Theoretical Studies on *Ab Initio* Models for O-H-O Hydrogen Bonds

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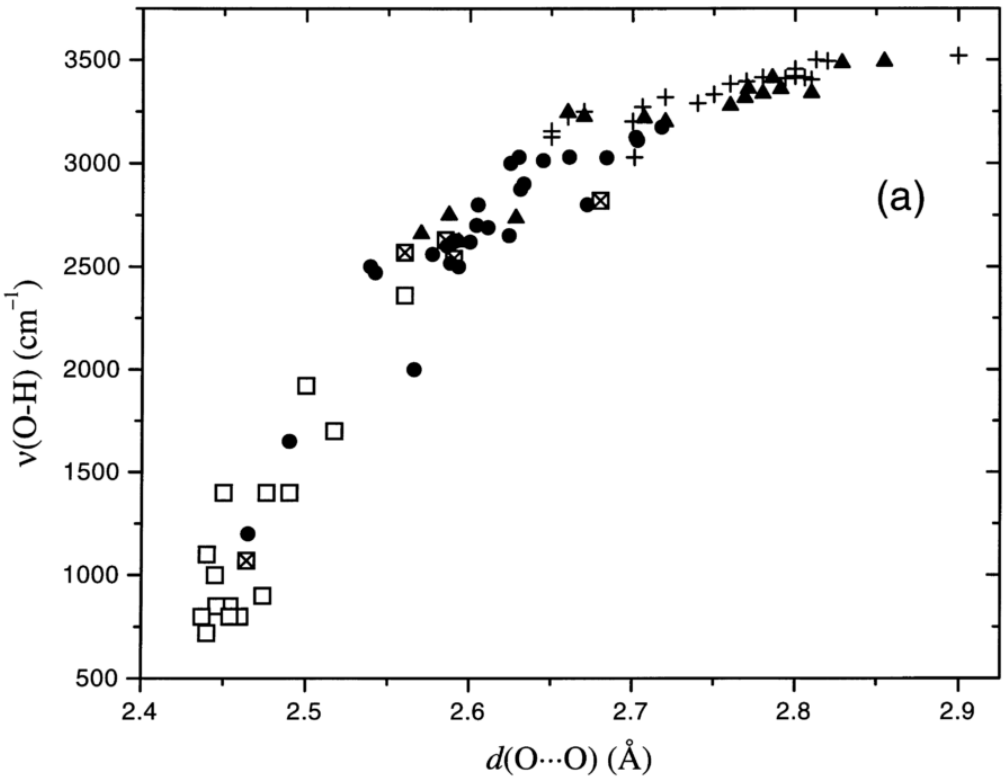
Outline

IR Frequencies vs. O-O Distance



There is a relationship in the O-O distance and the O-H-O asymmetric stretching frequencies.[1]

O H O

[1] Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1–15.

A Two-Morse-Potential Model

Hamiltonian describing the two interacting diabatic state is:[2, 3]

$$H = \begin{pmatrix} V_D(r) & \Delta_{DA}(R,\phi) \\ \Delta_{DA}(R,\phi) & V_A(r^*) \end{pmatrix} \tag{1}$$

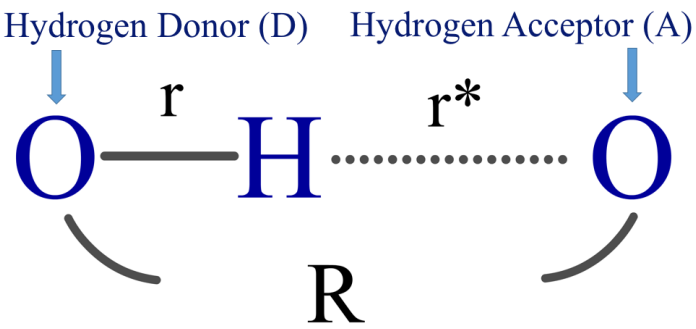
where V is the Morse potential for the 2 O-H bonds:

$$V_i(r) = D_i\Big(\exp\left(-2a_i(r-r_{0i})\right) - 2\exp\left(-a_i(r-r_{0i})\right)\Big) \tag{2}$$

The coupling term:

$$\Delta_{DA}(R,\phi) = \Delta_0 \cos(\phi)\cos(\phi^*)\exp(-bR) \tag{3}$$

ϕ and ϕ^*: the two O-O-H angles respectively.
Two fitting parameters: Δ_0 and b.

