Automatically Assigning Thousands of Vibrational Eigenstates

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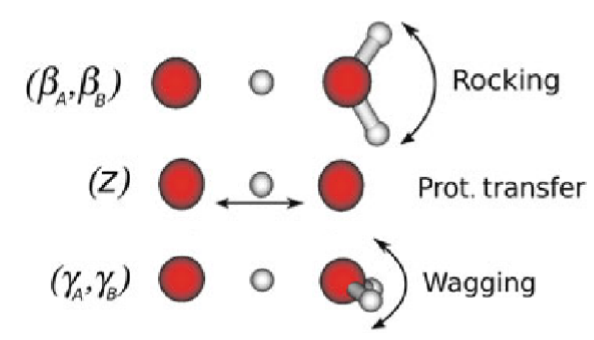
Motivation

- Characterize and understand quantum mechanical effects with vibrational spectroscopy
- Effects such as: degeneracies, strong coupling, anharmonicities, and Fermi resonances[1]
- Systems such as Zundel ion ($H_5O_2^+$) & Acetonitrile (CH_3CN)



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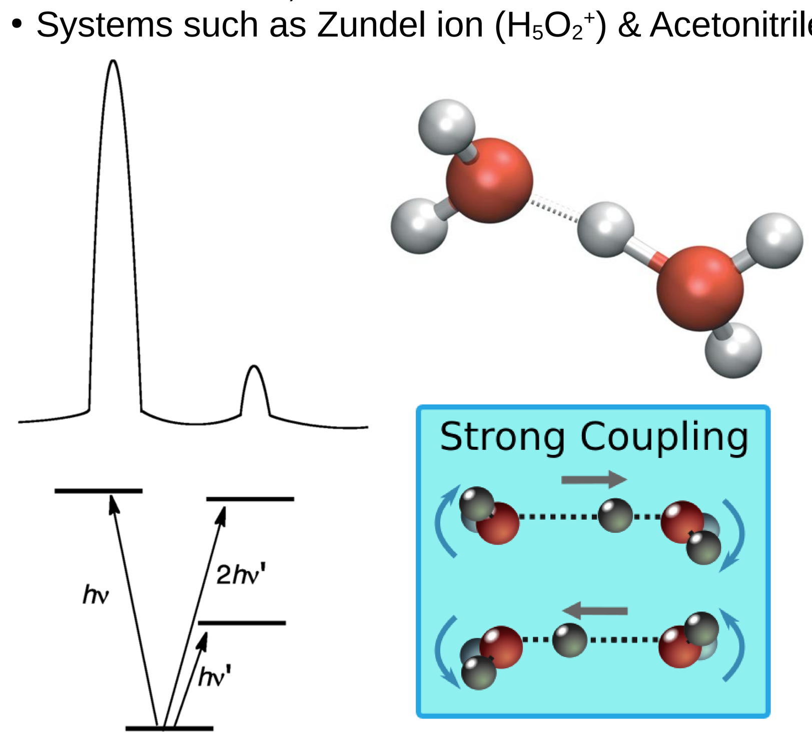

