

Adiabatic-hindered-rotor treatment of parahydrogen-water complex

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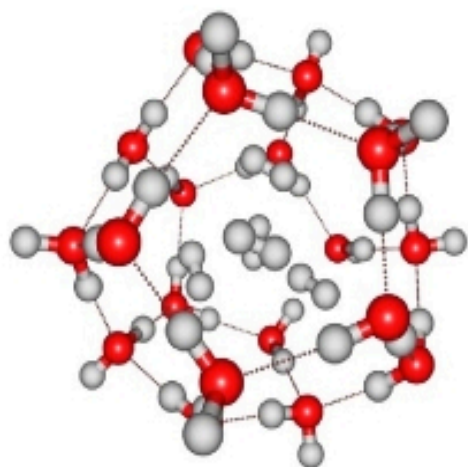
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Molecular Spectroscopy

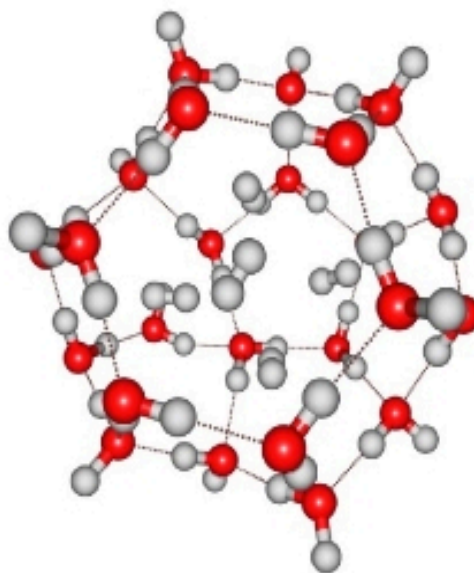
Columbus, Ohio, USA

H_2O-H_2 , a scientifically interesting interaction

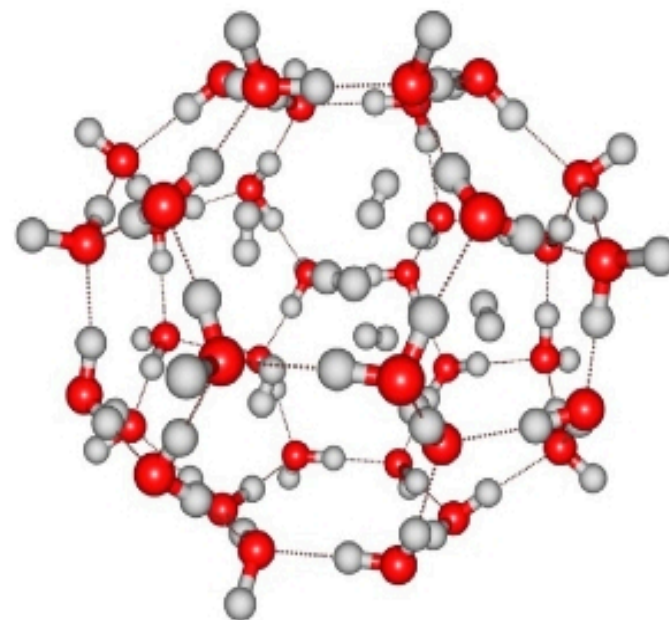
- Astrophysics:
- Hydrogen storage:
 - H_2 in H_2O cages (clathrates).
 - Clean energy in clean carrier.