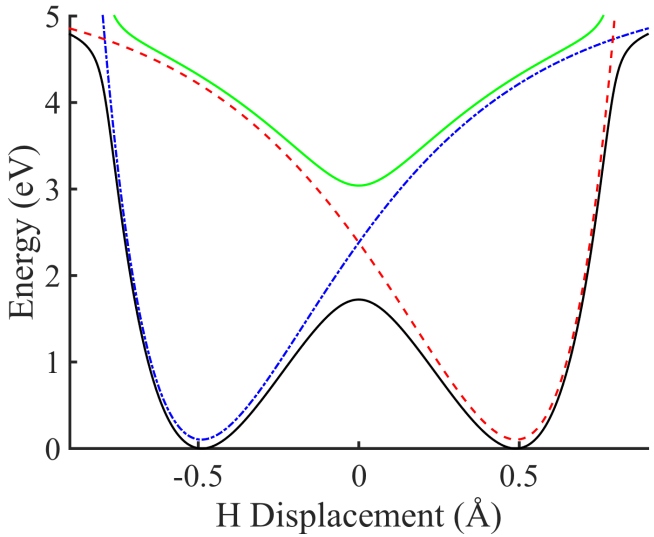


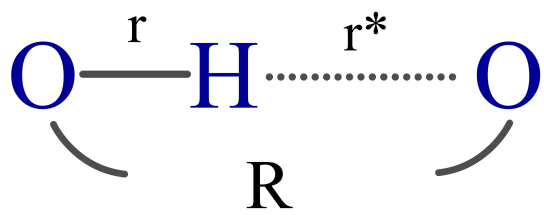
[2] McKenzie, R. H. *Chem. Phys. Lett.* **2012**, *535*, 196–200.

[3] McKenzie, R. H.; Bekker, C.; Athokpam, B.; Ramesh, S. G. *J. Chem. Phys.* **2014**, *140*, 174508.

Adiabatic Potential

$$V_{\pm}(r,R) = \frac{1}{2}(V_D(r)+V_A(R-r)) \pm \frac{1}{2}\left((V_D(R)-V_A(R-r))^2+4\Delta_{DA}(R)^2\right)^{\frac{1}{2}} \quad (4)$$





