VIBRATIONAL TUNNELING SPECTRA OF THE WATER HEXAMER PRISM

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INTRODUCTION

The water hexamer is an assembly of six water molecules that are weakly-bound by hydrogen bonds. This particular cluster is probably the most intriguing one out of a plethora of other studied water clusters because it is the smallest one with 3D structure. At very low temperatures, molecules in the cluster can rearrange and generate new, equivalent structures. These structures are connected to one another by some symmetry operation. It is observed that the water hexamer system has a great number of possible minima, but only the ones connected by short and energetically accessible tunneling paths cause observable splittings, which exhibit a characteristic doublet-of-triplets pattern.

Using isotopic substitution to analyze these structures reveals that the splitting pattern in the spectrum remains unchanged for three instances of oxygen isotope substitution: A&D, C&E, B&F [1]. In contrast, it has been shown that performing any other oxygen substitution destroys the pattern, indicating that the tunneling motion must include regrouping of the A21 and D78 water molecules.

Upon the $^{16}O - ^{18}O$ isotopic substitution, it is observed that the TM elements reduce up to approximately 85%, which points to the movement of oxygen atoms along the tunneling pathway [1]. In the water hexamer prism, there are two rearrangement motions which cause an observable tunneling splitting.
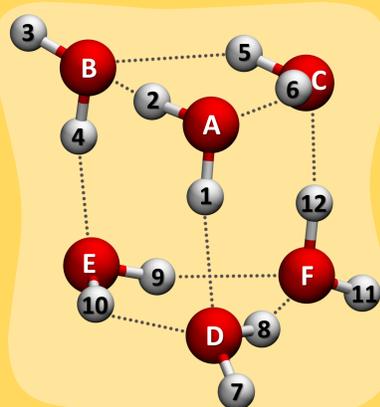
METHOD

The semiclassical method involves the construction of the tunneling matrix (TM) as the Hamiltonian matrix in the basis of localized states. The diagonal elements are zero-point energies of these states, and the off-diagonal elements contain information about minima coupling. The off-diagonal elements are calculated using the Herring formula with the WKB wavefunction at the minimum action path (MAP) and its quadratic neighbourhood. In order to calculate the splittings of the excited states, it is necessary to construct the excited-state wavefunction in the WKB approximation.

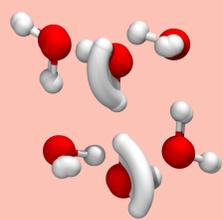The tunneling matrix elements are given by the following formulas [2]:

$$h_{GS} = \sqrt{\frac{det\, A_0}{\pi^N}}\, e^{-\int_0^{S_{tot}} p_0\, dS - W_1^L - W_1^R} \int \left(\frac{\partial W_0^L}{\partial S} - \frac{\partial W_0^R}{\partial S}\right) e^{-\Delta x^T \frac{A^L - A^R}{2} \Delta x} \delta(f(x)) dx$$

$$h_{ES} = h_{GS}(2\omega_e)\left(F^L F^R + \frac{1}{2} U^L \bar{A}^{-1} U^R\right)$$

We used the MB-Pol potential energy surface and the string method with L-BFGS algorithm for finding the minimum action path. **A** is calculated at the dividing plane by propagating the Riccati equation from both minima along the MAP. When determining the excited state elements h_{ES}, we calculate **U** by propagating the equation $p_0\, \partial U/\partial S = \omega_e U - AU$ from the minima to the dividing plane along the MAP.

RESULTS

Several motions with insignificant tunneling splitting values were observed. There are two main pathways - antigeared (AG) and geared (G) - that can explain the specific doublet-of-triplets splitting in spectrum obtained by experiment [3].
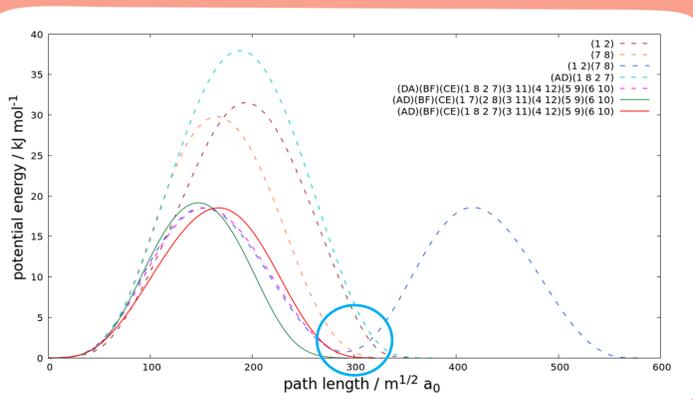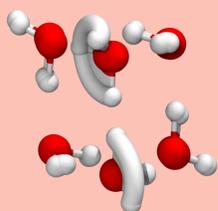
GEARED PATHWAY
P_g = (AD)(BF)(CE)(1 8 2 7)(3 11)(4 12)(5 9)(6 10)
double flip + bifurcation (breaks 2 hydrogen bonds)
triplet splitting pattern

