INCORPORATION OF A ROVIBRATIONAL ANALYSIS OF OC-H$_2$O INTO 6-D MORPHED POTENTIALS OF THE COMPLEX

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Motivation

- Non-covalent interactions of water with different molecules are poorly understood at the molecular level.

- Water and carbon monoxide are common and important molecules found in:
  - The earth's atmosphere
  - The products of combustion reactions
  - The interstellar medium
  - Comets

Motivation

- Detailed knowledge of OC-H_2O pairwise interaction can be of considerable significance in:
    - Modeling a wide range of phenomena
    - A pathway to understanding the properties of water complexes in more complex environments

- 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-H$_2$O

$\Sigma \leftarrow \Sigma$ OC-H$_2$O
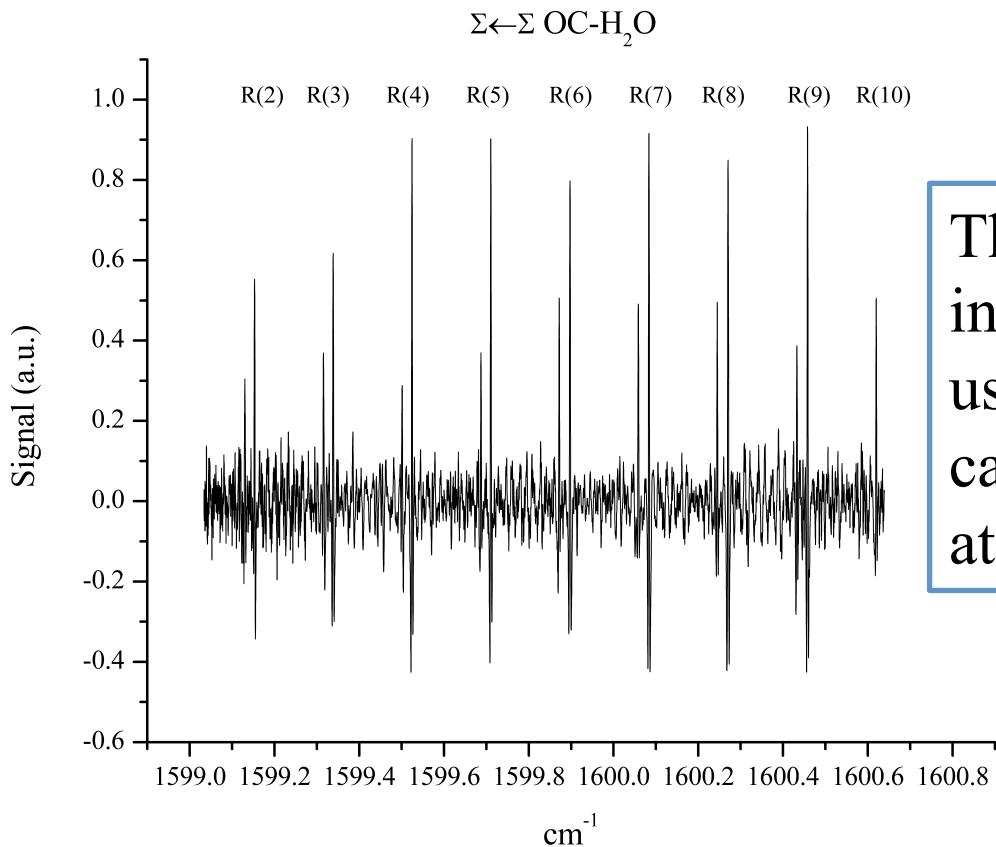
The H$_2$O bending spectrum in the complex has been recorded using a cw supersonic jet quantum cascade laser spectrometer at 6.2 μm.

The effective resolution of the spectrum is 80 MHz (0.003 cm^{-1}).

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$\times 10^3$	-0.0571(49)	-0.0755(53)
H2KJ$\times 10^3$	-0.0363(34)	-0.03574(14)
H2JJ$\times 10^6$	-0.03(14)	-0.0268(43)
F2$\times 10^3$	0.0478(19)	0.0564(26)
F2J$\times 10^6$	-	0.0271(32)
ν	1598.6810(3)	-
A	20.46392(50)	19.277226(13)
B	0.092383(19)	0.09209971(15)
C	0.091557(19)	0.09135137(40)
$c_{kj}\times 10^3$	1.013(11)	0.75664(21)
$c_{jj}\times 10^6$	-0.712(15)	-0.68032(47)
d1$\times 10^6$	0.071(99)	0.0281(11)
$c_{kjj}\times 10^6$	-0.193(52)	-0.13169(43)
h1$\times 10^9$	-0.19(27)	-0.0177(55)