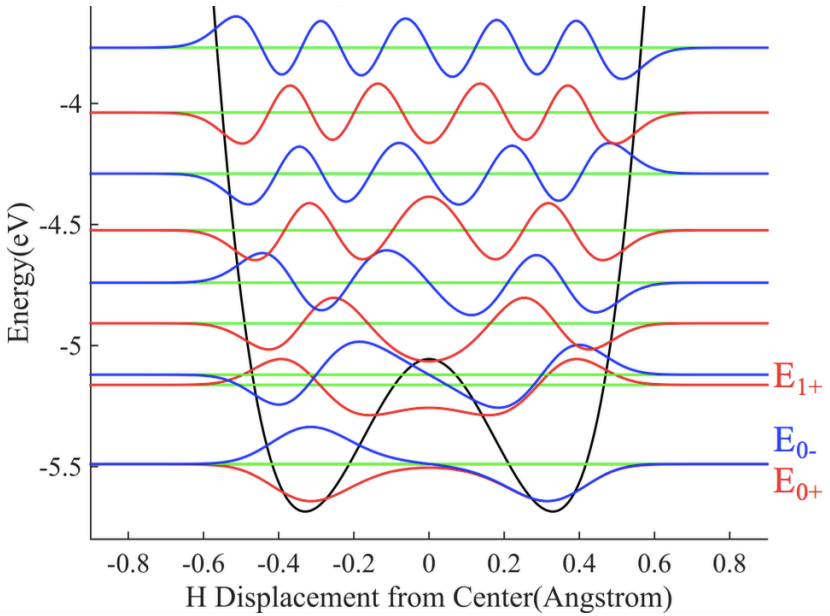
where the H displacement is $r - R/2$

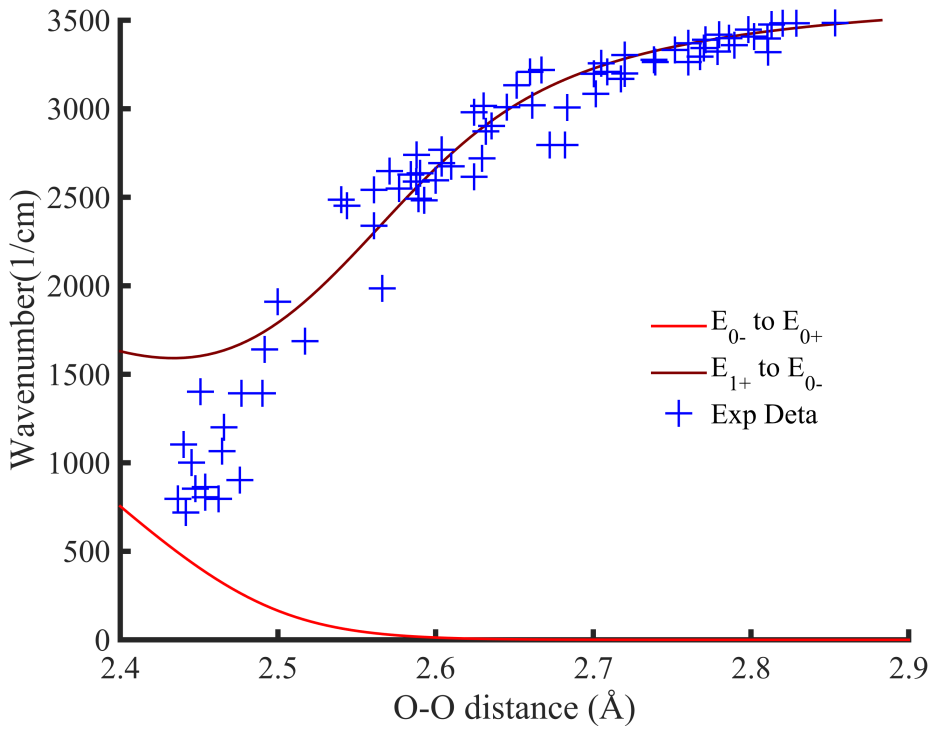
Use the lower eigenvalue as electronic effective PES to solve the proton motion on the O-O axis:

$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dr^2} + V_-(r,R)\right)\Psi_n(r) = E_n\Psi_n(r) \quad (5)$$

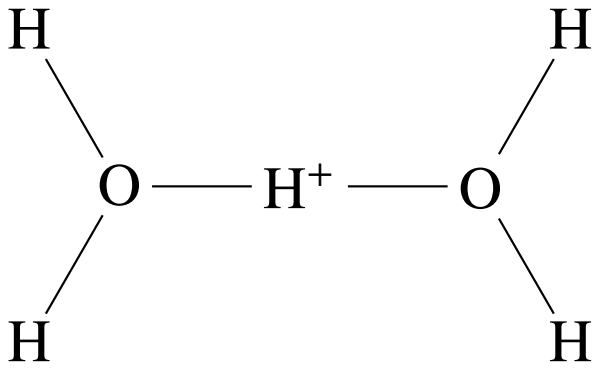
O-H Stretching vs. IR Experimental Data

- Repeat the calculation for R form 2.4 Å to 2.9 Å.
- Use the ΔE of states with different parity (+ even, - odd) to simulate the absorption frequency.
- Compare with the experimental data from various O-H-O hydrogen bonds.

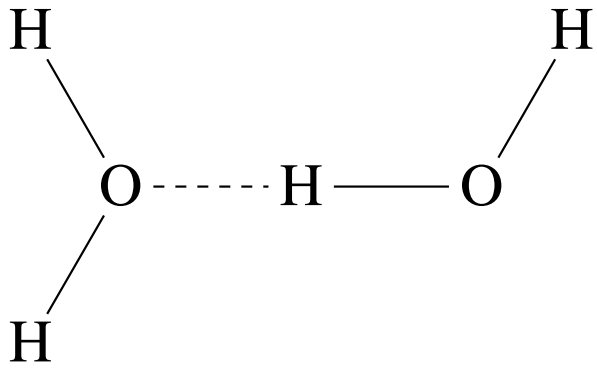




Ab Initio Model



(a) $H_5O_2^+$, Zundel-type hydronium ion



(b) H_4O_2, water dimer

- Optimized structure:

System	O-O distance	O-H distance	O-H distance	νOHO_{asym}
$H_5O_2^+$	2.40	1.20	1.20	1002[4]
H_4O_2	2.92	1.95	0.97	3755[5]

