

A ROVIBRATIONAL ANALYSIS OF THE WATER BENDING VIBRATION IN OC-H₂O AND A MORPHED POTENTIAL OF THE COMPLEX

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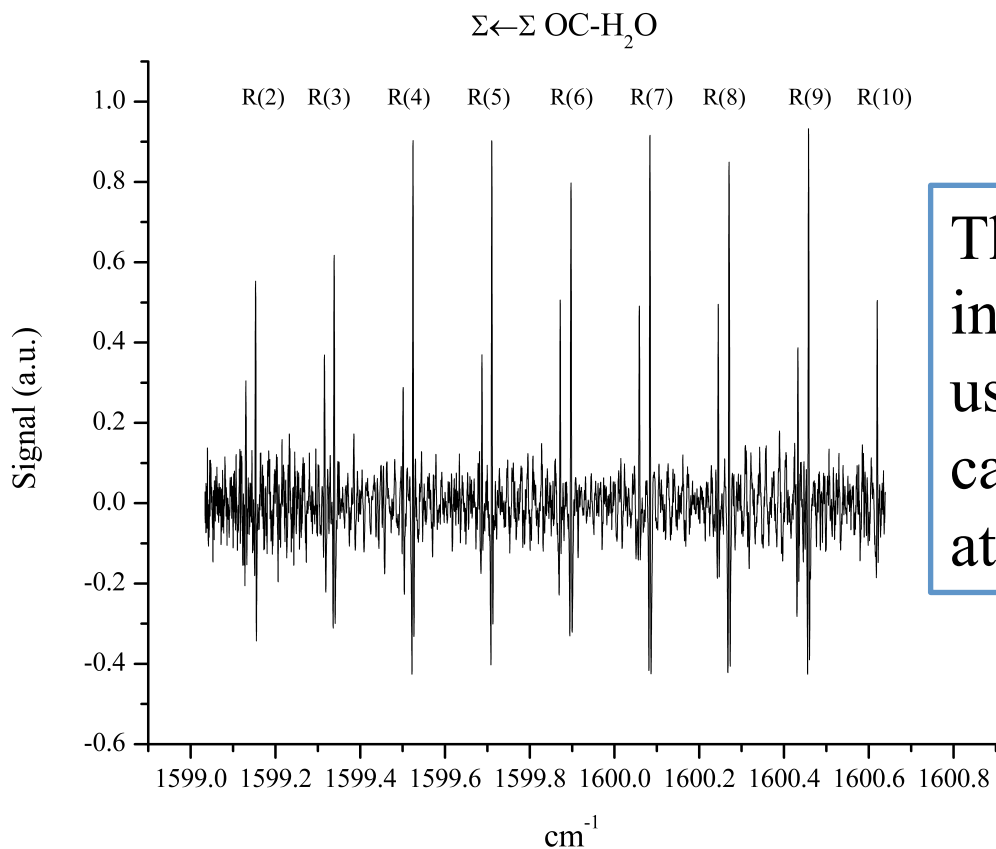
Motivation

- Water and carbon monoxide are common and important molecules found in the earth's atmosphere, in the products of combustion reactions and in the interstellar medium.
- Detailed investigation of a prototypical heteromolecular pairwise water interaction.
- A pathway to understanding the properties of water complexes in more complex environments.

Motivation

- The current investigation represents the first application of non-linear Compound Model Morphing methods.
- Compound Model Morphing which integrates spectroscopic and computational investigations have provided powerful methods for direct characterizations of non-covalent interactions.

