

Overtone vibrational spectroscopy and dynamics
in H₂-H₂O complexes:
a combined theoretical and experimental study

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H₂-H₂O

- H₂ most abundant molecule in interstellar medium (ISM), H₂O third (after CO)
- H₂-H₂O interactions important
 - collisions ⇒ state populations of H₂O (maser)
 - complex formation?
 - H₂ formation on icy grains
- Infrared spectrum H₂-H₂O |02⁻) ← |00⁺)
dimer lines observed, but not understood

H₂-H₂O

9D potential surface from Valiron *et al.* (2008)

⇒ 5D intermolecular potentials for various vibrational states of H₂/D₂ and H₂O/D₂O by averaging over monomer wave functions

VRT levels calculated for H₂-H₂O and D₂-H₂O ground states, and for H₂-H₂O |02⁻)

Basis with $j_A \leq 10$ and $j_B \leq 8$

Symmetry group G_8 generated by P_{12} , P_{34} , E^*

Also H₂O |02⁻) ← |00⁺) transition line strengths calculated

Calculation of VRT states

Hamiltonian

$$H = \left[A j_{A_a}^2 + B j_{A_b}^2 + C j_{A_c}^2 \right] + B j_B^2 - \frac{\hbar^2}{2\mu_{AB}R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu_{AB}R^2} \left[J^2 + j_{AB}^2 - 2\mathbf{j}_{AB} \cdot \mathbf{J} \right] + V(R, \omega_A, \omega_B)$$

