Supplementary material for "Rotation-Tunneling Spectrum of the Water Dimer Using Semiclassical Instanton Theory": Derivation of the tunneling matrix

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In order to extract the tunneling splittings from the path-integral formulation presented in the main text, it is necessary to insert the results of the instanton calculation into a tunneling matrix. The original tunneling matrix was derived using simple graph theory [1]. We show here a more detailed derivation, based on the use of density matrices.

We consider a full molecular Hamiltonian of the simple form

$$\begin{aligned}\hat{H} &= \sum_{i=1}^{f} \frac{\hat{p}_i^2}{2m_i} + \sum_{j=1}^{N_{\mathrm{at}}} V(\vec{x_j}) \\ &= \hat{T} + \hat{V}\end{aligned} \tag{S1}$$

where f is the number of degrees of freedom and N_{at} is the number of atoms. We have implicitly assumed the Born-Oppenheimer approximation is valid, meaning that all the electronic degrees of freedom are contained within the potential $V(\vec{x})$. For a prolate symmetric top molecule undergoing rotations and vibrations in free space (taking the space-fixed and molecule-fixed frames to be aligned), the nuclear wavefunction with the centre of mass translations removed may be written as a function of relative coordinates $\vec{r}$ and overall rotations $\vec{\eta}$ (as defined in the main text) in the form [2]

$$\psi_\nu^{JK}(\vec{r}_{\vec{\eta}}) = \sqrt{\frac{2J+1}{8\pi^2}} \left[D^J_{KK}(\vec{\eta})\right]^* \psi_\nu^{JK}(\vec{r}). \tag{S2}$$

The labels νJK denote the vibrational level, the rotational quantum number and the projection of the angular momentum on the principal axis, respectively. The properties of Wigner D matrices implies that for two successive rotations $\hat{R}_1(\vec{\Omega})\hat{R}_2(\vec{\eta}) = \hat{R}_{12}(\vec{\Theta})$, $D^J_{KK'}(\vec{\Theta}) = \sum_M D^J_{KM}(\vec{\Omega}) D^J_{MK'}(\vec{\eta})$. In terms of the vibrational functions in (S2), the density matrix can be written

$$\begin{aligned}\rho(\vec{r}, \vec{r}_{\vec{\Omega}}) = \sum_\nu \sum_{JKK'} &\frac{2J+1}{8\pi^2} |\psi_\nu^{JK}(\vec{r})|^2 e^{-\beta E_\nu^{JK}} \\ &\times \left[D^J_{KK'}(\vec{\eta})\right]^* \sum_M D^J_{KM}(\vec{\Omega}) D^J_{MK'}(\vec{\eta}).\end{aligned} \tag{S3}$$

Using the property of Wigner D matrices that $\sum_{K'} \left[D^J_{KK'}(\vec{\eta})\right]^* D^J_{MK'}(\vec{\eta}) = \delta_{KM}$, we obtain the expression for the density matrix in Eq. (6) of the main text. In the rest of this section, we assume the integral over angles has already been performed according to Eq. (7) of the main text and we drop the rotational state labels for brevity.

We introduce the tunneling matrix, $\mathbf{W}$, which has matrix elements

$$\begin{aligned}W_{ij} &= \frac{\langle \vec{r}_i | e^{-\beta H} | \vec{r}_j \rangle}{\langle \vec{r}_i | e^{-\beta H} | \vec{r}_i \rangle} - \delta_{ij} \\ &= \frac{\rho(\vec{r}_i, \vec{r}_j, \beta)}{\rho(\vec{r}_i, \vec{r}_i, \beta)} - \delta_{ij},\end{aligned} \tag{S4}$$

where i and j label the wells and range from 0 to $G-1$, with G being the order of the molecular symmetry group. We wish to relate the eigenvalues of the tunneling matrix to the tunneling splittings of the system, which is most easily done by finding the trace of $\mathbf{W}$. With the definition in (S4), however, the trace is simply a constant, which reflects the symmetric nature of the tunneling splittings. We must therefore change the basis of the tunneling matrix before taking the trace in order to obtain an expression in terms of the energy levels. Each row i of the tunneling matrix can be mapped on to the first row with appropriate reordering of the columns j, due to the properties of finite groups (the mapping can be worked out using the multiplication table for the molecular symmetry group). We can combine this principle with the invariance of the trace of the matrix to unitary transformations to simplify our task, resulting in a transformed tunneling matrix $\bar{\mathbf{W}}$

$$\begin{aligned}\mathrm{Tr}\left[\bar{\mathbf{W}}\right] &= \frac{1}{G} \sum_\mu \sum_{i>0} \sum_{j>0} a^*_{j\mu} W_{ij} a_{i\mu} = \sum_\mu \sum_{j>0} a^*_{j\mu} W_{0j} \\ &= \frac{\sum_\mu \left[\sum_{j>0} \sum_\nu a^*_{j\mu} a_{j\nu} e^{-\Delta_\nu(\beta - \bar{\beta}_\nu)}\right]}{1 + \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}},\end{aligned} \tag{S5}$$

where ν labels the eigenvalues, and μ labels the diagonal matrix elements of $\bar{\mathbf{W}}$. As the symmetry properties of the tunneling matrix are the same as for the molecular symmetry group the eigenstates have the same symmetry as the irreps, meaning that the $a_{j\nu}$ coefficients are in fact the corresponding characters. In the following few steps,

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we will make use of the orthogonality of the characters, rearranged as

$$\sum_{j>0} a^*_{j\nu} a_{j\mu} = G\delta_{\mu\nu} - 1. \tag{S6}$$

Separating out the ground state in the sum over ν and explicitly writing out $\rho(\vec{r}_i, \vec{r}_i)$, we find

$$\mathrm{Tr}\left[\mathbf{W}\right] = \frac{\sum_\mu \sum_{j>0} \left[1 + \sum_{\nu>0} a^*_{j\mu} a_{j\nu} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}\right]}{1 + \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}. \tag{S7}$$

Using (S6), we can evaluate the sum over j for each diagonal element of $\bar{\mathbf{W}}$,

$$\bar{W}_{\mu\mu} = \frac{G\delta_{\mu 0} + \sum_{\nu>0} \left(G\delta_{\mu\nu} - 1\right) e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}{1 + \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}. \tag{S8}$$

Considering $\mu = 0$ separately from the $\mu > 0$ values and evaluating the δ functions, the first term is

$$\bar{W}_{00} = \frac{G - \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}{1 + \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}, \tag{S9}$$

which can be approximated in the low temperature limit by

$$\bar{W}_{00} \approx \sum_\nu \tanh\left[\frac{\Delta_\nu}{2}\left(\beta - \bar{\beta}_\nu\right)\right]. \tag{S10}$$

All the higher terms for $\mu > 0$ take the general form

$$\bar{W}_{\mu\mu} = \frac{\sum_{\nu\neq\mu}\left[e^{-\Delta_\mu(\beta-\bar{\beta}_\mu)} - e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}\right]}{1 + \sum_{\nu>0} e^{-\Delta_\nu(\beta-\bar{\beta}_\nu)}}. \tag{S11}$$

When we then sum over all the values of $\mu > 0$, we find that each term involving μ in the numerator matches up with a term involving ν, and thus cancel out. The total trace is therefore only given by the first term in (S10), as required.

[1] J. O. Richardson, S. C. Althorpe, and D. J. Wales, J. Chem. Phys. **135**, 124109 (2011).

[2] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley & Sons: New York, 1988).