. In Table VII, differences of selected pairs of experimental IR A and B transitions, ν_A and ν_B , are reported. These differences correspond to either the sum or the difference of $v_2=0$ and $v_2=1$ tunneling splittings. The first pair, ${}^QR_0(0)$, given on the first line of Table VII, is also shown in Fig. 6. For this pair, $\tilde{\Delta}_1(0) - \Delta_0(0) = -(\nu_A - \nu_B) = -0.038 \text{ cm}^{-1}$. We therefore obtain $\tilde{\Delta}(0) - \Delta(0) = -0.038 \text{ cm}^{-1}$, neglecting the J -dependence. This means that the $K=0$ tunneling splitting is reduced by vibrational excitation. The same result can also be obtained from other pairs with higher J (because of the weak J dependence).

TABLE VII. Deduce the tunneling splitting for the $v_2=1$ state of $\text{N}_2\text{-D}_2\text{O}$ using IR transitions. The numerical value of the splitting in the Splitting column is $\nu_A - \nu_B$ in the previous column. The splitting in the third line can be used with $\Delta_0(0) + \Delta_1(1) = 0.327 \text{ cm}^{-1}$ of Table VI to reproduce the first line of this table.

Sub-bands	Lines	ν_A	ν_B	$\nu_A - \nu_B$	Splitting
$K=0 \leftarrow 0$	${}^QR_0(0)$	1179.830	1179.792	0.038	$-(\tilde{\Delta}_1(0) - \Delta_0(0))$
$K=1 \leftarrow 0$	${}^RQ_0(1)$	1191.587	1191.293	0.295	$\Delta_1(0) + \tilde{\Delta}_1(1)$
$K=0 \leftarrow 1$	${}^PQ_1(1)$	1168.241	1168.530	-0.289	$-(\tilde{\Delta}_1(0) + \Delta_1(1))$

The difference $\tilde{\Delta}(1) - \Delta(1)$ could be computed in the same fashion from a pair of transitions in the $K=1 \leftarrow 1$ subband; however, that subband is not observed by Zhu *et al.*³² $\tilde{\Delta}(1) - \Delta(1)$ can nevertheless be determined from the experimental data. First, from the ${}^RQ_0(1)$ pair in the second line of Table VII, we find $\Delta_1(0) + \tilde{\Delta}_1(1) = (\nu_A - \nu_B) = 0.295 \text{ cm}^{-1}$. Second, this is combined with $\Delta_0(0) + \Delta_1(1) = 0.327 \text{ cm}^{-1}$, derived previously from GSCD (in Table VI), assuming $\Delta_0(0) = \Delta_1(0)$ to obtain $\tilde{\Delta}(1) - \Delta(1) = -0.032 \text{ cm}^{-1}$ (dropping the $J=1$ subscript). Therefore, the $K=1$ tunneling splitting is also reduced in the vibrational excited state. Combining these experimental splitting differences with the calculated splittings in the ground state, $\Delta(0) = 0.220$ and $\Delta(1) = 0.101 \text{ cm}^{-1}$, one finds $\tilde{\Delta}(0) = 0.182$ and $\tilde{\Delta}(1) = 0.069 \text{ cm}^{-1}$ (Table VIII).

Zhu *et al.* reported an average tunneling splitting of $0.12850(25) \text{ cm}^{-1}$ for the $v_2=1$ state, also obtained from the experimental A rotational constants. Their average agrees again very well with the average of our $K=0$ and $K=1$ splittings, $\tilde{\Delta}(0)$ and $\tilde{\Delta}(1)$ (see Table VIII). In conclusion, combining the calculated $v_2=0$ tunneling splittings with observed IR transitions, we find that both the $K=0$ and $K=1$ tunneling splittings are reduced upon vibrational excitation, by 0.038 and 0.032 cm^{-1} , or 17% and 32%, respectively.

There are no experimental data on the $K=0$ and $K=1$ H-H exchange tunneling splittings of $\text{N}_2\text{-H}_2\text{O}$. By averaging the $1/2$ and $+/-$ calculated levels, we find that $\Delta(0) = 2.800$ and $\Delta(1) = 0.658 \text{ cm}^{-1}$ (Table VIII). Zhu *et al.*³² estimated the $K=0$ and $K=1$ averaged tunneling splittings to be about $2.5\text{--}3.0 \text{ cm}^{-1}$. This estimate is based on the assumption that the

TABLE VIII. H–H or D–D exchange tunneling splittings (in cm^{-1}) of $\text{N}_2\text{--H}_2\text{O}$ and $\text{N}_2\text{--D}_2\text{O}$.