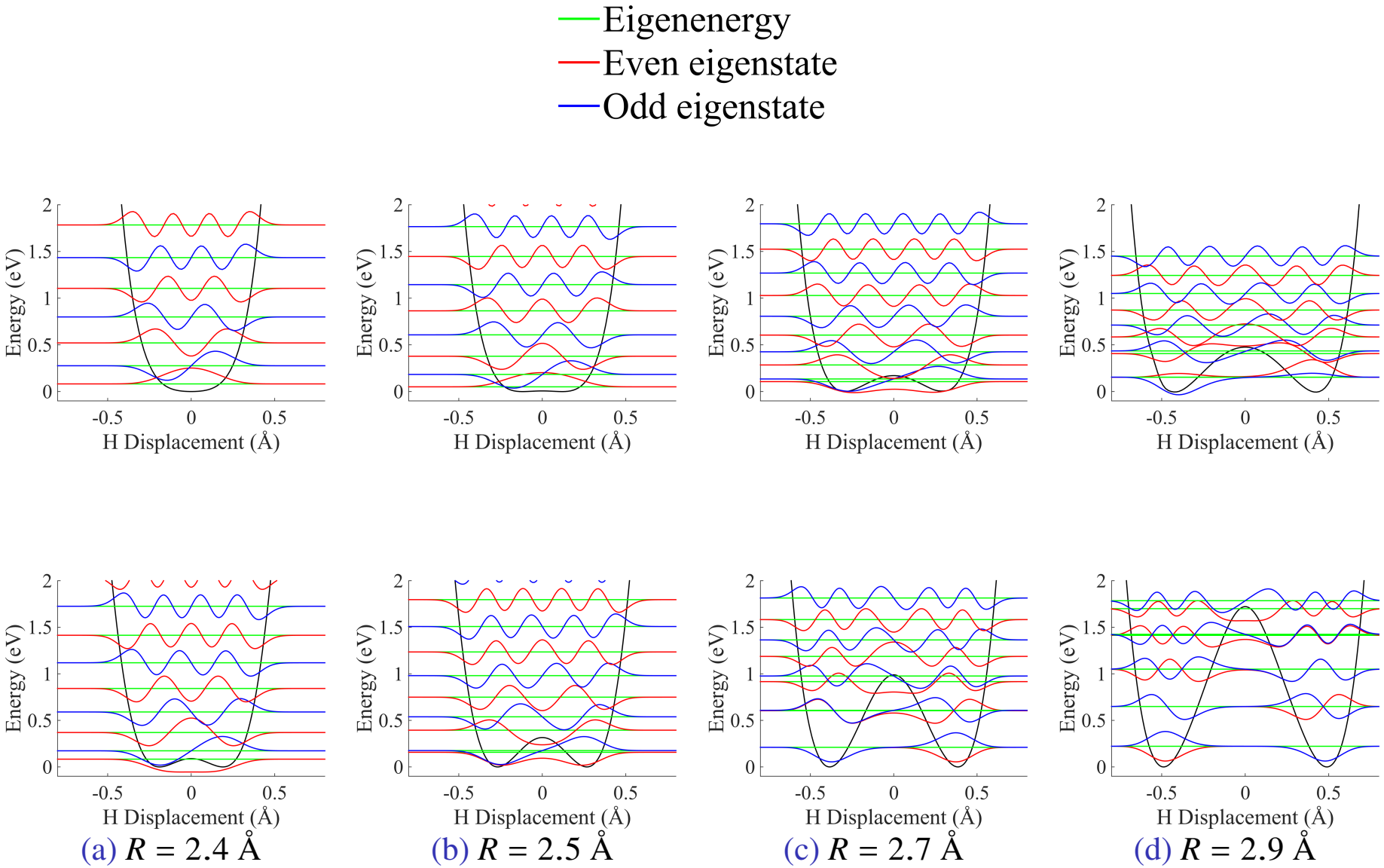
[4] Roscioli, J. R.; McCunn, L. R.; Johnson, M. A. *Science* **2007**, *316*, 249–254.

[5] Mineo, H.; Niu, Y. L.; Kuo, J. L.; Lin, S. H.; Fujimura, Y. *J. Chem. Phys.* **2015**, *143*, 084303.