6-D Ab Initio Calculations

- CCSD(T)/aug-cc-pVTZ (BSSE corrected)
- CCSD(T)/aug-cc-pVTZ (Not BSSE corrected)
- MP2/aug-cc-pVTZ (BSSE corrected)
- MP2/aug-cc-pVQZ (BSSE corrected)
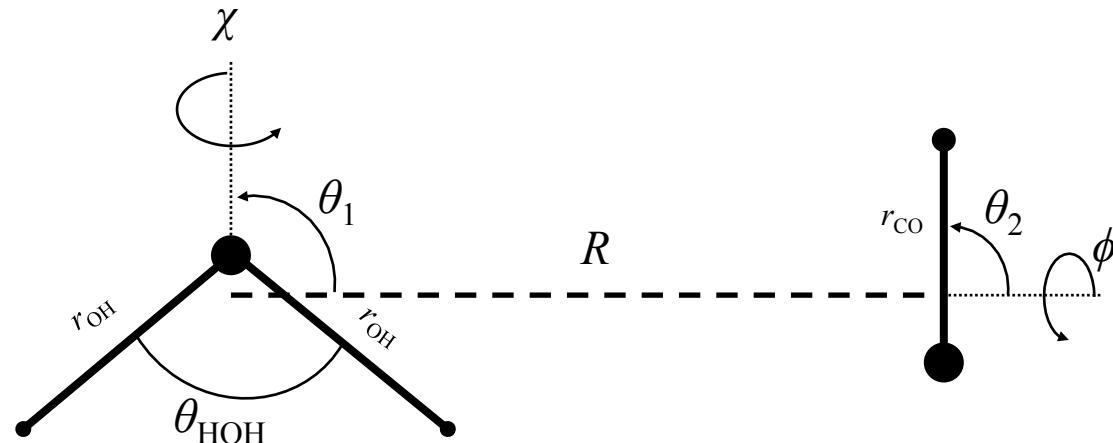
6-D Ab Initio Calculations

- 6-D potentials of 336,000 $(R, \theta_{HOH}, \theta_1, \theta_2, \phi, \chi)$ points
  - $r_{OH} = 0.9753$ Å; $r_{CO} = 1.1283$ Å
  - Frozen CO
  - H_2O bending vibration

- 6-D potentials of 560,000 $(R, r_{CO}, \theta_1, \theta_2, \phi, \chi)$ points
  - $r_{OH} = 0.9753$ Å; $\theta_{HOH} = 104.0$ deg
  - Frozen H_2O
  - CO stretching vibration
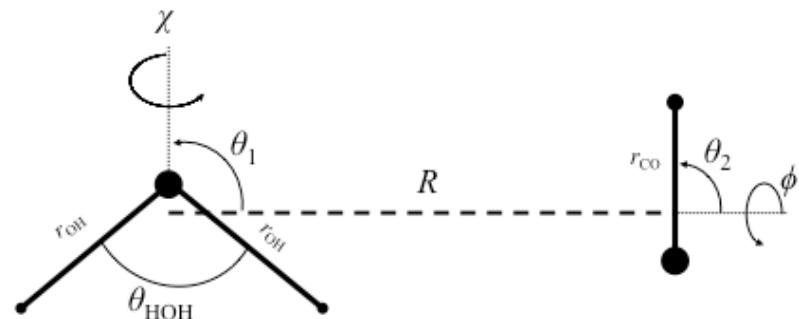
Interpolation of the Ab Initio PES

- R, r_{CO}, and θ_{HOH} coordinates
  - Reproducing Kernel Hilbert Space (RKHS)
  - Ho and Rabitz, J. Chem. Phys. 104 (1996) 2584.

- Angular coordinates $(\theta_1, \theta_2, \phi, \chi)$
  - IMLS

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

Morphing the PES

- Hamiltonian

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

- CMM-RC

$$V_{\text{CMM-RC}}\left(R\right) = C_1\left[V_{\text{MP2}}\left(R'\right)\right]_{\text{QZ}}^{\text{CP}} + C_2\left\{\left[V_{\text{CCSD(T)}}\left(R'\right)\right]_{\text{TZ}}^{\text{CP}} - \left[V_{\text{CCSD(T)}}\left(R'\right)\right]_{\text{TZ}}^{\text{NO CP}}\right\}$$

$$+ C_3\left\{\left[V_{\text{CCSD(T)}}\left(R'\right)\right]_{\text{TZ}}^{\text{CP}} - \left[V_{\text{MP2}}\left(R'\right)\right]_{\text{TZ}}^{\text{CP}}\right\}$$

$$R' = C_4\left(R - R_{\text{f}}\right) + \left(1.0 + C_5\right)R_{\text{f}}$$

Initial Values: $C_1 = 1.0$, $C_2 = 0.0$, $C_3 = 1.0$, $C_4 = 1.0$, and $C_5 = 0.0$