	Observed	Calculated
$\text{N}_2\text{--H}_2\text{O}$		
$\Delta_0(0)$		2.800
$\Delta_1(1)$		0.658
$\text{N}_2\text{--D}_2\text{O}$		
$\Delta_0(0)$		0.220
$\Delta_1(1)$		0.101
$\Delta_0(0) + \Delta_1(1)$	0.327	0.321
$\tilde{\Delta}_0(0)$		0.182
$\tilde{\Delta}_1(1)$		0.069
$\tilde{\Delta}_0(0) + \tilde{\Delta}_1(1)$	0.257 ^a	0.251

^aDifference of the A constants between A and B states for $v_2 = 1$ state, computed from the experimental data of Zhu *et al.*³²

ratio of the average splittings for $\text{N}_2\text{--H}_2\text{O}$ and $\text{OC--H}_2\text{O}$ should be equal to the ratio for $\text{N}_2\text{--D}_2\text{O}$ and OC--D_2 (about 5), for both of which there are experimental data. The average value from our calculation is 1.729 cm^{-1} , below the estimated value of Zhu *et al.*

C. The vibrational band center shift of $\text{N}_2\text{--D}_2\text{O}$

Zhu *et al.*³² also report A and B $v_2 = 1$ band centers of $\text{N}_2\text{--D}_2\text{O}$ and from them one easily obtains shifts from the $v_2 = 1$ vibration of D_2O . These shifts are a measure of the strength of the hydrogen bond. The experimental band origin is blue shifted by 1.266 and 1.227 cm^{-1} for A and B states, respectively. We calculate the vibrational band center shift from $\Delta_{\text{shift}} = E_{v_2=1}^{\text{zpe}} - E_{v_2=0}^{\text{zpe}}$, where each zero-point energy (ZPE) is relative to its own dissociation limit. See, for example, Ref. 14. To do this calculation properly, we need a PES averaged over the $v_2 = 1$ monomer vibrational wavefunction and a $v_2 = 1$ rotational constant. For $\text{H}_2\text{--H}_2\text{O}$, the $v_2 = 1$ PES is available,⁴⁰ and for $\text{N}_2\text{--D}_2\text{O}$, it is not. We can nonetheless compute $v_2 = 1$ levels using the $v_2 = 0$ PES in place of the missing $v_2 = 1$ PES and using the rotational constants of the $v_2 = 1$ state of D_2O . The $v_2 = 1$ band centers we obtain in this fashion are blue shifted by 0.936 and 0.944 cm^{-1} for A and B states, respectively. This shows that about 75% of the band center shift is due to the change of the rotational constant of the monomer. The other 25% must be due to the change of the PES. However, the calculated band center shift for the B state is slightly larger than for the A state, in contradiction with the experimental data, presumably due to the approximate $v_2 = 1$ PES.

VI. UNDERSTANDING WAVEFUNCTIONS IN PLANAR CONFIGURATIONS

It is difficult to understand wavefunctions of $\text{N}_2\text{--H}_2\text{O}$ if they are plotted in the dynamical coordinates. We wish to show all planar geometries on one plot. There are planar configurations with $\alpha_A - \alpha_B = 0$ or $\pm\pi$ and $\gamma_A = 0$ or π . We divide the planar configurations into four cases: $(\alpha_A - \alpha_B, \gamma_A)$ equal to (a) $(0, 0)$, (b) (π, π) , (c) $(\pi, 0)$, and (d) $(0, \pi)$. A $(\beta_A, \beta_B, \alpha_A - \alpha_B = 0, \gamma_A = 0)$ wavefunction cut does not show the tunneling clearly because it covers only one fourth of the planar

configuration space. This makes it difficult to trace motion or link wavefunction amplitude between different cases. For example, one does not see that a point with coordinates $\alpha_A - \alpha_B = 0, \beta_A = \pi - \epsilon, \gamma_A = 0$ in case (a) is close to the point with coordinates $\alpha_A - \alpha_B = \pi, \beta_A = \pi - \epsilon, \gamma_A = \pi$ in case (b).