ANTIGEARED PATHWAY
P_a = (AD)(BF)(CE)(1 7)(2 8)(3 11)(4 12)(5 9)(6 10)
double flip (breaks 1 hydrogen bond)
doublet splitting pattern

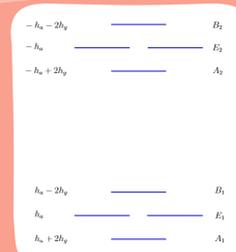Symmetry analysis of the hexamer cluster reveals that the eigenvectors of the tunneling matrix transform as irreducible representations of a group isomorphic to the D_{2d} point group [1]. The eigenvalues and eigenvectors of the TM define the energy diagram and vibrational states of the system. It is evident that the triplet width is equal to ($-4h_g$), while the doublet width is ($-2h_a$).

The calculated ground-state TM elements (**O**) are in relatively good agreement with the results obtained in article **A1** [1], but with those of article **A2** [2] and experimental reference values **EXP** [3] only to a mediocre extent. All h values are expressed in MHz.

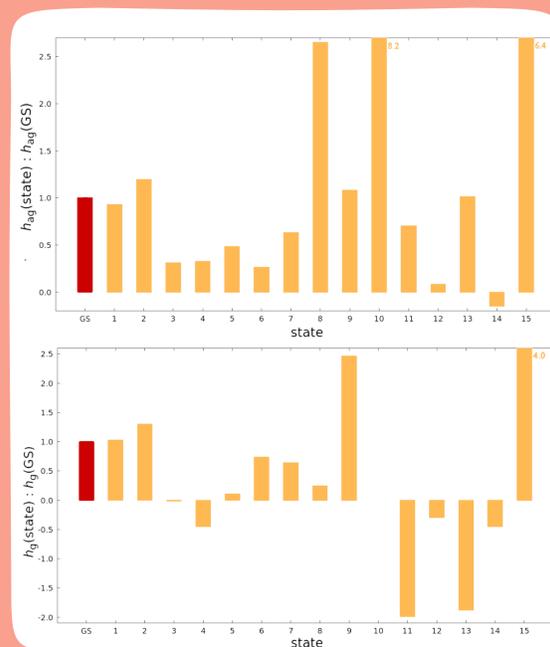|	$|h_{ag}|$	$|h_g|$
O	1.02	0.14
A1	0.88	0.15
A2	0.4	0.12
EXP	0.382	0.073

The AG pathway is somewhat shorter than the G pathway, namely: 294.2 a. u. and 320.6 a. u. Therefore, the calculated action values are S_{ag} = 18.76 $\hbar$, and S_g = 20.92 $\hbar$.

These graphs show the ratio of excited and ground state TM elements for AG and G pathways, which are proportional to the doublet and triplet widths.

The splittings in a few excited modes (12th in AG, 3rd and 5th in G) are lessened, whereas in others substantially enlarged (10th and 15th in AG, 15th in G), e.g. up to 8x in mode 10 (AG). Ref. [5] reported dramatically enhanced tunneling splittings (1000x) in an excited librational mode.

In some excited modes, the energy levels invert the order. For example, in the 14th excited mode both the doublet and triplet are inverted.

$\tilde{\nu} = 62.2\ cm^{-1}$ $\tilde{\nu} = 72.1\ cm^{-1}$ $\tilde{\nu} = 74.4\ cm^{-1}$ $\tilde{\nu} = 110.1\ cm^{-1}$ $\tilde{\nu} = 119.9\ cm^{-1}$ $\tilde{\nu} = 149.9\ cm^{-1}$ $\tilde{\nu} = 172.5\ cm^{-1}$ $\tilde{\nu} = 178.8\ cm^{-1}$

CONCLUSION

To conclude, the goal of this work was to calculate the tunneling splittings of ground and vibrationally excited states using a variant of the WKB approximation along the minimum action path and the Herring formula. The main advantage of this method is in its applicability to determining both ground- and excited-state splittings. Ring polymer instanton theory and path integral molecular dynamics can only calculate tunneling splittings in the ground state. Future work includes performing symmetry analysis to see how symmetry affects the size of the splittings in the excited states and adapting the method to the excitations of higher frequencies (librational modes).

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