5 H_2 in 5^{12}



5 H_2 in $5^{12}6^2$



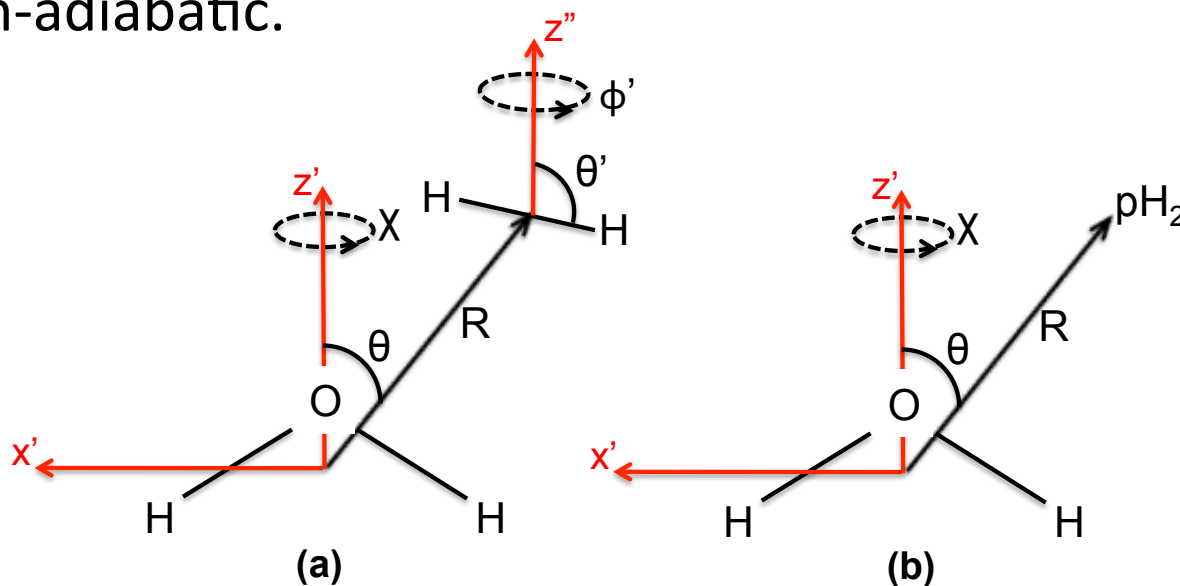
6 H_2 in $5^{12}6^8$

Chattaraj et al. J. Phys. Chem. A **115**, 187 (2011)

Valiron potential energy surface

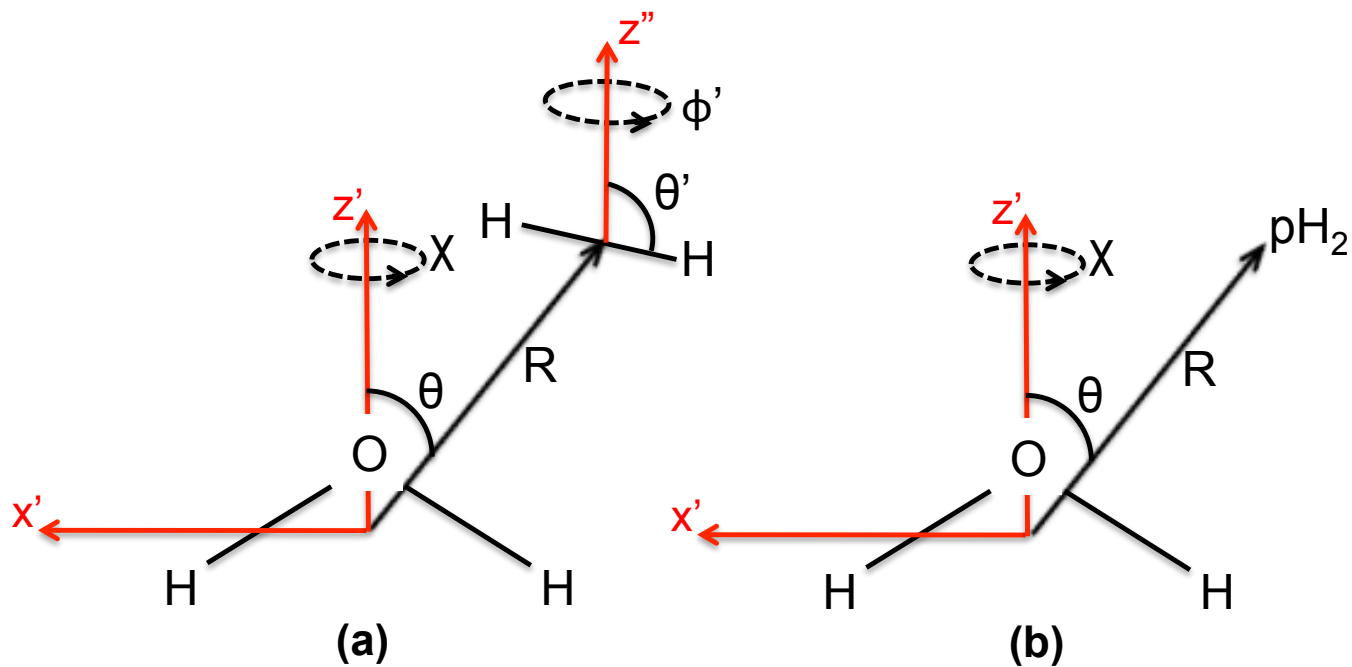
Valiron et al. J. Chem. Phys. **129**, 134306 (2008)

- 5-D rigid-rotor potential.
- CCSD(T) reference + CCSD(T)-R12 calibration + average over vibrational ground state: 9-D to 5-D.
- Highly accurate; not efficient enough for large scale studies.
- Our objective: 5-D to 3-D for para- H_2 - H_2O interaction.
- pH_2 : superfluidity.
- Ortho- H_2 : non-adiabatic.