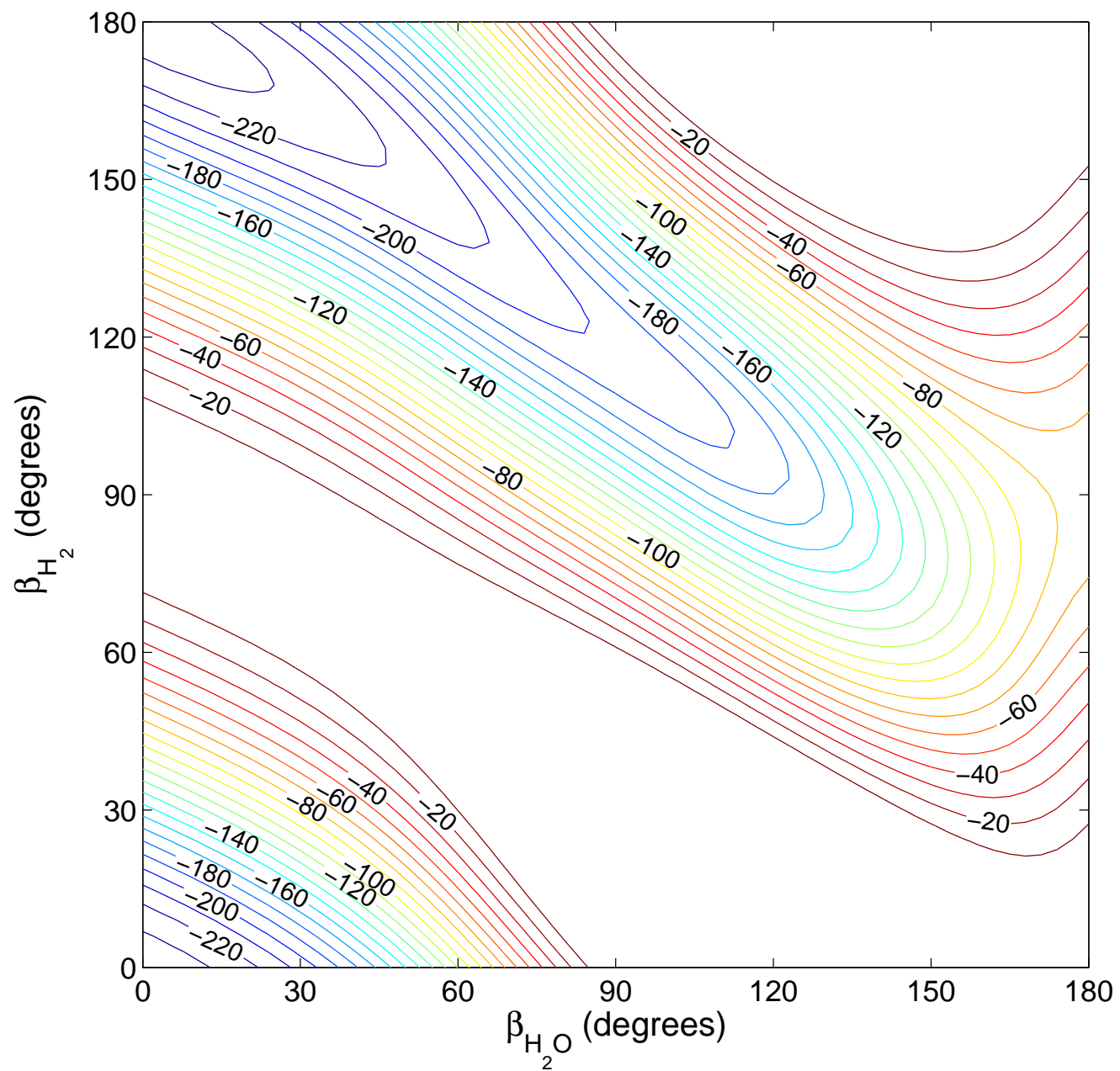
Analytic basis

$$\chi_n(R) \sum_{m_A m_B} D_{m_A k_A}^{(j_A)}(\omega_A)^* Y_{j_B, m_B}(\omega_B)^* \langle j_A m_A; j_B m_B | j_{AB} K \rangle D_{MK}^{(J)}(\alpha, \beta, 0)^*$$