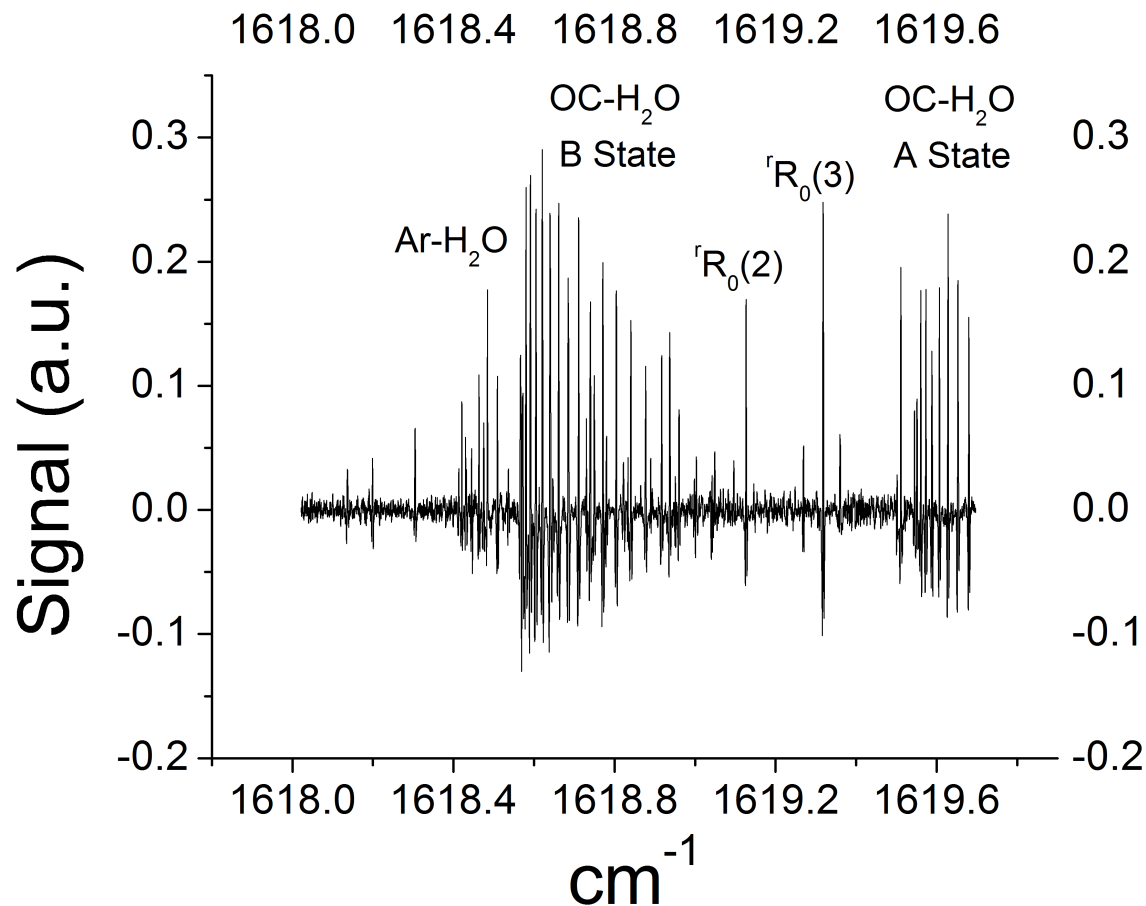
QCL cw supersonic jet spectrum of Σ - Σ transition in OC-H₂O



The H₂O bending spectrum in the complex has been recorded using a cw supersonic jet quantum cascade laser spectrometer at 6.2 μm .

The effective resolution of the spectrum is 80 MHz (0.003 cm⁻¹).