Adiabatic-hindered-rotor approximation

- Approximation foundation: fast H_2 rotation vs slow motions of the rest leads to adiabatic separation; adiabatically hindered H_2 rotation



How adiabatic is it?

- Bound states for a van der Waals complex: slow radial motion.
- Large R_e and $\mu \approx m_{\text{H}_2}$: $B_{\text{H}_2} \gg B_{\text{H}_2\text{O}-\text{H}_2}$; slow end-over-end rotation.
- Rotational constants of H_2O and H_2 are at the same order (30 vs 60 cm^{-1}): non-adiabatic?
- pH_2 : only even / numbers are allowed; 350 vs 25 cm^{-1} ; adiabaticity restored.
- Ultimate test: compared to non-adiabatic spectroscopic calculations.
 - Wang and Carrington J. Chem. Phys. **134**, 044313 (2011);
 - van der Avoird and Nesbitt J. Chem. Phys. **134**, 044314 (2011).

Formalism

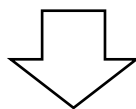
- Total Hamiltonian operator in DF:

$$\hat{H}_{\text{total}} = \hat{T}_{\text{H}_2\text{O}} + \hat{T}_{\text{H}_2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu R^2} \left[\hat{\vec{J}} - \left(\hat{\vec{j}}_{\text{H}_2\text{O}} + \hat{\vec{j}}_{\text{H}_2} \right) \right]^2 + V(R, \theta, \chi, \theta', \phi')$$

- Adiabatic hindered rotor (AHR) approximation:

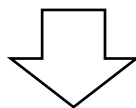
AHR Equation:

$$\left(\hat{T}_{\text{H}_2} + \frac{\hbar^2}{2\mu R^2} \hat{j}_{\text{H}_2}^2 + V(R, \theta, \chi, \theta', \phi') \right) \psi(\theta', \phi'; R, \theta, \chi) = V^{\text{AHR}}(R, \theta, \chi) \psi(\theta', \phi'; R, \theta, \chi)$$



H₂O-atom Hamiltonian

$$\hat{H}^{BO} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \hat{T}_{\text{H}_2\text{O}} + \frac{\left(\hat{\vec{J}} - \hat{\vec{j}}_{\text{H}_2\text{O}} \right)^2}{2\mu R^2} + V^{\text{AHR}}(R, \theta, \chi)$$