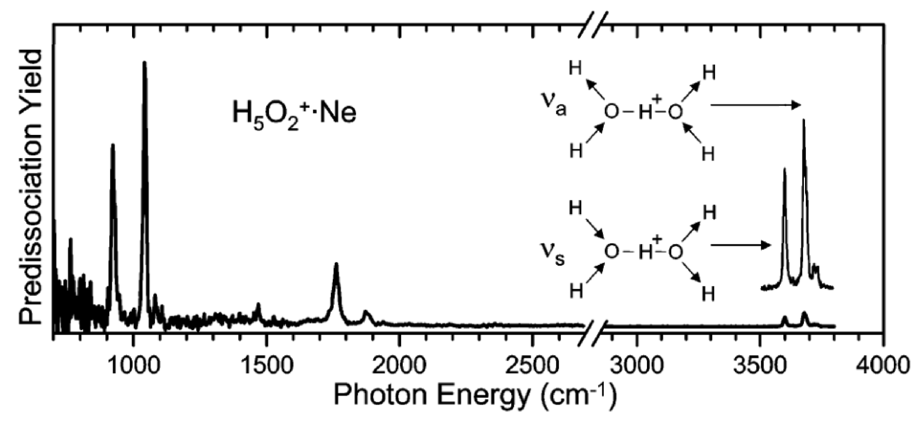

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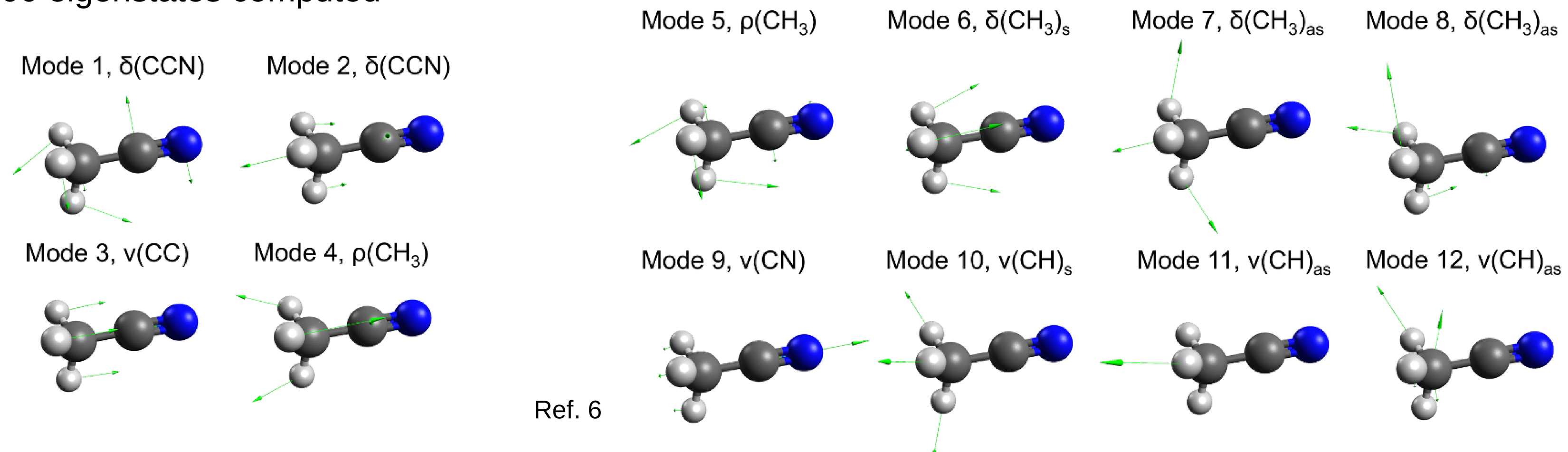
Acetonitrile

- A prototypical model exemplary of degeneracies, resonances, and couplings[4]
- 12 degrees of freedom
- Choose commonly used Avila and Carrington potential energy surface of the multiple surfaces to choose from due to the quartic force field expansion[5,9]
- 5000 eigenstates computed[4]