contracted DVR for $\chi_n(R)$

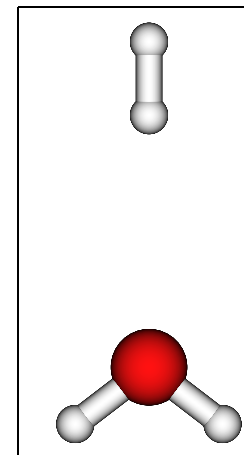
Basis adapted to irreps of PI group G_8

Potential surface

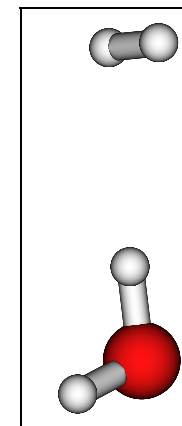


Minima

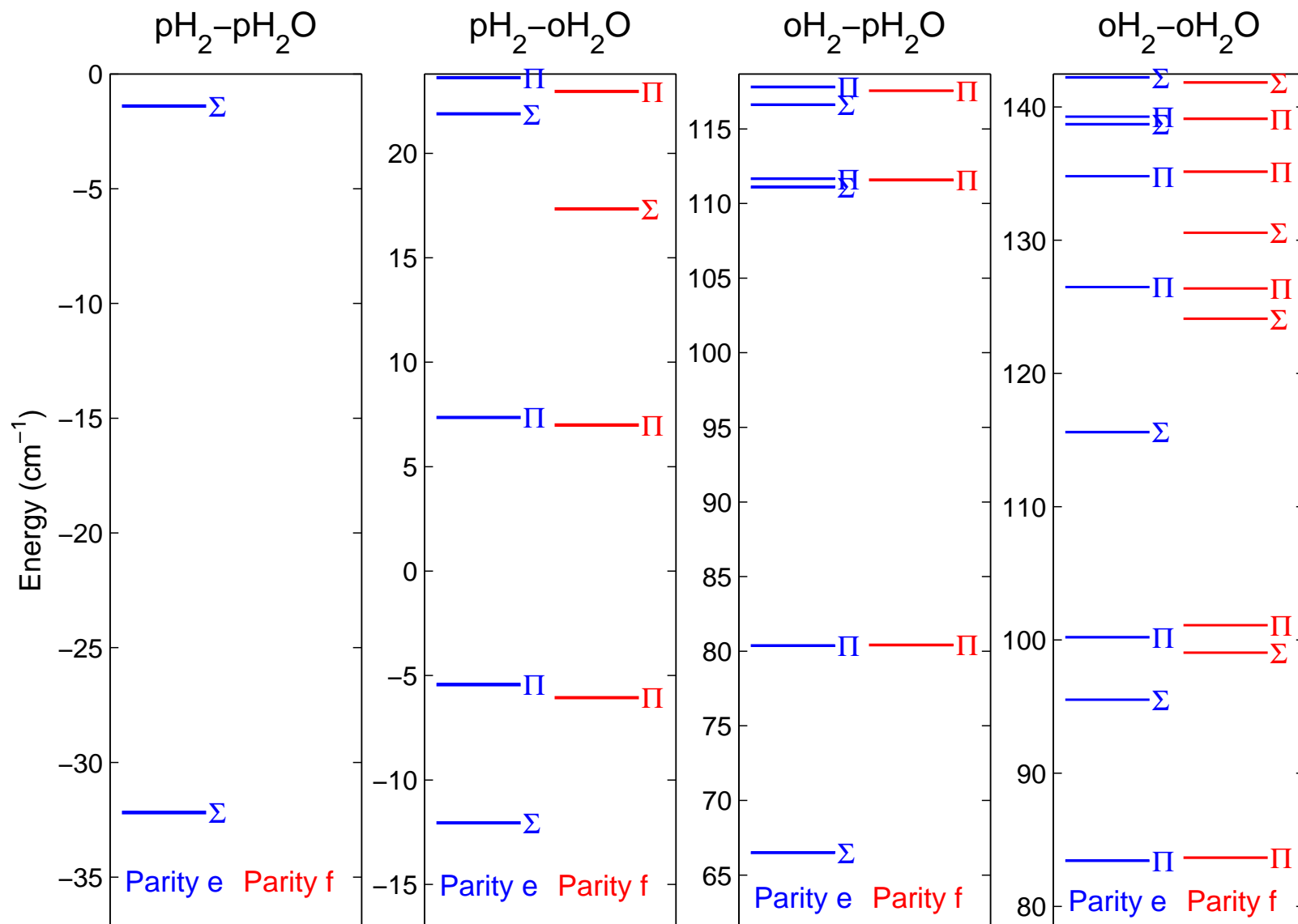
Global



Local

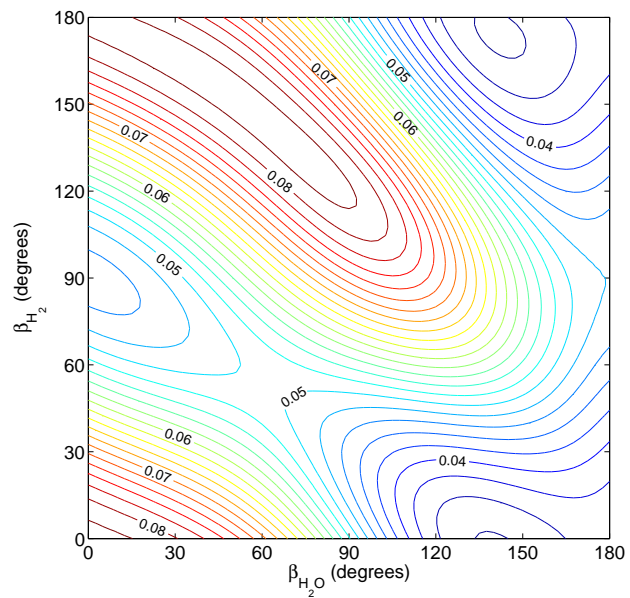


Calculated energy levels ($J = 1$)

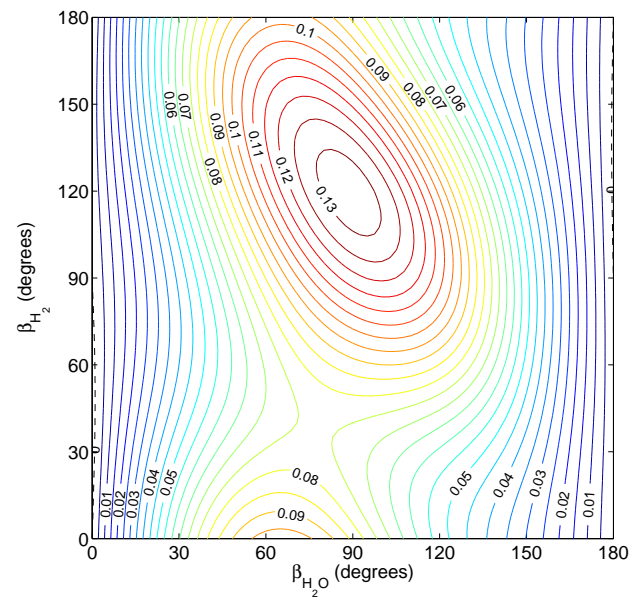


Wave functions ($J = 0$)