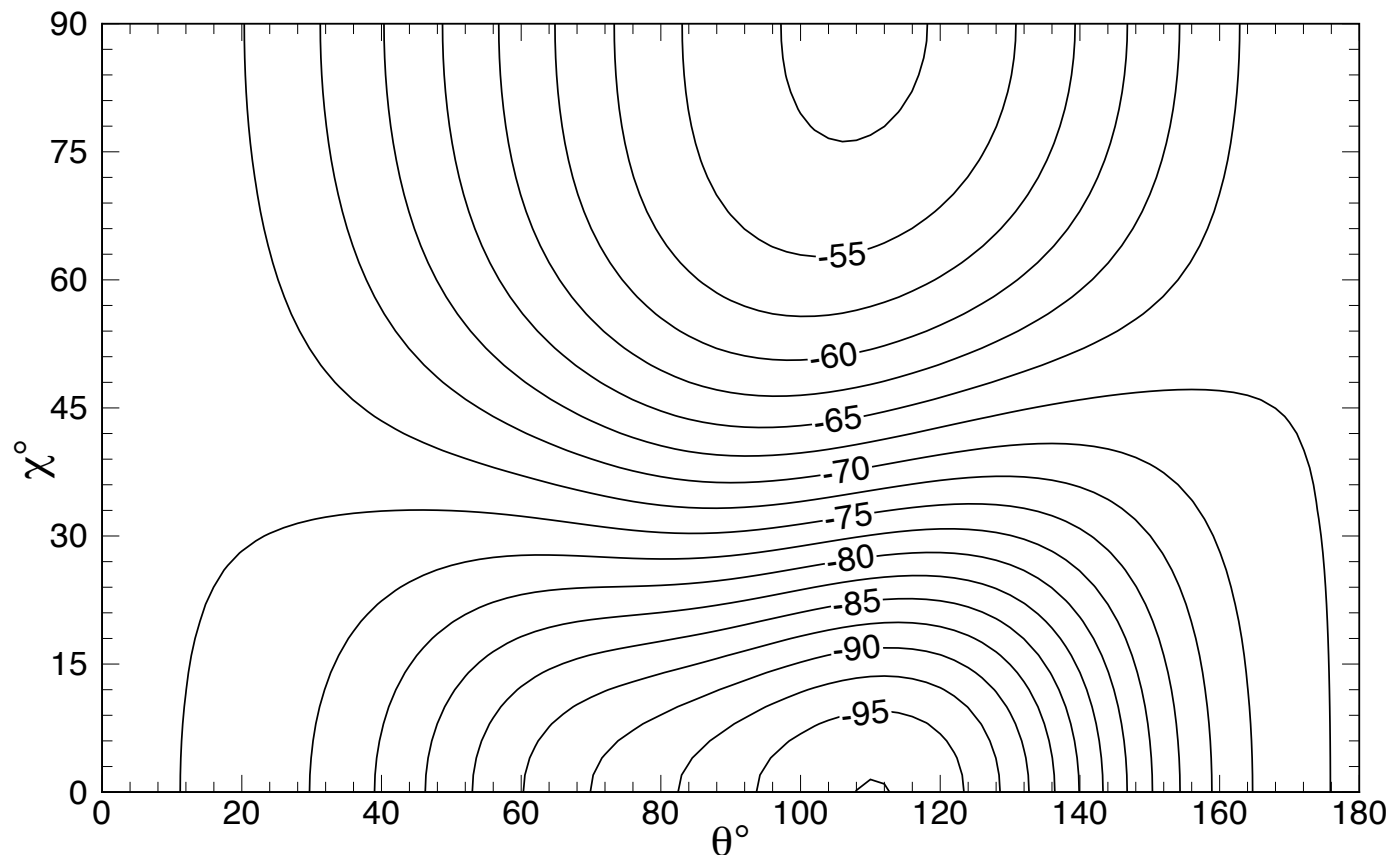


Adiabatic Rovibrational Equation

$$\hat{H}^{BO} |\Phi\rangle = E |\Phi\rangle$$

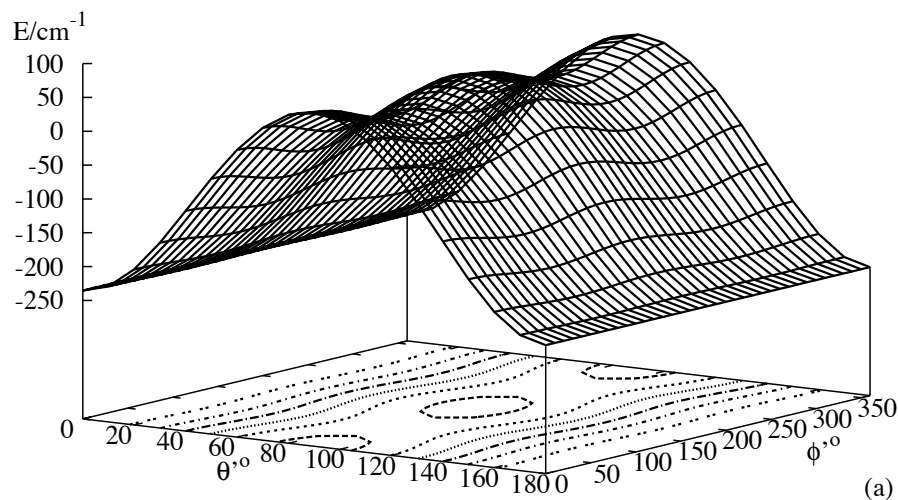
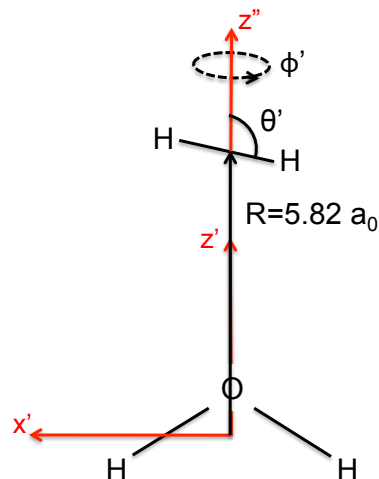
The AHR 3-D potential

- There is only one minimum on the AHR potential energy surface (PES) versus two on the Valiron 5-D one.
- Closely related to the ground state AHR wave function.