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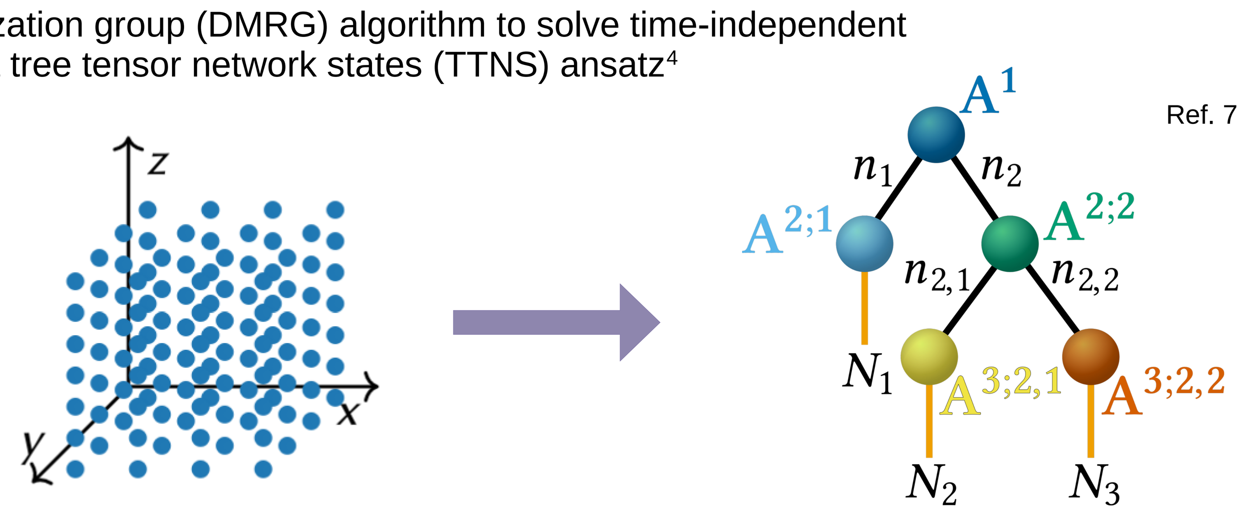
Schrodinger Equation

- Use density matrix renormalization group (DMRG) algorithm to solve time-independent Schrodinger equation using a tree tensor network states (TTNS) ansatz[4]
- Determine eigenstates $|\psi_N\rangle$

$$H|\Psi\rangle = E|\Psi\rangle$$



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$$\Psi(x_p, y_q, z_r) = \sum_i^{n_1}\sum_j^{n_2}\sum_k^{n_{2,1}}\sum_l^{n_{2,2}} A^1_{ij} A^{2;1}_{ip} A^{2;2}_{jkl} A^{3;2,1}_{kq} A^{3;2,1}_{lr}$$

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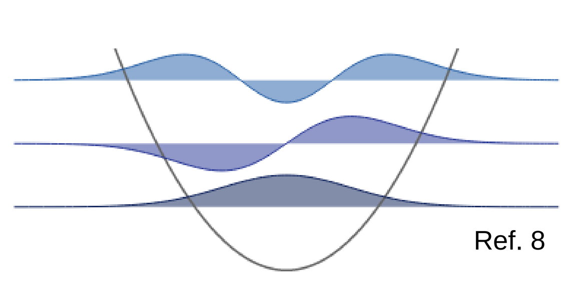
Eigenstate Assignment

$$|\psi_N\rangle = |n_1\rangle \otimes |n_2\rangle \otimes ... \otimes |n_F\rangle = \bigotimes_\kappa^F |n_\kappa\rangle$$

- Assign principal quantum number based on excitations
- Assignments tell us which modes are active and give deep insights into modal couplings and resonances
- Angular momentum is a key feature of degenerate coordinates, assign this too

