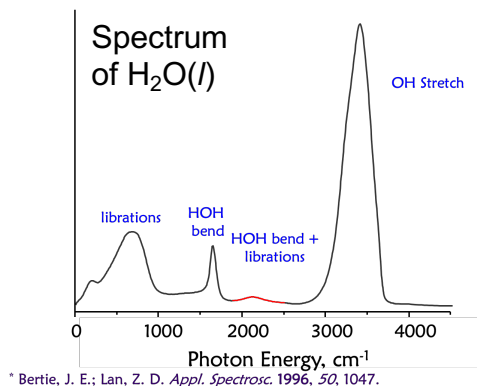# P5450: GUIDED DIFFUSION MONTE CARLO APPROACHES FOR STUDIES OF WATER CLUSTERS: APPLICATIONS TO WATER HEXAMER
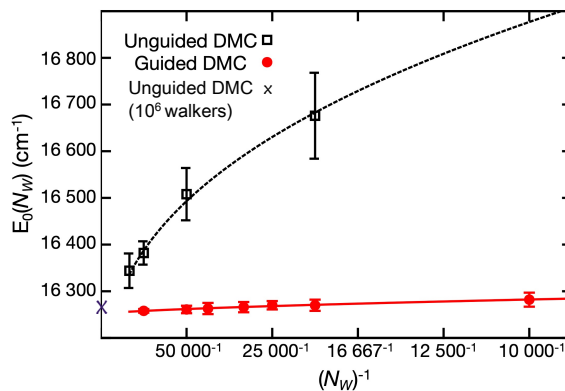
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McCoy Group

Origin of the problem:

Spectrum of $H_2O(l)$

OH Stretch

librations

HOH bend

HOH bend + librations

Photon Energy, cm^{-1}

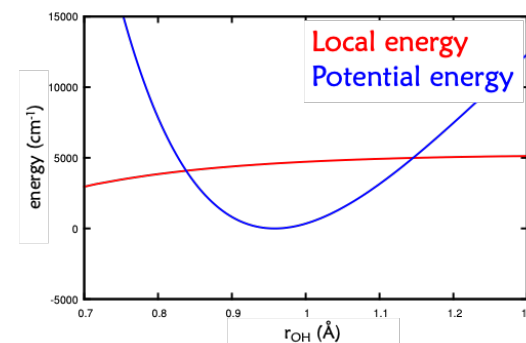* Bertie, J. E.; Lan, Z. D. *Appl. Spectrosc.* 1996, *50*, 1047.

OH frequency depends on the environment; range of frequencies is similar to the frequencies of the intermolecular vibrations

Problem: DMC converges slowly with ensemble size for larger clusters

Unguided DMC □
Guided DMC ●
Unguided DMC × (10^6 walkers)

$E_0(N_w)$ (cm^{-1})

$(N_w)^{-1}$

Conclusion: Adding well-chosen guiding functions improves this dramatically!

Solution:

Local energy
Potential energy

energy (cm^{-1})

r_{OH} (Å)

Introduce guiding functions, which are products of one-dimensional functions of OH stretch and HOH bend; replace V with local energy
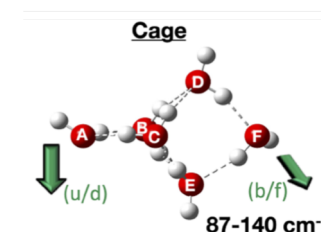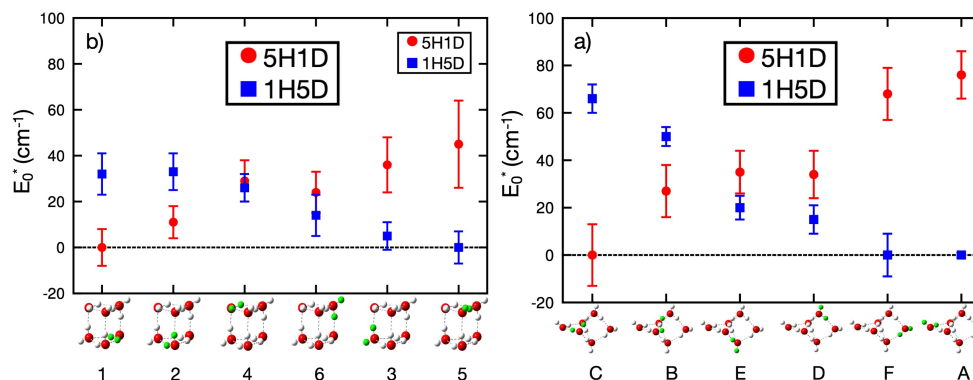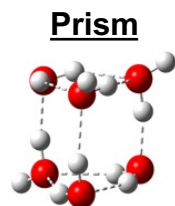
Results:

Energy of cage relative to prism (w/ ZPE):

$(H_2O)_6$: **-50** cm^{-1}

$(D_2O)_6$: **~0** cm^{-1}

$(H_2O)_5(D_2O)$: **-60** cm^{-1}

$(H_2O)(D_2O)_5$: **-22** cm^{-1}

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Prism

b) 5H1D ● 1H5D ■

E_0^* (cm^{-1})

1 2 4 6 3 5

a) 5H1D ● 1H5D ■

E_0^* (cm^{-1})

C B E D F A

Cage

(u/d) (b/f)

87-140 cm^{-1}

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WA10
WK05