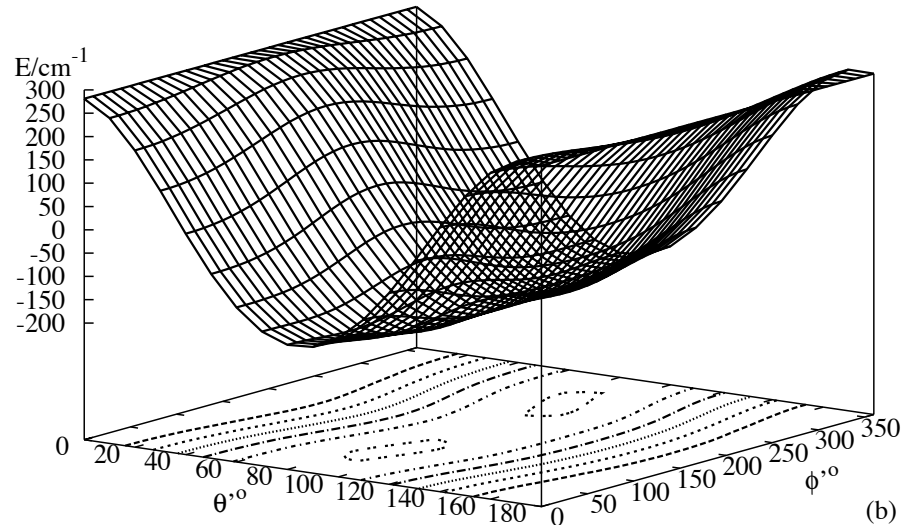
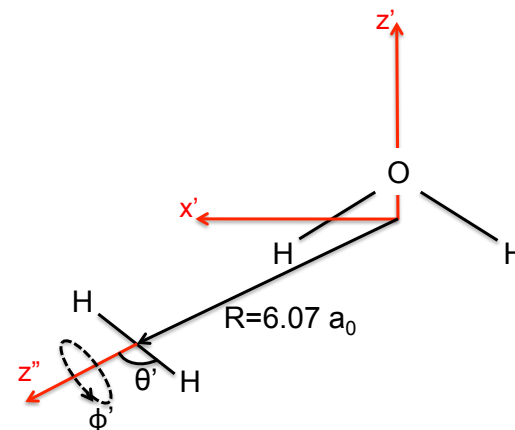


Minimum AHR potential energy contour at orientation space.

PES for H₂ rotation at the two configurations



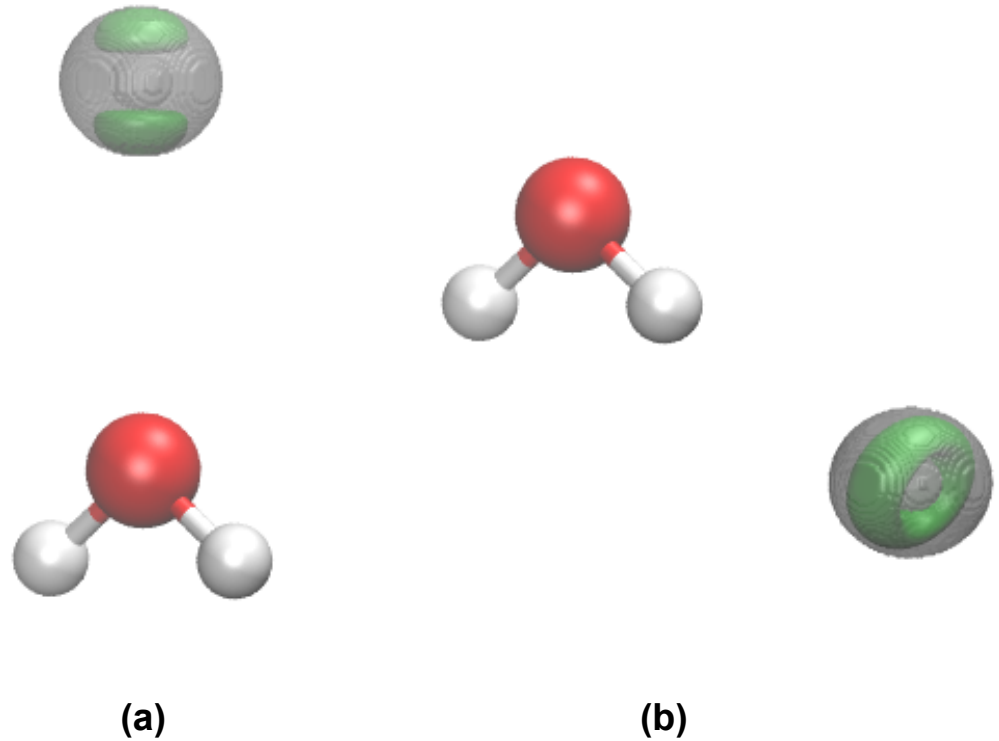
5-D global minimum (proton donor),
about -240 cm^{-1}