Ex: $|\psi_N\rangle = \bigotimes_\kappa^F |n_\kappa\rangle = |02...1\rangle$



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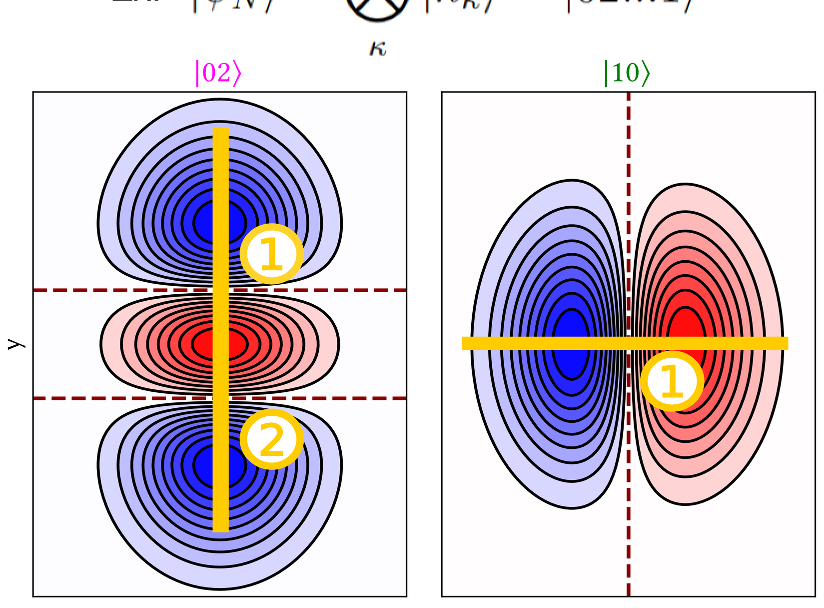

$$|n_\kappa^{(S)}\rangle = |(vl)_\kappa^{(S)}\rangle = \sum_{i=1}^\infty c_i |v_\kappa^{(i,S)}\rangle \otimes |l_\kappa^{(i,S)}\rangle$$

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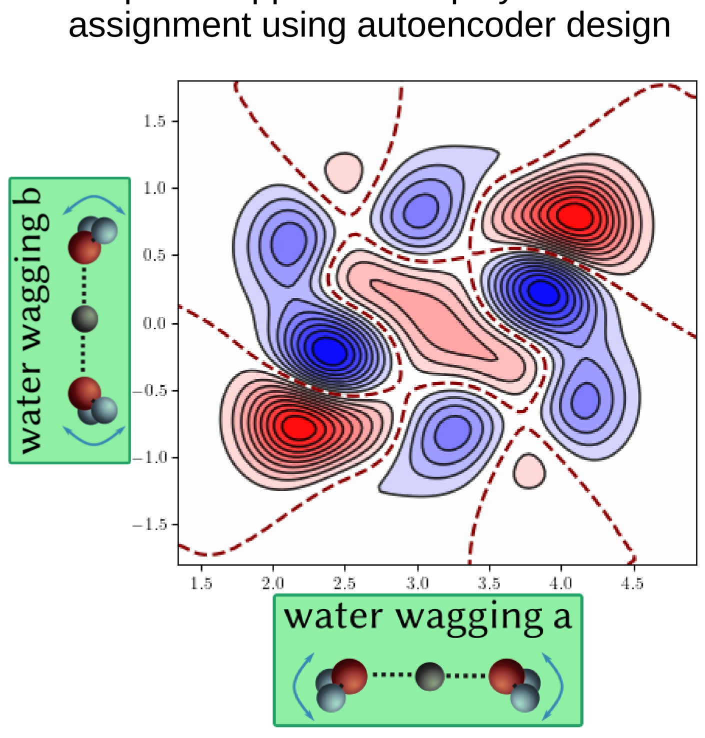
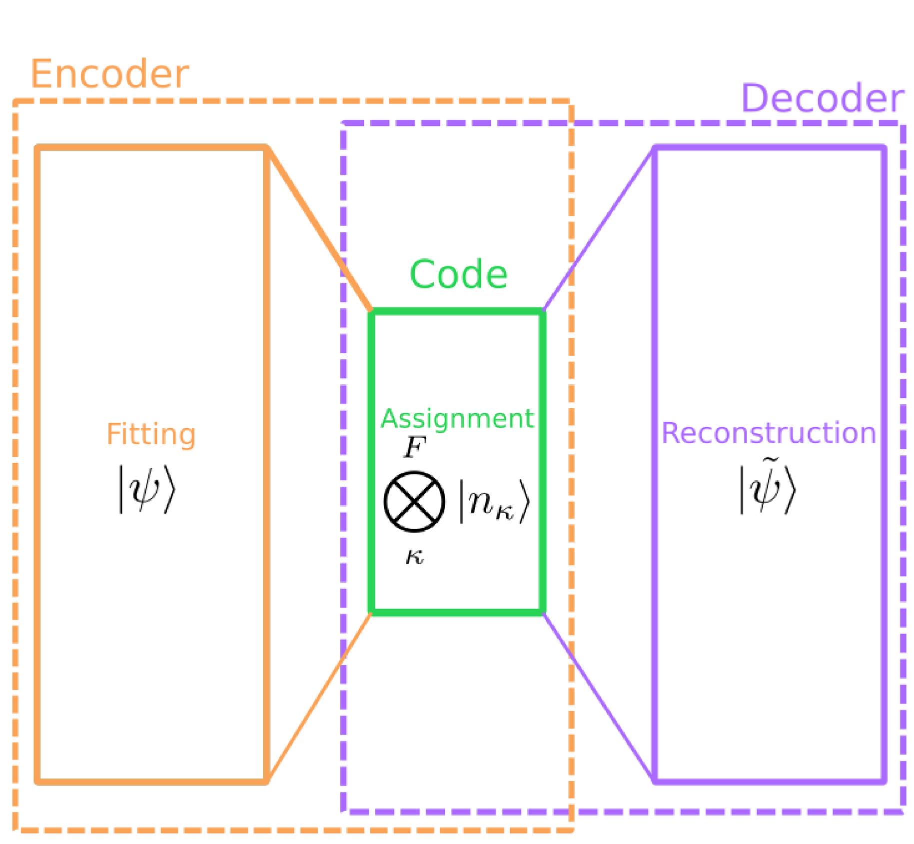
Automated Assignment