QCL cw supersonic jet spectrum of Σ - Σ transition in OC-H₂O

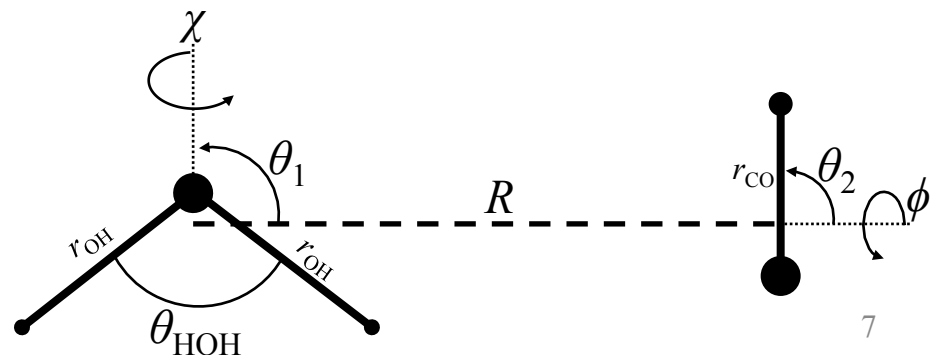


Rovibrational Constants for the Water Bending Vibration in OC-H₂O

	Excited	Ground
H2	-0.19694(33)	-0.2782393(26)
TH2	-	0.0275077(14)
H2K	-0.01344(40)	-
H2J×10 ³	-0.0571(49)	-0.0755(53)
H2KJ×10 ³	-0.0363(34)	-0.03574(14)
H2JJ×10 ⁶	-0.03(14)	-0.0268(43)
F2×10 ³	0.0478(19)	0.0564(26)
F2J×10 ⁶	-	0.0271(32)
v	1598.6810(3)	-
A	20.46392(50)	19.277226(13)
B	0.092383(19)	0.09209971(15)
C	0.091557(19)	0.09135137(40)
c _{kj} ×10 ³	1.013(11)	0.75664(21)
c _{jj} ×10 ⁶	-0.712(15)	-0.68032(47)
d1×10 ⁶	0.071(99)	0.0281(11)
c _{kij} ×10 ⁶	-0.193(52)	-0.13169(43)
h1×10 ⁹	-0.19(27)	-0.0177(55)

7-D Ab Initio Calculations

- CCSD(T)/aug-cc-pVTZ MP2/aug-cc-pVTZ
- MP2/aug-cc-pVQZ (in progress)
- 10 R points from 3.50 to 7.00 Å
- 5 r_{CO} points from 1.00 to 1.30 Å
- 7 θ_{HOH} points from 74.0 to 134.0 deg
- $r_{\text{OH}} = 0.9753$ Å
- 11,200 angular points ($\theta_1, \theta_2, \phi, \chi$)
- 3,920,000 total points



Interpolation *Ab Initio* PES

- R , r_{CO} , and θ_{HOH} coordinates
 - Reproducing Kernel Hilbert Space (RKHS)
 - T.-S. Ho, H. Rabitz, J. Chem. Phys. 104 (1996) 2584.
- Angular coordinates $(\theta_1, \theta_2, \phi, \chi)$
 - IMLS

$$V(R_i, r_{\text{CO}j}, \theta_{\text{HOH}k}, \theta_1, \theta_2, \phi, \chi) = \sum_{L_1 K_1 L_2 L} v_{L_1 K_1 L_2 L, i, j, k}(\theta_1, \theta_2, \phi, \chi) A_{L_1 K_1 L_2 L}(\theta_1, \theta_2, \phi, \chi)$$

Morphing the PES

- Hamiltonian

$$H = T_1 + T_2 + \frac{1}{2\mu_{1,2}R^2} \left[-\hbar^2 \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + J^2 + j_{1,2}^2 - 2\mathbf{j}_{1,2} \cdot \mathbf{J} \right] + V^{v_1, v_2} (R, \theta_1, \theta_2, \phi, \chi)$$

- CMM-RC

$$\begin{aligned} V_{\text{CMM-RC}}(R) = & C_1 [V_{\text{MP2}}(R')]_{\text{QZ}}^{\text{CP}} + C_2 \left\{ [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{CP}} - [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{NO CP}} \right\} \\ & + C_3 \left\{ [V_{\text{CCSD(T)}}(R')]_{\text{TZ}}^{\text{CP}} - [V_{\text{MP2}}(R')]_{\text{TZ}}^{\text{CP}} \right\} \\ R' = & C_4 (R - R_f) + (1.0 + C_5) R_f \end{aligned}$$

Morphed 5-D PES for H₂O-CO and D₂O-CO

$$V_{\text{S-RC}}(R) = C_1 \left[V_{\text{CCSD(T)}} \left(C_2 (R - R_f) + (1.0 + C_3) R_f \right) \right]_{\text{TZ}}^{\text{CP}}$$