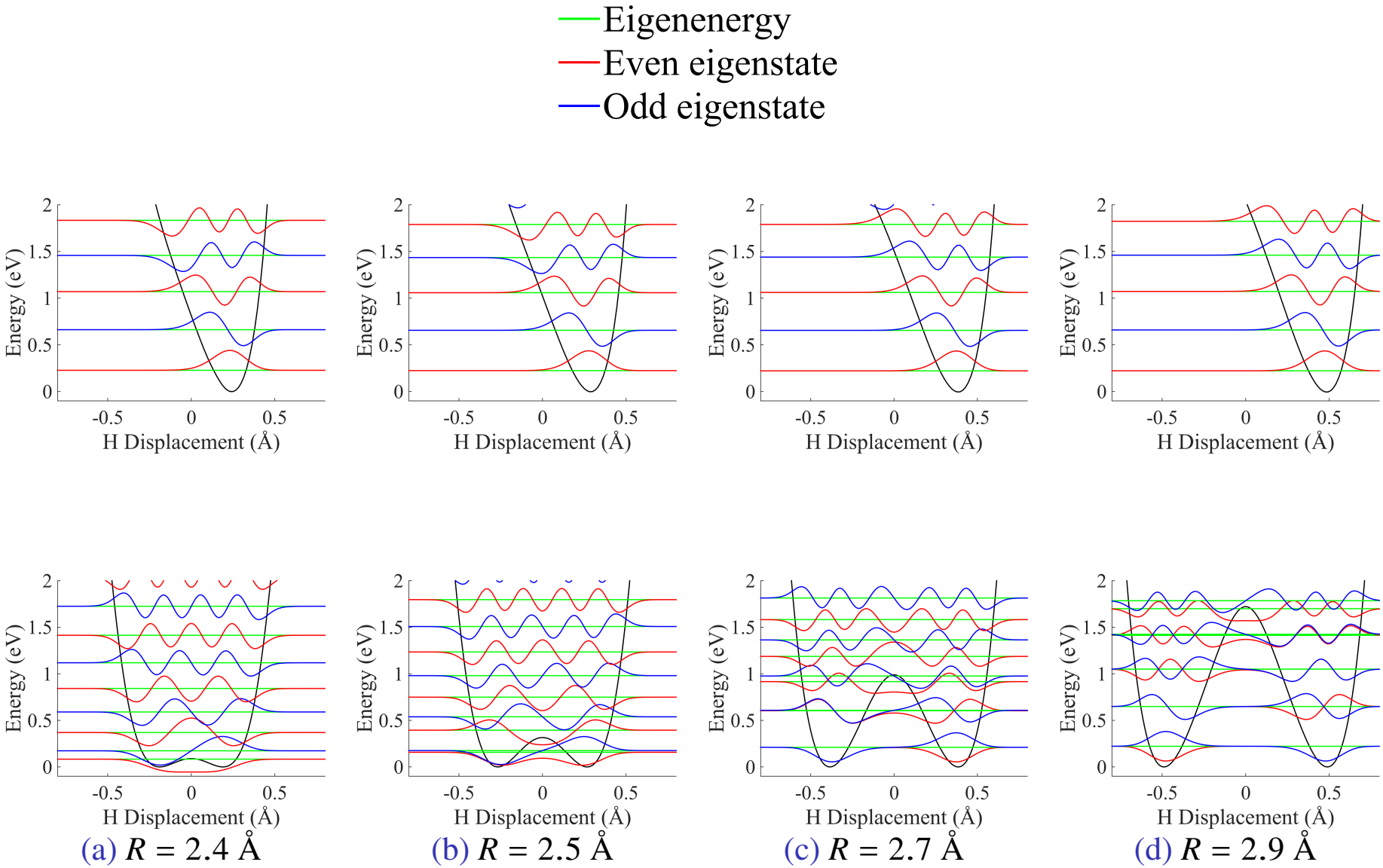
PES Scan

- G09 program
- Relaxed Scan:
  1. Fix the O-O distance as 2.4, 2.5, 2.7, 2.9 Å respectively.
  2. **Move the H atom** within the O-H-O bond and perform **partial geometry optimization** to obtain the optimized geometries via **DFT** methods (ωB97X-D/Aug-cc-pVTZ).
  3. Use **CCSD(T)/Aug-cc-pVTZ** to calculate energetic properties.

Solve Schrödinger Equations on *Ab Initio* PES ($H_5O_2^+$)

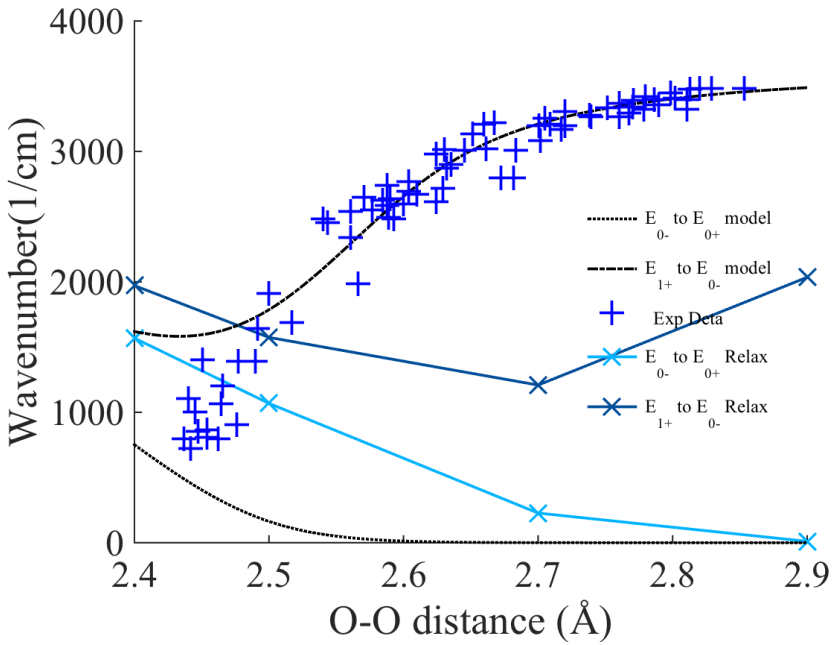


Solve Schrödinger Equations on *Ab Initio* PES (H_4O_2)