(a)

(b)

(c)

(d)

FIG. 7. Definition of the extended angles $\tilde{\beta}_A$ and $\tilde{\beta}_B$ appropriate for visualizing the wavefunction of $\text{N}_2\text{--H}_2\text{O}$ in planar configuration. The relation between the pair of extended angles $(\tilde{\beta}_A, \tilde{\beta}_B)$ and the dynamical angles is given in this figure for each of the four cases (a), (b), (c), and (d) (see text). In each case, the extended angles are obtained by equating the arguments of Ψ with $(\alpha_B, \beta_A, \gamma_A; \alpha_B, \beta_B; \alpha, \beta)$. The H_2O MF frame (in blue) and N_2 MF frame (in blue) are obtained with the dynamical angles indicated as the arguments of Ψ in the figure. The red dashed frame is obtained by rotating the space-fixed frame by Euler angles $(\alpha, \beta, \alpha_B)$. The orientation of the two MF frames can be obtained by rotating the red dashed frame by $\tilde{\beta}_A$ and $\tilde{\beta}_B$. To obtain the N_2 MF frame in panels (c) and (d), one must rotate the frame whose orientation is specified (with respect to the DF frame) by $\alpha_B + \pi$ and $2\pi - \tilde{\beta}_B$, by a third Euler angle $\gamma_B = \pi$, but the wavefunction is independent of this angle.

One remedy is to plot in so-called extended angles which we denote $\tilde{\beta}_A$ and $\tilde{\beta}_B$. Values of $\tilde{\beta}_A$ and $\tilde{\beta}_B$ specify a planar shape, but not its orientation. $\tilde{\beta}_k$ is defined as the positive (counterclockwise) angle from $\mathbf{r}_0$ to the z axis of the MF frame attached to monomer k , $k = A, B$, and monomer A is on the left, see Fig. 7. To describe all planar configurations, it is necessary that the extended coordinates have the range $[0, 2\pi]$, extended beyond the range $[0, \pi]$ of β_k . When one adds to $\tilde{\beta}_A$ and $\tilde{\beta}_B$ coordinates that specify the orientation of the molecule $(\alpha, \beta, \alpha_B)$, one obtains a full set of coordinates specifying all planar configurations. Note that for a planar configuration, $\alpha_B + \pi$ and α_B specify the same orientation because N_2 is linear. The extended coordinates of a point in one quadrant and the extended

coordinates of a point close to it, but in a neighboring quadrant, correspond to two very similar molecular shapes. A quadrant corresponds to a case (see Fig. 7). Extended coordinates were used for the HF dimer by Hougen and Ohashi.⁶⁵

To find values of a function, e.g., a wavefunction, in all four quadrants, one must establish relationships between the dynamic and extended coordinates. We denote a wavefunction on the plane and in quadrant q as $\tilde{\Psi}_q(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B)$, $q = a, b, c, d$. Note that on the plane $\tilde{\Psi}_q$ has only five arguments. Values of $\tilde{\Psi}_a$ are exactly equal to values of Ψ which we compute, because the dynamic and extended coordinates are the same in quadrant a . We must also determine $\tilde{\Psi}_b, \tilde{\Psi}_c, \tilde{\Psi}_d$. We find

$$\begin{aligned}\tilde{\Psi}_a(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B) &\equiv \Psi(\alpha_B, \tilde{\beta}_A, 0; \alpha_B, \tilde{\beta}_B; \alpha, \beta) && \text{for case (a),} \\ \tilde{\Psi}_b(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B) &\equiv \Psi(\alpha_B + \pi, 2\pi - \tilde{\beta}_A, \pi; \alpha_B, \tilde{\beta}_B; \alpha, \beta) && \text{for case (b),} \\ \tilde{\Psi}_c(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B) &\equiv \Psi(\alpha_B, \tilde{\beta}_A, 0; \alpha_B + \pi, 2\pi - \tilde{\beta}_B; \alpha, \beta) && \text{for case (c),} \\ \tilde{\Psi}_d(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B) &\equiv \Psi(\alpha_B + \pi, 2\pi - \tilde{\beta}_A, \pi; \alpha_B + \pi, 2\pi - \tilde{\beta}_B; \alpha, \beta) && \text{for case (d).}\end{aligned}\quad (7)$$

The wavefunction on the right has 7 arguments and is what we compute. By setting $(\alpha_B, \beta_A, \gamma_A; \alpha_B, \beta_B; \alpha, \beta)$ equal to the arguments of Ψ on the right side of Eq. (7), one obtains, case by case, the relation between the dynamical and extended coordinates. For the four cases, (a), (b), (c), and (d), the ranges of $(\tilde{\beta}_A, \tilde{\beta}_B)$ are $([0, \pi], [0, \pi])$, $([\pi, 2\pi], [0, \pi])$, $([0, \pi], [\pi, 2\pi])$, and $([\pi, 2\pi], [\pi, 2\pi])$, respectively. The relationship between the two sets of coordinates is explained in Fig. 7. When a wavefunction or the PES is plotted in the extended coordinates, the cases correspond to quadrants of the plot.