- Manual inspection difficult in the case of complicated resonances
- Thousands of states to assign
- Proposed approach: employ automated assignment using autoencoder design





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Hartree Product Decomposition and Change of Basis

- Decompose eigenstate, ψ_N, into simpler, orthogonal Hartree product states, truncate terms with small contributions
- Discrete variable representation basis, m_α

$$|\psi_N\rangle = \sum_R d_R |m_1^{(R)} m_2^{(R)} m_3^{(R)} m_4^{(R)} m_5^{(R)} m_7^{(R)} m_9^{(R)} m_{11}^{(R)}\rangle$$

Change of Basis

Non-degenerate | Degenerate

Vibrational self-consistent field (VSCF) basis

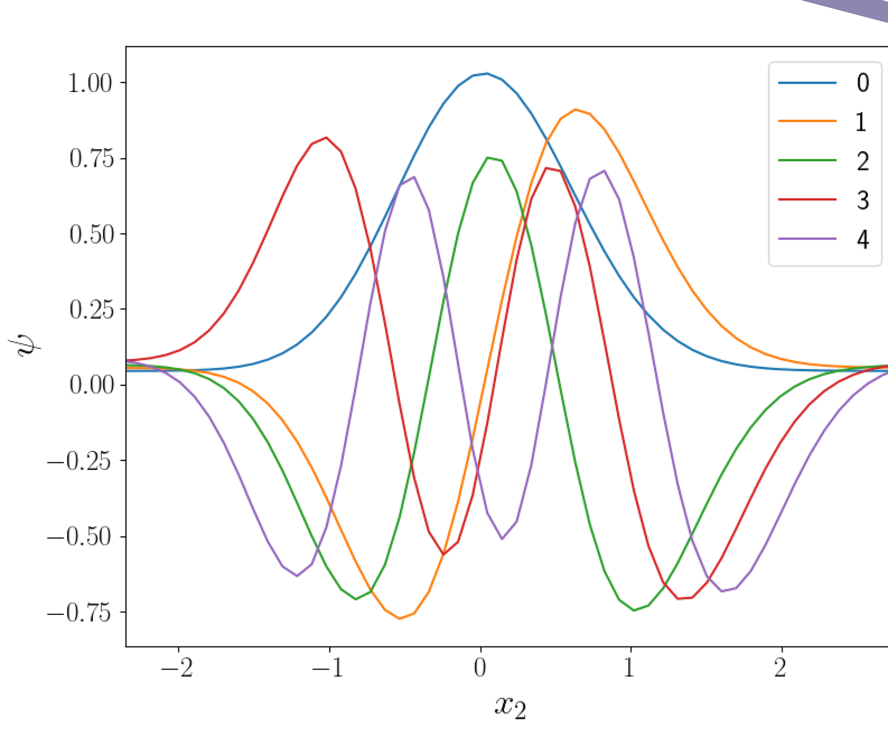
$$\sum_x |n_x^{(R,\alpha)}\rangle\langle n_x^{(R,\alpha)}|$$