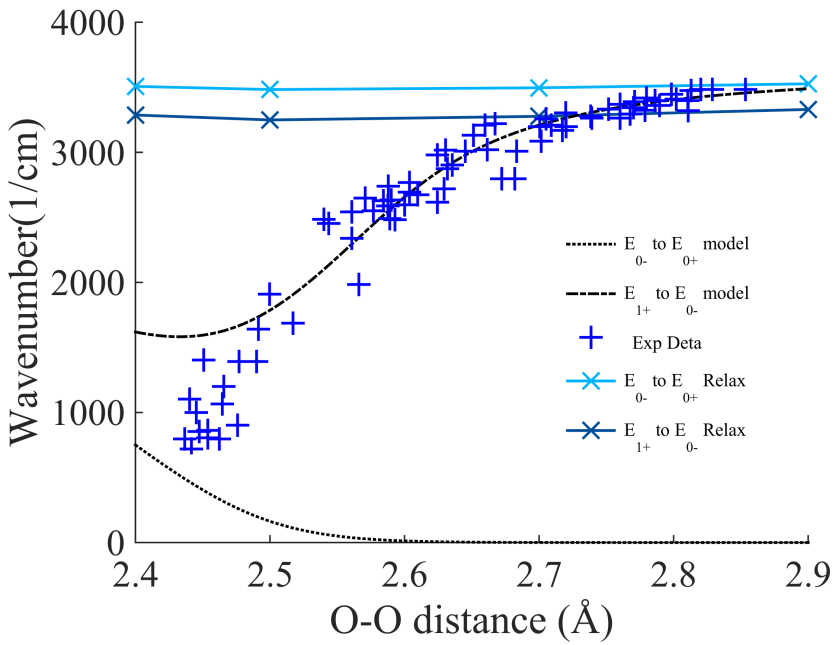


(a) R = 2.4 Å (b) R = 2.5 Å (c) R = 2.7 Å (d) R = 2.9 Å

Spectrum of *Ab Initio* Model ($H_5O_2^+$ and H_4O_2)



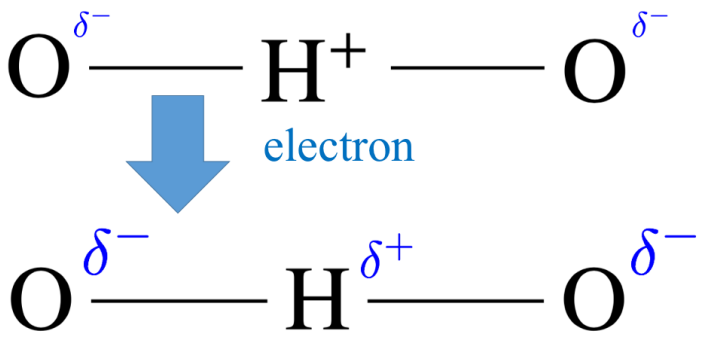
(a) $H_5O_2^+$

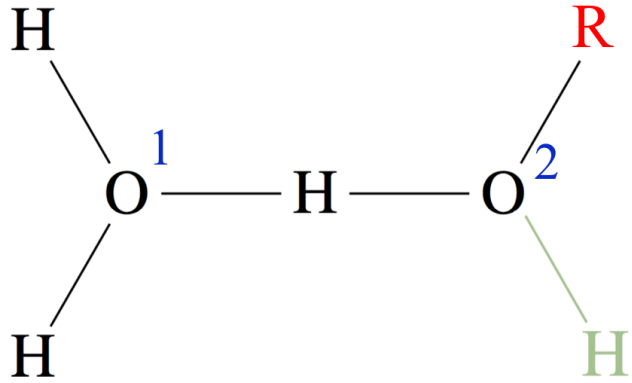


(b) H_4O_2

It is probably that including charges into the effective potential model will be a way to find a better and physically acceptable potential model.