5-D local minimum (proton acceptor),
About -200 cm^{-1}

Polarization of pH_2 rotation

- H_2O hinders pH_2 rotation:
 - mixing rotational excited states to the ground state.
 - s-d hybridization.
 - sphere-quadrupole polarization.
- Strong polarization:
 - at configuration (a)
 $0.9357s + 0.0639d + 0.0003g$
 - at configuration (b)
 $0.9239s + 0.0757d + 0.0004g$



pH₂O Adiabatic rovibrational levels (cm⁻¹)

Parity (j _{KaKc})	J=0	J=1	J=2	J=3	J=4	J=5
e (0 ₀₀)	-34.75 -33.57	-33.35 -32.18	-30.57 -29.43	-26.44 -25.34	-21.00 -19.96	-14.32 -13.35
e (0 ₀₀)*	-2.30 -2.06	-1.62 -1.40	-0.33 -0.16			

- **Reference data:**
 - van der Avoird and Nesbitt J. Chem. Phys. **134**, 044314 (2011)
- Adiabatic levels are qualitatively consistent with the non-adiabatic reference.
- Adiabatic levels are lower.
- Maximum deviation: $\sim 1.2 \text{ cm}^{-1}$ (3.5% of D_0).

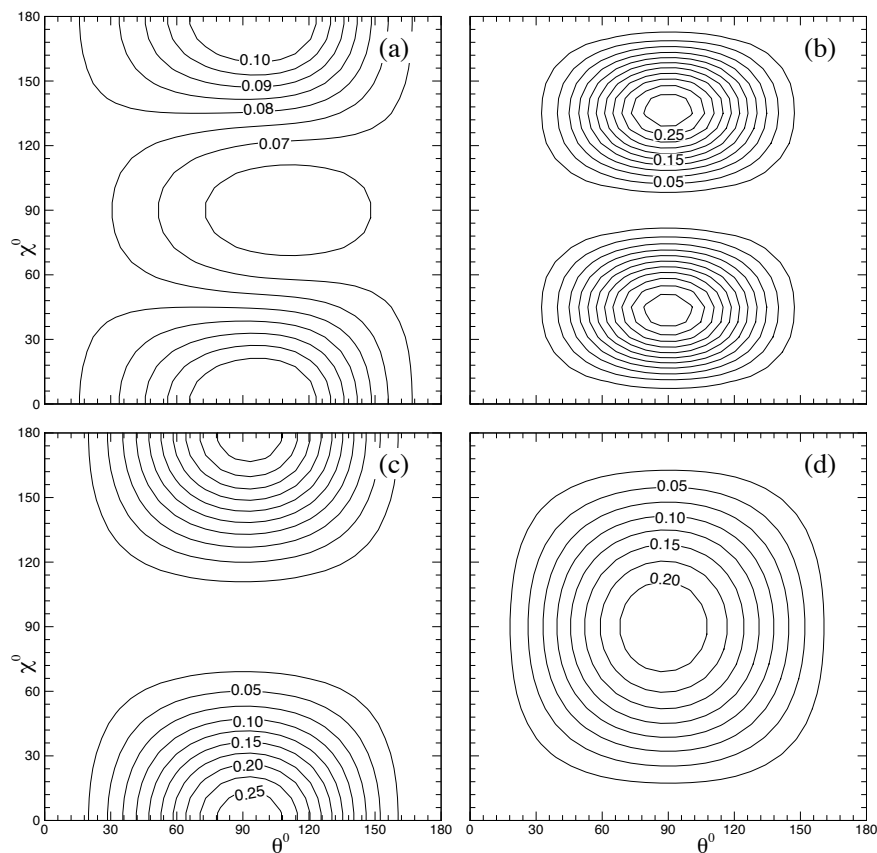
oH₂O Adiabatic rovibrational levels (cm⁻¹)