The extended angles presented here are a generalization of the extended angles for the planar configurations of a complex composed of two linear monomers (see Fig. 2 of Ref. 66 and also Refs. 16 and 67). They can be further extended for a system of two non-linear monomers such as $(H_2O)_2$. Smit *et al.*⁶⁸ plotted wavefunctions of $(H_2O)_2$ using extended β_A and β_B angles. The range is extended to $[0, 2\pi]$. However, they did not explain how wavefunctions at points in the extended angles were computed.

The relations of Eq. (7) are true regardless of the symmetry of monomers A and B . Exploiting the symmetry, it is possible to obtain a wavefunction $\tilde{\Psi}_q$, $q = a, b, c, d$, at a point in quadrant q from the wavefunction at a point in quadrant a . This is done by operating on the full-dimensional wavefunction which when projected onto the plane is $\tilde{\Psi}_q$. For quadrant (b), we find, for example,

$$\begin{aligned}\tilde{\Psi}_b(\tilde{\beta}_A, \tilde{\beta}_B; \alpha, \beta, \alpha_B) &\equiv \Psi(\alpha_B + \pi, 2\pi - \tilde{\beta}_A, \pi; \alpha_B, \tilde{\beta}_B; \alpha, \beta) \\ &= \sigma_{HH}\sigma_{NN}C_2^\pi(r_0)\Psi(\alpha_B, 2\pi - \tilde{\beta}_A, 0; \alpha_B, \pi - \tilde{\beta}_B; \alpha, \beta) \\ &= \sigma_{HH}\sigma_{NN}C_2^\pi(r_0)\tilde{\Psi}_a(2\pi - \tilde{\beta}_A, \pi - \tilde{\beta}_B; \alpha, \beta, \alpha_B),\end{aligned}\quad (8)$$

where $C_2^\pi(r_0)$ is a rotation by π along the $\mathbf{r}_0$ vector. Note that in general $C_2^\pi(r_0)$ is not a symmetry operation. Operating on the basis functions, it has the property $C_2^\pi(r_0)|j_A k_A m_A; j_B(m_B); JKM\rangle = (-1)^K |j_A k_A m_A; j_B(m_B); JKM\rangle$.

Due to the symmetry of H_2O and N_2 , it is also true that every point in quadrants (b), (c), and (d) has the same potential value as a point in quadrant (a). See Fig. 3. The point in quadrant (b) with the same potential value as a point in quadrant (a) can be obtained from Eq. (8) by dropping the operators on the left of the RHS (they do not affect the potential). In this fashion, we find

$$\begin{aligned}V^{(b)}(\tilde{\beta}_A, \tilde{\beta}_B) &= V^{(a)}(2\pi - \tilde{\beta}_A, \pi - \tilde{\beta}_B), \\ V^{(c)}(\tilde{\beta}_A, \tilde{\beta}_B) &= V^{(a)}(\tilde{\beta}_A, \tilde{\beta}_B - \pi), \\ V^{(d)}(\tilde{\beta}_A, \tilde{\beta}_B) &= V^{(a)}(2\pi - \tilde{\beta}_A, 2\pi - \tilde{\beta}_B).\end{aligned}\quad (9)$$

These relations enable one to plot the potential in all quadrants when it is known in quadrant a (Fig. 3). Potential contours in the extended coordinates facilitate understanding of the wavefunction plots of Figs. 8 and 9.

The four nearly degenerate tunneling wavefunctions for the ground state and the first excited state are plotted in extended angles in Figs. 8 and 9, respectively. Clearly the extended coordinates make it much easier to understand the tunneling that occurs in planar configurations. The more facile H–H exchange tunneling occurs mostly along $\tilde{\beta}_A$. In the vicinity of the global minima, the ground state wavefunction contours and the potential contours are similar. Important tunneling occurs between versions 1 and 2 and between versions 3 and 4, where the wavefunction has large amplitude. The dominant tunneling path between these wells is in the region between the minima. The largest amplitude is not along

FIG. 8. Wavefunction cuts for the four tunneling states of the ground state of $\text{N}_2\text{-H}_2\text{O}$. These wavefunctions are obtained by projecting the wavefunctions onto the extended angles $(\tilde{\beta}_A, \tilde{\beta}_B)$ appropriate for visualizing continuously changing wavefunctions in planar configuration and fixing $r_0 = 6.30a_0$ and $\alpha_B = 45^\circ$. α_B is chosen to avoid nodes in the wavefunction. The plotted states are A_1^+ , A_2^+ , B_1^+ , and B_2^+ for (a), (b), (c), and (d), with energies 0, 0.0017, 2.8008, and 2.8005 cm^{-1} , respectively. The contour interval is 0.2.