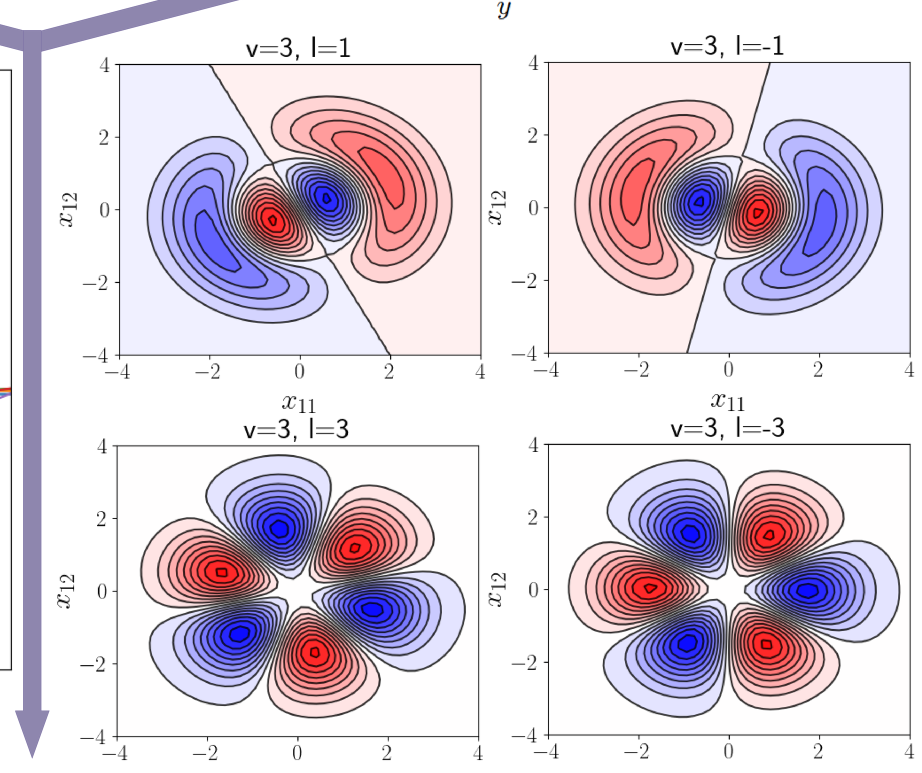
$$|m_\alpha^R\rangle = \sum_x a_x^{(R,\alpha)} |n_x^{(R,\alpha)}\rangle$$

2D isotropic harmonic oscillator basis

$$\sum_y |v_y^{(R,\alpha)} l_y^{(R,\alpha)}\rangle\langle v_y^{(R,\alpha)} l_y^{(R,\alpha)}|$$

$$|m_\alpha^R\rangle = \sum_y b_y^{(R,\alpha)} |v_y^{(R,\alpha)} l_y^{(R,\alpha)}\rangle$$





$$|\psi_N\rangle = \sum_R d_R \bigotimes_\alpha \sum_x c_x |q_x^{(R,\alpha)}\rangle$$