Parity (j _{KaKc})	J=0	J=1	J=2	J=3	J=4	J=5
e (1 ₀₁)	-14.28	-13.45 (92%)	-11.59 (82%)	-8.52 (76%)	-4.17 (70%)	1.43 (66%)
	-12.83	-12.05 (91%)	-10.26 (81%)	-7.23 (74%)	-2.95 (69%)	2.59 (65%)
e (1 ₀₁) [*]	21.86	21.66 (63%)	22.33 (56%)	23.56 (52%)		
	21.95	21.89 (60%)	22.53 (55%)	23.72 (51%)		
f (1 ₁₀)	14.79	16.49 (97%)	19.80 (91%)			
	15.66	17.34 (97%)	20.62 (91%)			

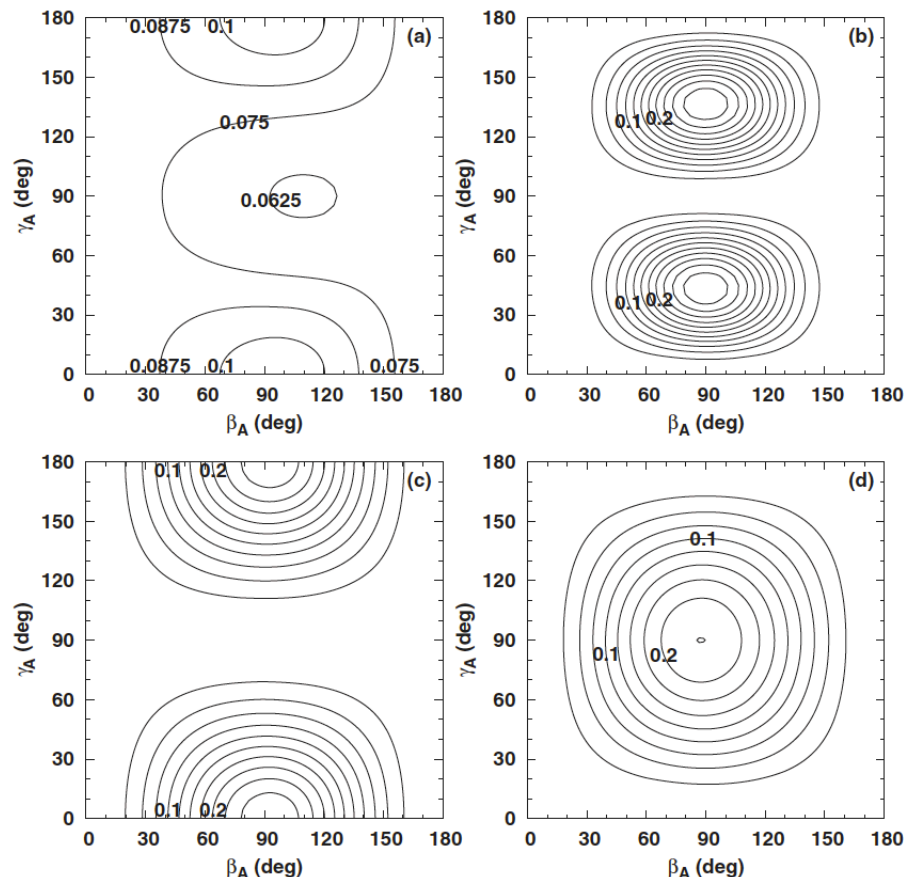
- Only $K=0$ states are shown.
- Maximum deviation: $\sim 1.4 \text{ cm}^{-1}$ (3.9% of D_0).

Adiabatic rovibrational wave functions

- Correct j_{KaKc} assignments.
- K -assignments: maximum deviation $\sim 3\%$.
- Angular density distributions: indiscernible from the reference.



VS



Angular density distributions of the ground states for even and odd parities and p and oH₂O complexes. Left: our results; right: reference from Wang and Carrington J. Chem. Phys. **134**, 044313 (2011).

Transition line strengths

$$S_{i'i} = 3 \sum_{M',M} \left| \langle \Phi'_i | \mu_Z^{SF} | \Phi_i \rangle \right|^2$$

Transition line strengths for pH₂O complex in the unit of $\mu_{\text{H}_2\text{O}}^2$.

	$\Sigma^e (0_{00})$	$\Sigma^e (0_{00})^*$
$\Sigma^e (0_{00})$	0.003 0.006	0.0198 0.0181
$\Sigma^e (0_{00})^*$	0.0531 0.0366	0.0000 0.0000

Transition line strengths for oH₂O complex in the unit of $\mu_{\text{H}_2\text{O}}^2$.