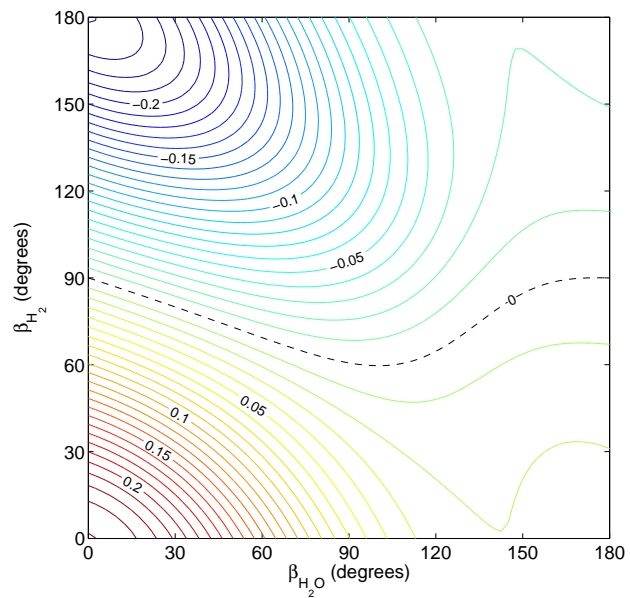
pH₂-pH₂O



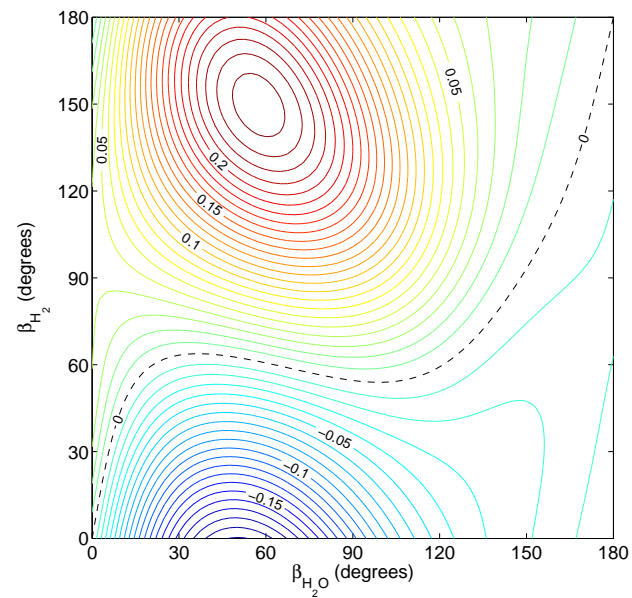
pH₂-oH₂O



oH₂-pH₂O



oH₂-oH₂O



Binding energies

Potential well depth $D_e = 235 \text{ cm}^{-1}$

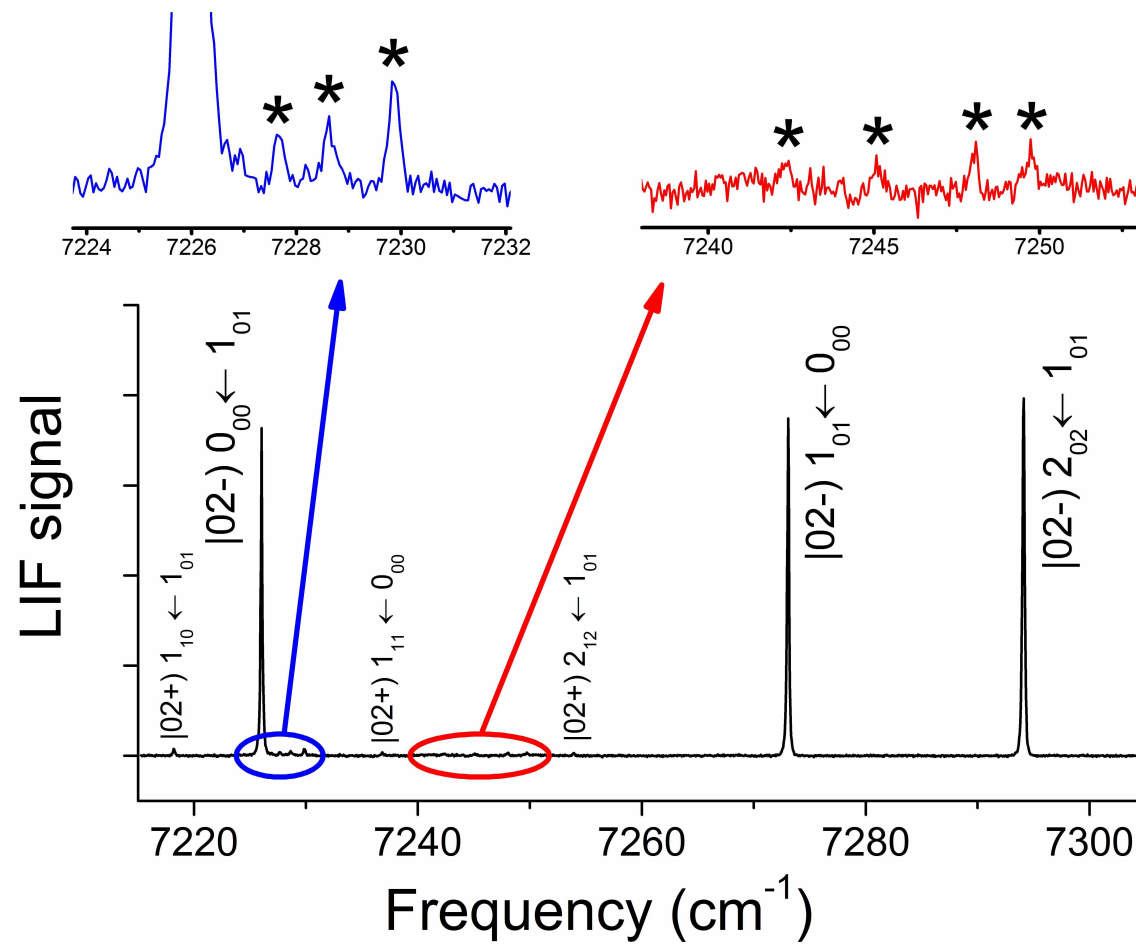
Dissociation energies D_0

para H ₂ - para H ₂ O	33.6 cm ⁻¹
para H ₂ - ortho H ₂ O	36.6 cm ⁻¹
ortho H ₂ - para H ₂ O	53.6 cm ⁻¹
ortho H ₂ - ortho H ₂ O	59.0 cm ⁻¹