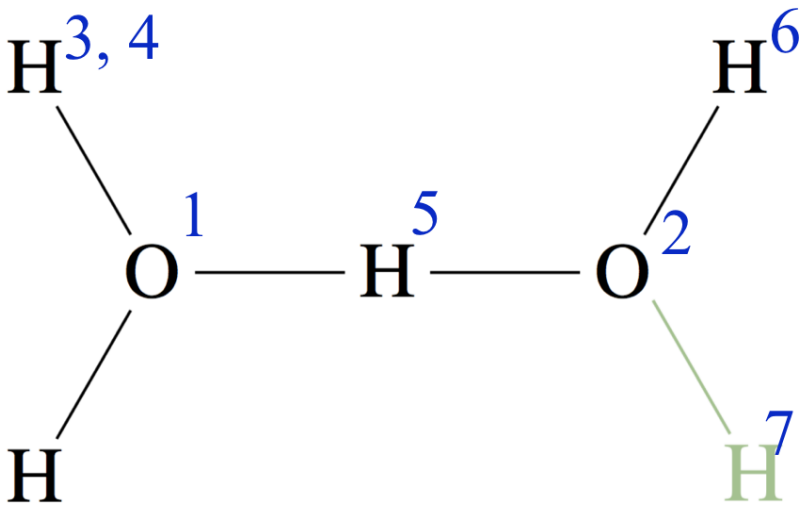
Idea





- Add 1 electron into the O-H-O hydrogen bond, and analyze where the charge will move to.
- Compare different optimized structure with different O-O distance to observe the move of charge.
- Method and basis set: ωB97X-D/6-31+G(d,p), ESP charges.

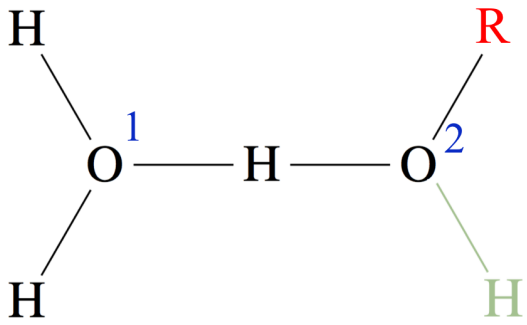
Add 1 Electron to the O-H-O Hydrogen Bond