a steepest descent path but rather more or less along a straight line linking the two minima. The wavefunction amplitude is larger along the path going through the $C_{2v}(\text{H})$ saddle point than the $C_{2v}(\text{O})$ saddle point. The N–N exchange tunneling is less facile. The two lobes of the wavefunctions are well separated along $\tilde{\beta}_B$, indicating a slow tunneling process. In Fig. 3, it is possible to follow motion of the atoms along a path between planar configurations. The path goes from version 1 $\rightarrow$ 2 $\rightarrow$ 3 $\rightarrow$ 4 $\rightarrow$ 1. Along this closed path, $\tilde{\beta}_A$ changes by 4π and $\tilde{\beta}_B$ changes by 2π . The H–H exchange tunneling links version 1 and version 2. Permuting the N atoms takes one from version 1 to version 3. Along the cyclic path this occurs by going through version 2. Although there is little tunnelling between

versions 1 and 3, wavefunction amplitude along the cyclic path seems to be larger than amplitude along a direct path from version 1 to 3. All paths from version 1 to version 3 are either long or have high barriers. This is part of the reason for the small N–N exchange tunneling splitting. Most of the tunneling dynamics occurs among planar configurations. However, at the $C_{2v}(\text{O})$ saddle point, N_2 can rotate out of the plane, passing through a C_{2v} saddle point (called structure V in Ref. 35) only 32 cm^{-1} higher according to Ellington and Tschumper³⁵ and only 33.6 cm^{-1} higher on TWHH PES.¹¹ Due to the fact that wavefunction amplitude at the $C_{2v}(\text{O})$ saddle point is small, the low barrier does not mean that non-planar dynamics is important.

FIG. 9. Same as Fig. 8 but for the excited bending state. The energies of the A_1^+ , A_2^+ , B_1^+ , and B_2^+ states are 33.78, 34.67, 37.57, and 37.29 cm^{-1} .

Finally, the nodes of the wavefunctions are in accord with what one expects on the basis of the symmetry labels. For example, B_1^+ and B_2^+ states have a node along the dominant H–H tunneling path (the bottom two panels of Fig. 8) because B labels states anti-symmetric with respect to H–H exchange. Similarly, for A_2^+ and B_2^+ states, there is a node along $\tilde{\beta}_B$ (the right two panels of Fig. 8) because “2” labels states anti-symmetric with respect to N–N exchange.

Plotting wavefunctions helps us to assign the vibrational excited states. For example, for the A_1^+ symmetry states, the second e vibrational state at 33.78 cm^{-1} is a bending excited state with a clear node (Fig. 9), both the third and fourth e vibrational states at 47.11 and 62.12 cm^{-1} have stretch excitation character, and the first f vibrational state at 58.94 cm^{-1}

has excitation in an out-of-plane mode with a node seen in γ_A coordinate.

VII. CONCLUSION

Spectra of van der Waals molecules are notoriously difficult to analyze because standard zeroth-order models work poorly. However, modern methods for making PESs and solving the rovibrational Schrödinger equation make it possible, within the approximation that monomers are rigid, to easily compute rovibrational spectra and analyze spectra. This is most easily done by using a large product basis and the symmetry adapted Lanczos algorithm. These methods make it possible to compute rovibrational levels of $\text{N}_2\text{--H}_2\text{O}$ and

$\text{N}_2\text{-D}_2\text{O}$. The PES of Tulegenov *et al.*¹¹ is very accurate. Eigenvectors computed with the Lanczos algorithm have been used to plot wavefunctions to understand the states. Sums and difference of some tunnelling splittings have been measured experimentally. We calculate the splittings themselves and our results should guide experimentalists working on $\text{N}_2\text{-H}_2\text{O}$ and $\text{N}_2\text{-D}_2\text{O}$. A striking result is the observation that the order of symmetric and anti-symmetric tunnelling states is inverted for $\text{N}_2\text{-D}_2\text{O}$ $K = 1$ levels, but not for $K = 0$ levels, in agreement with the experiment. The order is normal (*A* below *B*) for both the $K = 0$ and $K = 1$ levels of $\text{N}_2\text{-H}_2\text{O}$, which should be tested by future experiments.

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