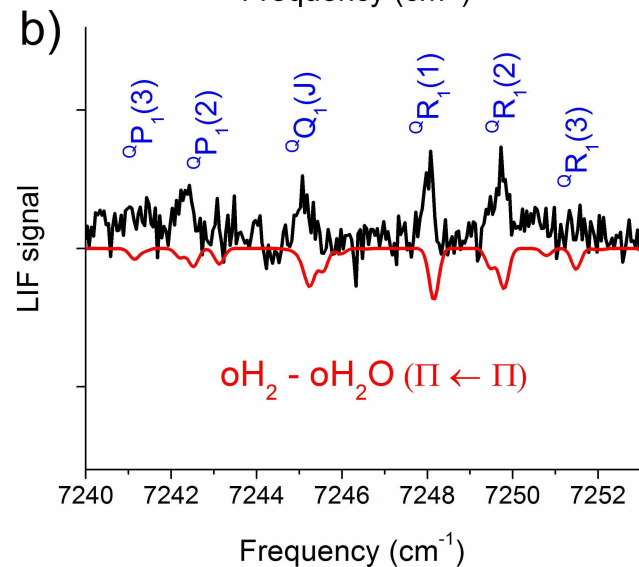
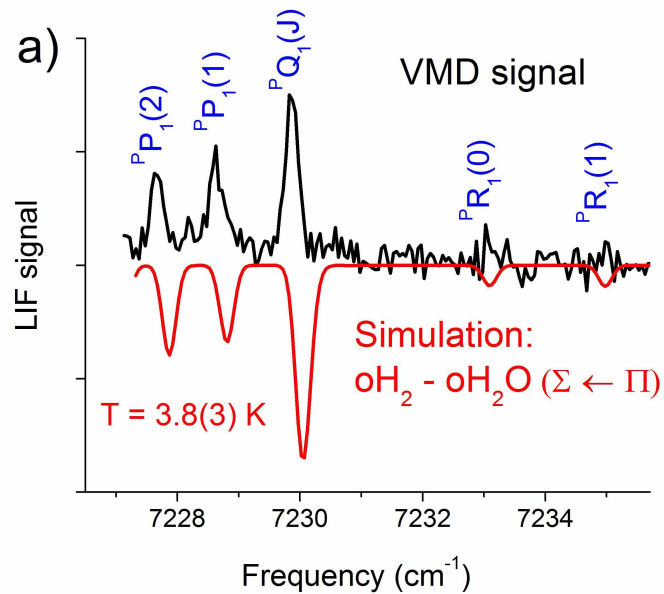
Selection rules

- H₂O |02⁻) odd under P_{12} , |00⁺) ground state even
- Overall dipole moment function even under permutations P_{12} , P_{34} , odd under inversion $E^* \Rightarrow$ symmetry A_1^-
- |02⁻) \leftarrow |00⁺) transition dipole function depends on intermolecular coordinates and has symmetry A_2^-
- Pure |02⁻) \leftarrow |00⁺) vibrational transition is forbidden
- Must be accompanied by internal rotor transition in the complex
- Sensitive to anisotropy of the intermolecular potential

H₂-H₂O |02⁻) ← |00⁺) excitation spectrum



Spectrum simulated from calculated levels and line strengths



Also predissociation dynamics
(lifetimes)