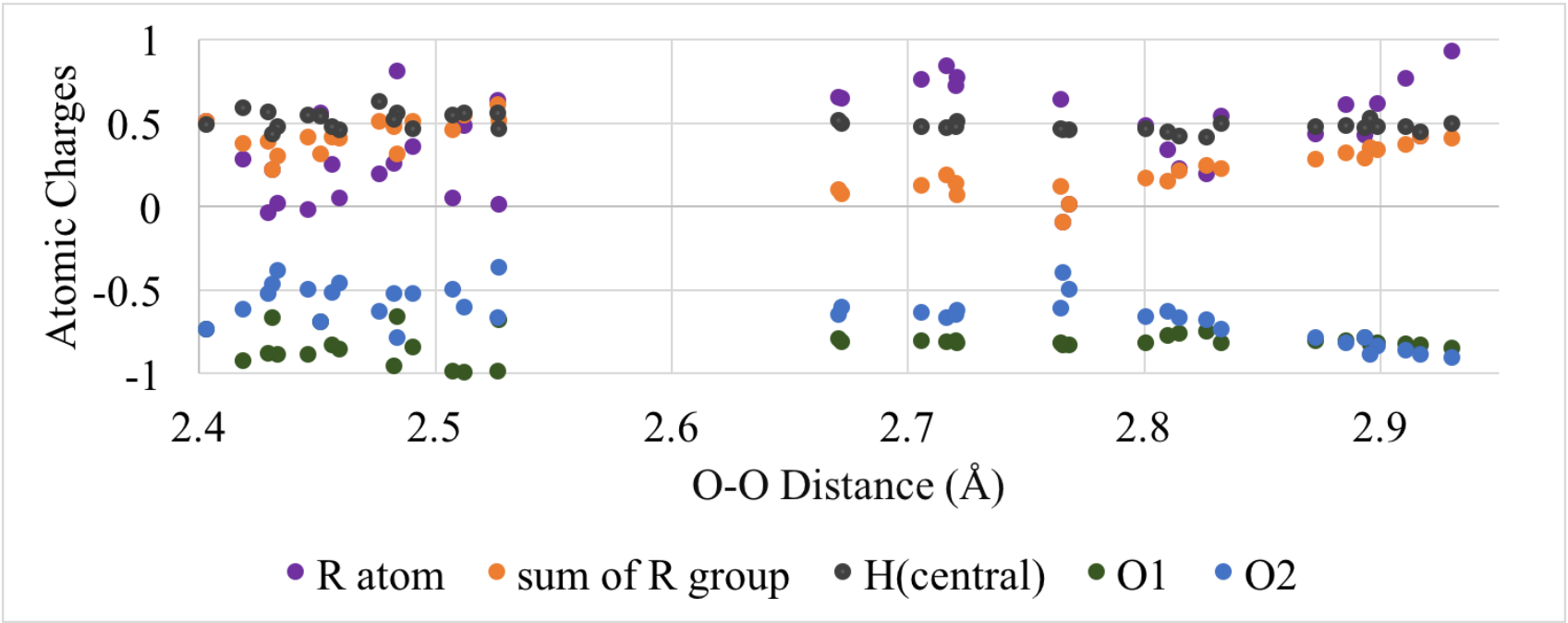


Model	1	2	3	4	5	6	7	sum 126	sum 26
$H_5O_2^+$	-0.67	-0.67	0.46	0.49	0.45	0.49	0.46	-0.89	-0.22
H_4O_2	-0.76	-0.80	0.39	0.38	0.39	0.39	none	-1.17	-0.41
difference	-0.09	-0.13	-0.06	-0.11	-0.06	-0.10	-0.46	-0.28	-0.19

Different Functional Groups

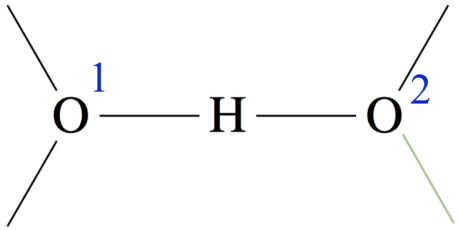
R = hydrocarbyl, phenyl, halogen, halocarbon, carboxyl

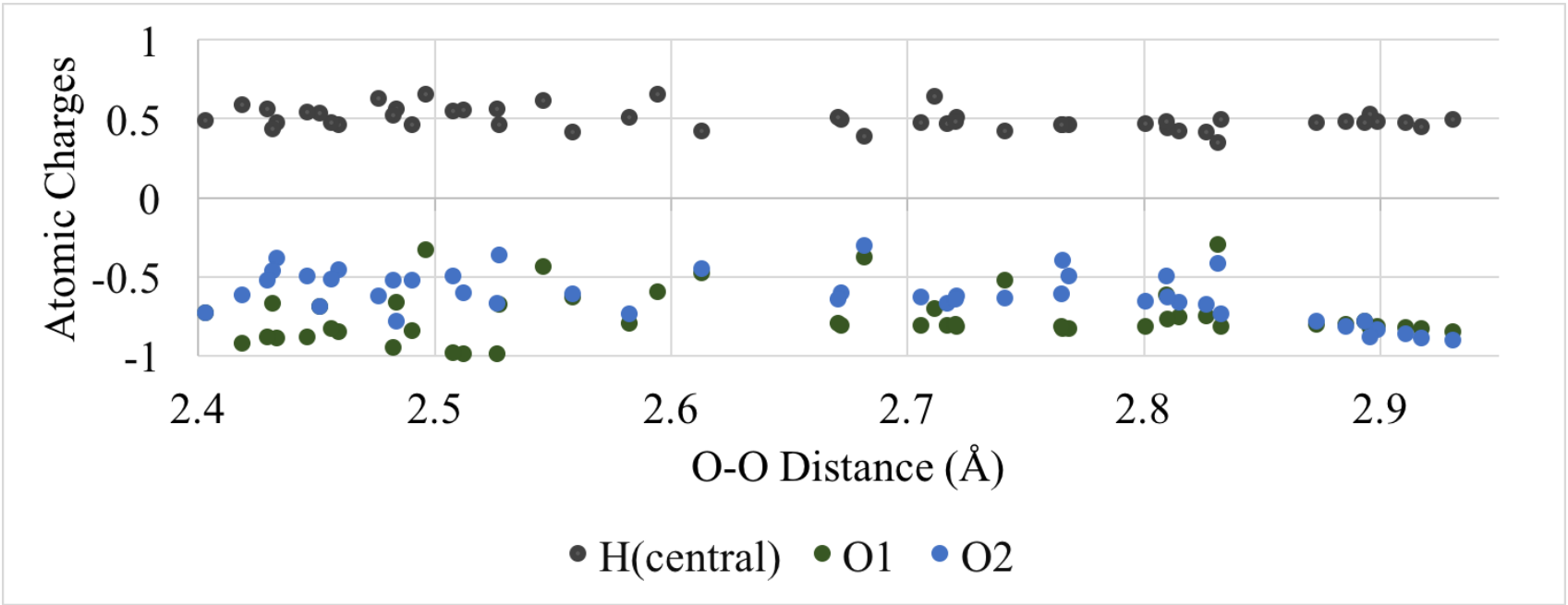




Atomic Charges in Different Kinds of HBs

- 2 or more substitutions





Summary

- Atomic charges in different O-H-O hydrogen bonds and O-O distance are almost independence.
- More attempts is needed to find a better and physically acceptable potential model.