OC-H$_2$O Morphed Potentials

Observable	6-D H$_2$O	6-D CO	Exp
A_0/cm^{-1}	19.83	19.82	19.833730(3)
A_0/cm^{-1}	18.72	18.73	18.720718(4)
B_0/10^{-2} cm^{-1}	9.171	9.171	9.170111(7)
B_0/10^{-2} cm^{-1}	9.175	9.175	9.174707(3)
v_3/cm^{-1}	---	2153.61	2153.5953(1)
v_3/cm^{-1}	---	2153.65	2153.6478(1)
v_5/cm^{-1}	1597.69	---	1598.6810(3)

OC-D$_2$O Morphed Potentials

Observable	6-D D$_2$O	6-D CO	Exp
A_0/cm^{-1}	11.71	11.73	11.78376(2)
A_0/cm^{-1}	11.65	11.67	11.716189(7)
B_0/10^{-2} cm^{-1}	8.736	8.734	8.73678(1)
B_0/10^{-2} cm^{-1}	8.735	8.733	8.73583(1)
v_3/cm^{-1}	---	2154.53	2154.5375(1)
v_3/cm^{-1}	---	2154.53	2154.5409(1)
v_5/cm^{-1}	1180.11	---	1180.6198(2)

Tunneling Splitting in OC-H$_2$O

- $K = 0$ state
  - 0.83 cm^{-1} (Morphed Potentials)
  - 0.557 cm^{-1} (Bumgarner *et al.* CPL 176 (1991) 123)

- $K = 1$ state
  - 0.27 cm^{-1} (Morphed Potentials)
  - 0.304 cm^{-1} (Oudejans and Miller, CPL 306 (1999) 214)

Plots of the Morphed PES
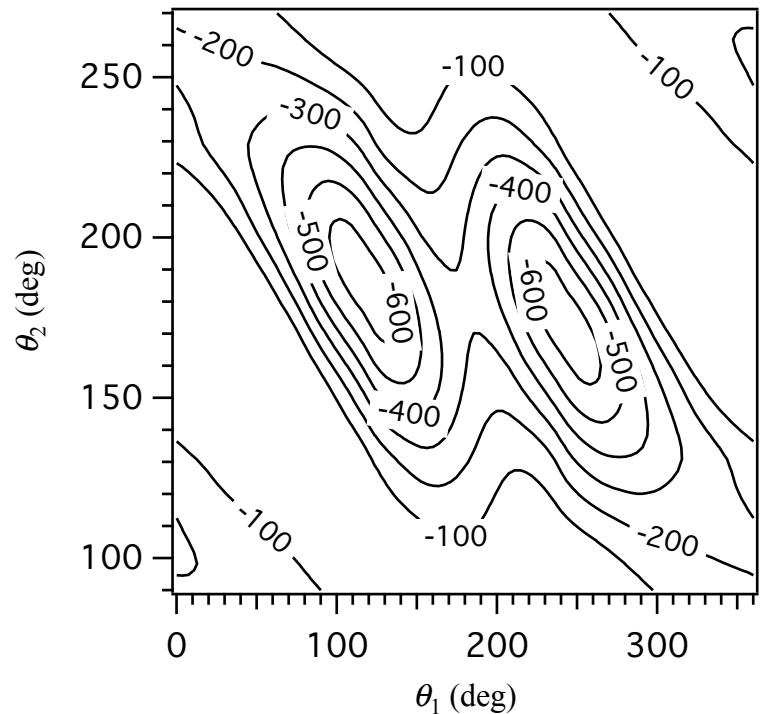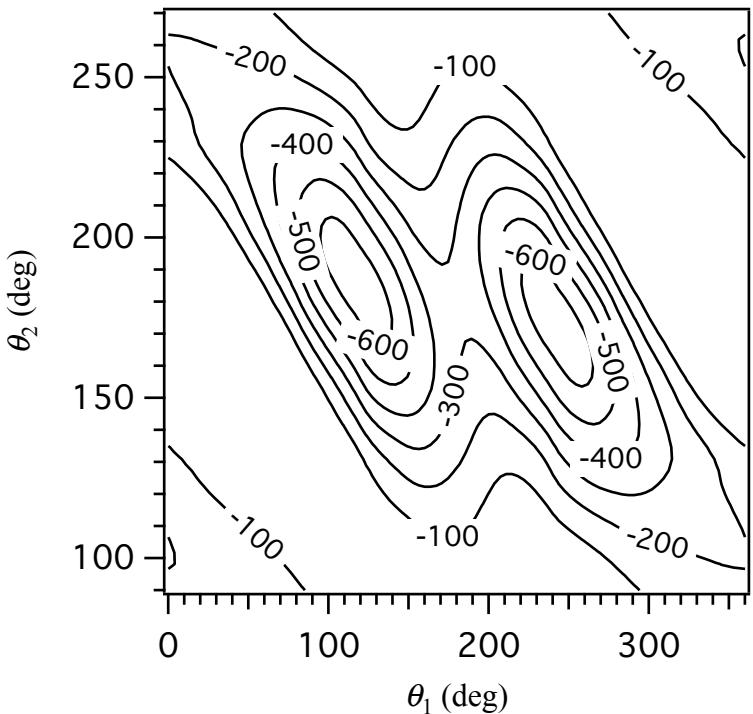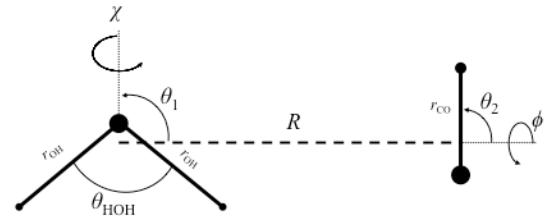
6-D H_2O D_e = 653(7) cm^{-1}
Barrier = 336(8) cm^{-1}