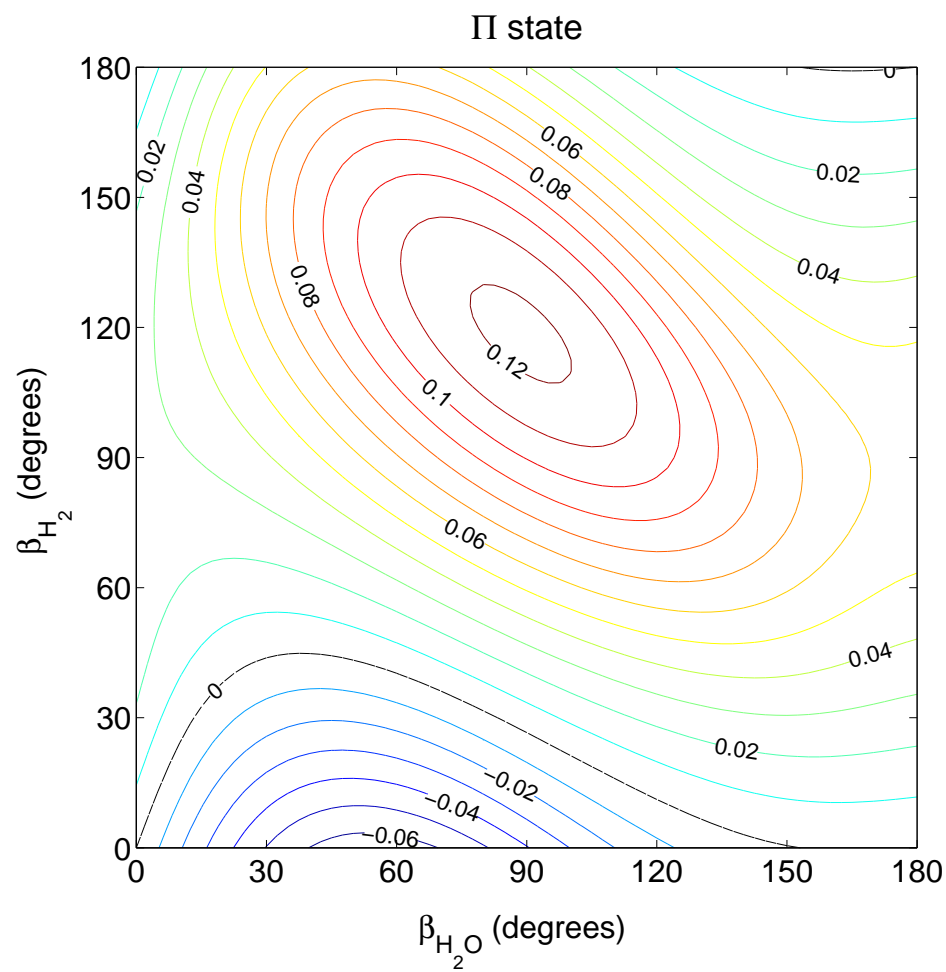
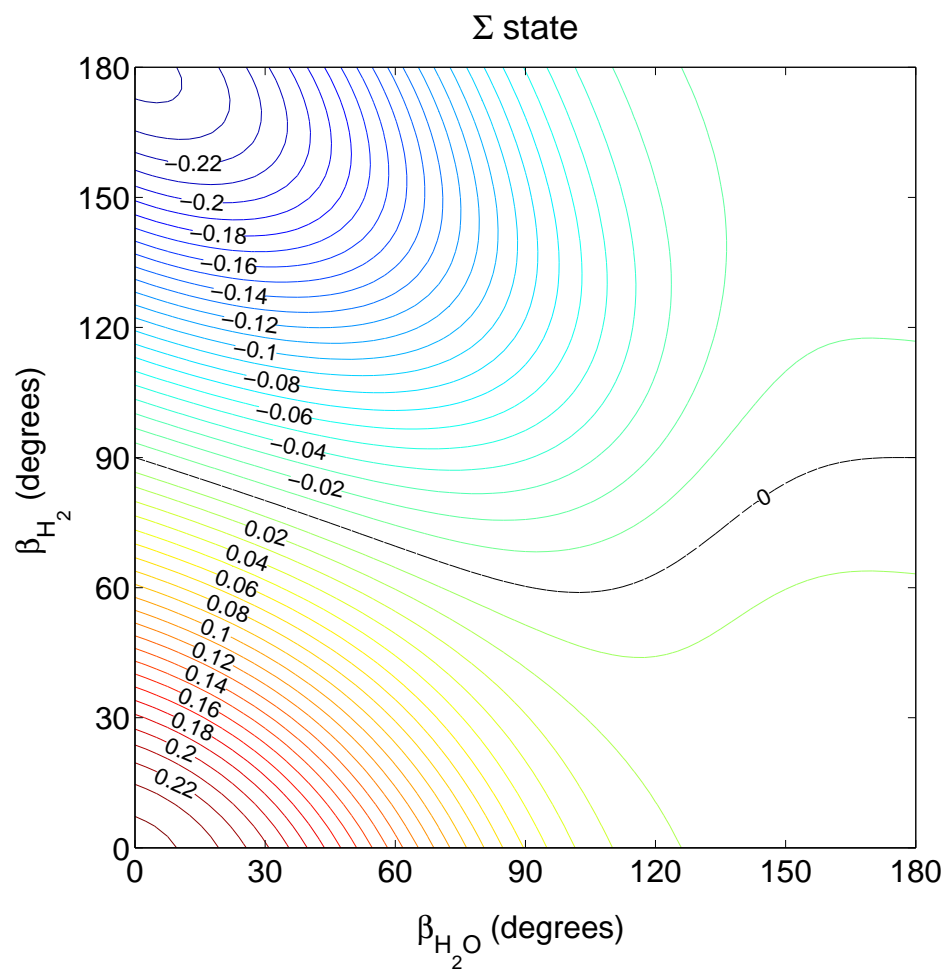
can be understood from
the relative stability of

different ortho/para H_2 and
ortho/para H_2O species

and the nature of
the excited state

wave functions

Wave functions of $\text{oH}_2\text{-oH}_2\text{O } |02^- \rangle$



For details, see:

J. Chem. Phys. (2012), the paper was accepted yesterday.

Acknowledgement

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