Expand and simplify

$$|\psi_N\rangle = \sum_{S=1}^\infty c_S |n_1^{(S)} n_2^{(S)} n_3^{(S)} n_4^{(S)} (vl)_5^{(S)} (vl)_7^{(S)} (vl)_9^{(S)} (vl)_{11}^{(S)}\rangle$$

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Automated Assignment Results

- Produce assignment that factors in principal and angular momentum quantum numbers
- Hartree product decomposition approximates the eigenstate due to truncation
- Assignment confirmed for 50 states
- (c_S) is the coefficient, n is the principal quantum number, v is the frequency, l is the angular momentum quantum number, α is the coordinate

Format: $(c_S)nv_\alpha^l$

State	Energy (cm^{-1})	Assignment	Ref. Assignment[9]	Ref. Assignment[10]
1	360.990	$(0.7+0.2i)v_{11}^{+1} + (0.7i)v_{11}^{-1}$	$v_{11}^{\pm1}$	v_{11}
2	360.990	$(0.7)v_{11}^{-1} + (-0.2+0.7i)v_{11}^{+1}$	$v_{11}^{\pm1}$	v_{11}
3	723.179	$(0.5-0.5i)2v_{11}^{-2} + (-0.4+0.6i)2v_{11}^{+2}$	$2v_{11}^{\pm2}$	$2v_{11}$
4	723.179	$(0.6+0.4i)2v_{11}^{+2} + (0.5+0.5i)2v_{11}^{-2}$	$2v_{11}^{\pm2}$	$2v_{11}$
5	723.825	$(-0.9-0.5i)2v_{11}^{0}$	$2v_{11}^{0}$	$2v_{11}$
⋮				
15	1388.967	$(-0.7-0.2i)v_3 + (0.5i)v_9^{-1}v_{11}^{+1} + (0.5i)v_9^{+1}v_{11}^{-1}$	v_3	$v_3+v_9+v_{11}$
⋮				
19	1397.680	$(-0.7-0.2i)v_3 + (-0.5i)v_9^{-1}v_{11}^{+1} + (-0.5i)v_9^{+1}v_{11}^{-1}$	$v_9^{\pm1}+v_{11}^{\mp1}$	$v_3+v_9+v_{11}$
⋮				
1000	4175.787	$(-0.7i)3v_9^{-3}3v_{11}^{-3} + (0.7+0.2i)3v_9^{+3}3v_{11}^{+3}$	N/A	N/A

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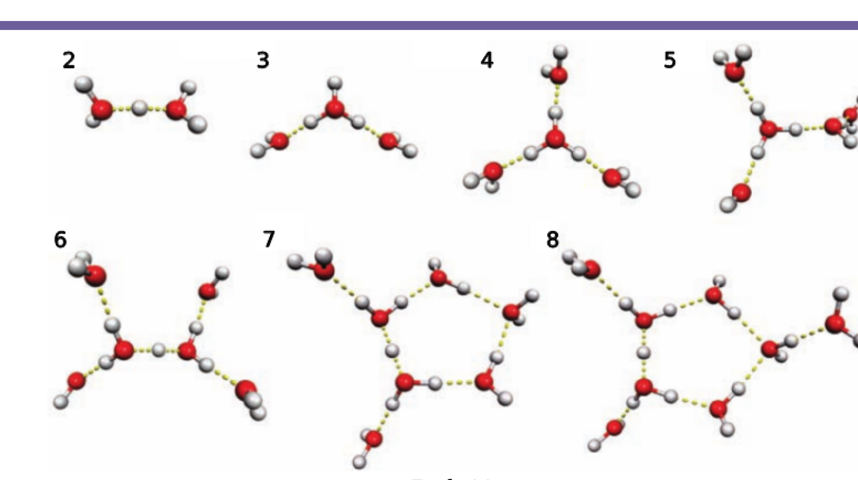
Outlook

- Confirm more results and analyze 5000 states
- Understand main couplings, resonances, anharmonicities, and select zero-order states to create best basis
- Apply to fluxional systems, such as protonated water clusters



Ref. 11

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Credits

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