	$\Pi^f (1_{01})$	$\Sigma^e (1_{01})$	$\Pi^e (1_{01})$
$\Sigma^e (1_{01})$	x	0.00008 0.00003	0.00079 0.00153
$\Pi^e (1_{01})$	x	0.00048 0.00021	0.00130 0.00244
$\Pi^f (1_{01})$	0.00230 0.00386	x	x

reference from Wang and Carrington J. Chem. Phys. **134**, 044313 (2011)

- Small transition dipoles:
 - Very sensitive to minute wave function errors, “Coulson’s captain”;
 - Errors magnified by taking square.
- The same order of magnitude as the reference: qualitatively satisfactory

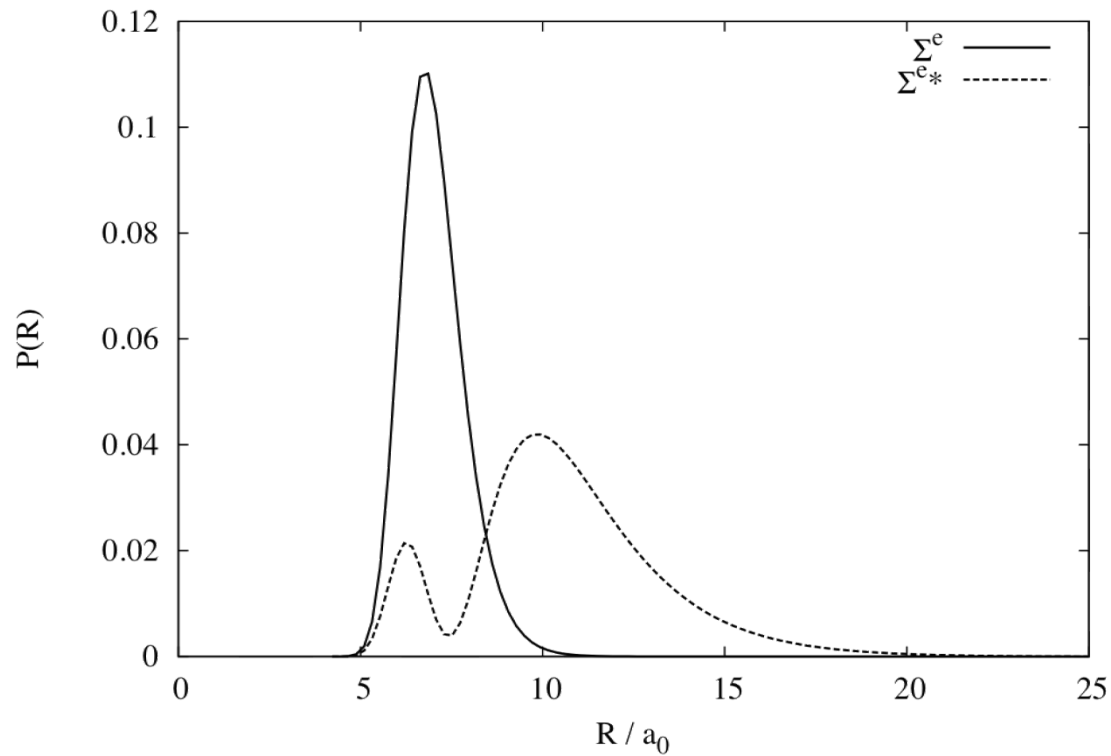
Conclusions

- AHR approximation reduces the $\text{H}_2\text{O}-\text{H}_2$ PES dimension from 5-D to 3-D.
- Only one minimum on the 3-D AHR PES.
- Accurate rovibrational levels:
 - Most errors $< 1 \text{ cm}^{-1}$;
 - Can not reach spectroscopic accuracy;
 - Good for large scale simulations.
- Accurate wave functions
 - Correct j_{KaKc} - and K -assignments;
 - Correct angular distribution;
 - Qualitatively correct transition line strengths.
- Treating pH_2 as a diabatic sphere leads to large error ($\sim 6\text{cm}^{-1}$).
- AHR PES will be used in path integral simulations for water-doped pH_2 clusters.
 - Rotational propagator of pH_2 is not needed;
 - Pair-product action approximation for point-like pH_2 .

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 - NSERC PDF for TZ

Radial stretching excited state



- Only one quantum can be excited.
- Weakly bound.
- Missing node?
 - Node blurred by small amount of angular excitation.