R = 3.97 Å
$\phi = \chi = 0.0°$

6-D CO D_e = 649(11) cm^{-1}
Barrier = 337(12) cm^{-1}

# The Badger-Bauer Rule Revisited

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

D_0 for H_2O-CO is predicted to be 355(13) cm^{-1}.

5-D Frozen H_2O and CO
D_0 = 337(5) cm^{-1}

6-D H_2O
D_0 = 342(5) cm^{-1}

6-D CO
D_0 = 339(5) cm^{-1}
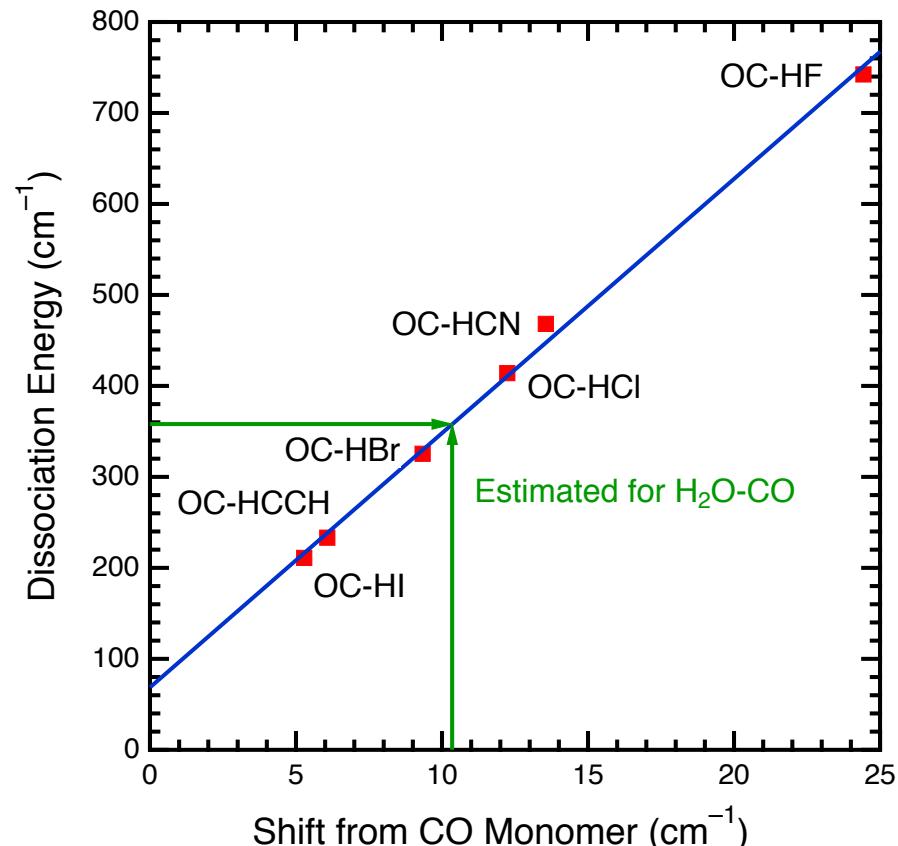
Rivera-Rivera et al.
J. Phys. Chem. A 117 (2013) 8477.

Conclusions

- Rovibrational analysis of the water bending vibrational spectrum in OC-H_2O complex has been completed.

- Potential morphing can now be applied to any dimer complex comprised of a non-linear and a linear molecule.

- It is now feasible to extend the methodology for studying pairwise complexes of non-linear molecules.

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