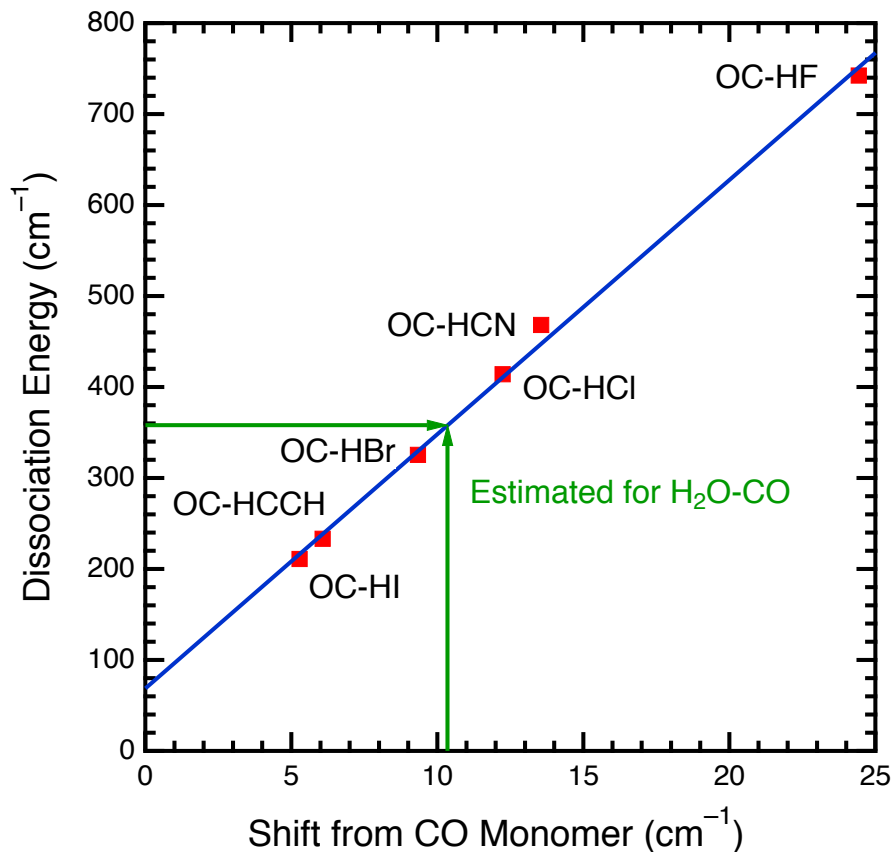
Observable	CCSD(T)/ aug-cc-pVTZ	Morphed	Exp
<i>B</i> (GS, A) 10 ⁻² cm ⁻¹	9.058	9.172	9.17011
<i>B</i> (GS, B) 10 ⁻² cm ⁻¹	9.065	9.177	9.17470
<i>D_J</i> (GS, A) 10 ⁻⁸ cm ⁻¹	73.5	68.0	69.7
<i>D_J</i> (GS, B) 10 ⁻⁸ cm ⁻¹	73.2	67.9	68.4
<i>D₀</i> cm ⁻¹	295	349	--
<i>B</i> (GS, A) 10 ⁻² cm ⁻¹	8.630	8.735	8.73678
<i>B</i> (GS, B) 10 ⁻² cm ⁻¹	8.630	8.734	8.73583
<i>D_J</i> (GS, A) 10 ⁻⁸ cm ⁻¹	59.5	55.8	55.0
<i>D_J</i> (GS, B) 10 ⁻⁸ cm ⁻¹	59.5	55.8	52.0
<i>D₀</i> cm ⁻¹	342	400	--

The Badger-Bauer Rule Revisited

S. H. Bauer and R. M. Badger
J. Chem. Phys. 5 (1937) 839.

D_0 for H₂O-CO is predicted
to be 355(13) cm⁻¹.

5-D Morphed PES
 $D_0 = 349(10)$ cm⁻¹



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Conclusion and Outlook

- Rovibrational analysis of OC-H₂O has been completed.
- A computer algorithm has been written for a compound model morphed calculations of non-linear systems, specific to prototypical water complexes.

Conclusion and Outlook

- Preliminary morphed potential of OC-H₂O has been completed at 5-D. The predicted D_0 for H₂O-CO agree with previous prediction using the Badger-Bauer rule.
- Refinement of the current treatment to 7-D morphed potential will include the H₂O bending and the CO stretch.

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