Vibrational Transitions of Isolated Alcohol

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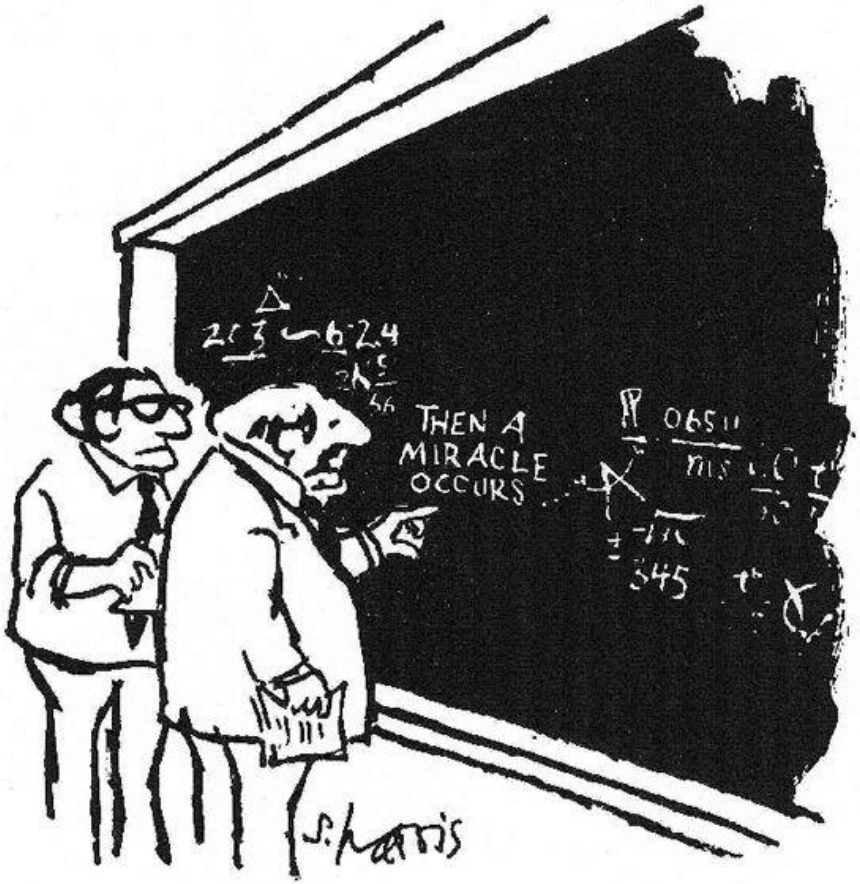
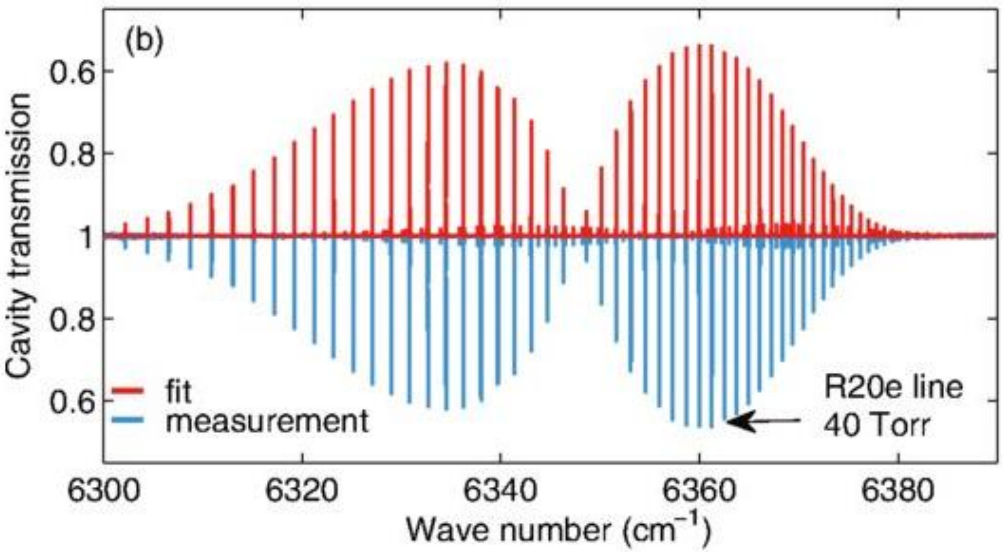
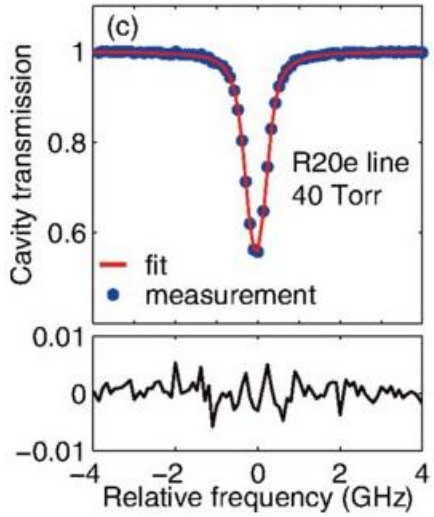
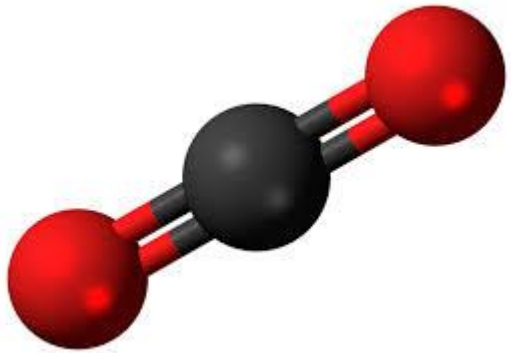
The Physical Chemistry (IR Spectroscopy) Community



"I think you should be more explicit here in step two."







High Resolution ~ 0.001 cm^{-1}

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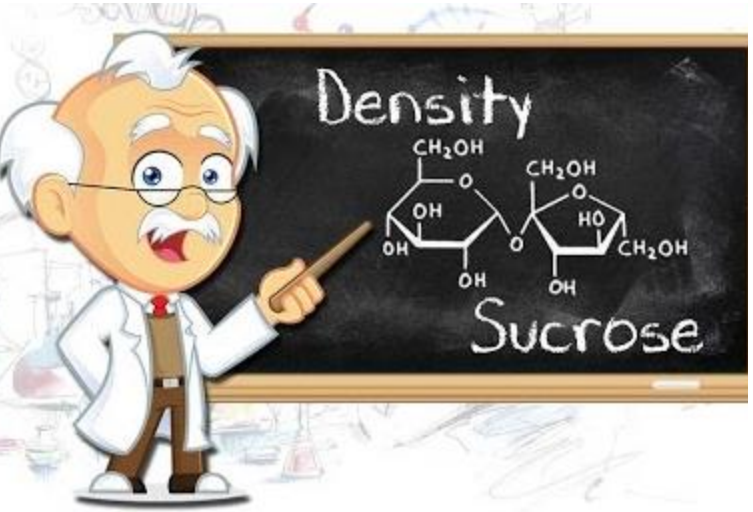
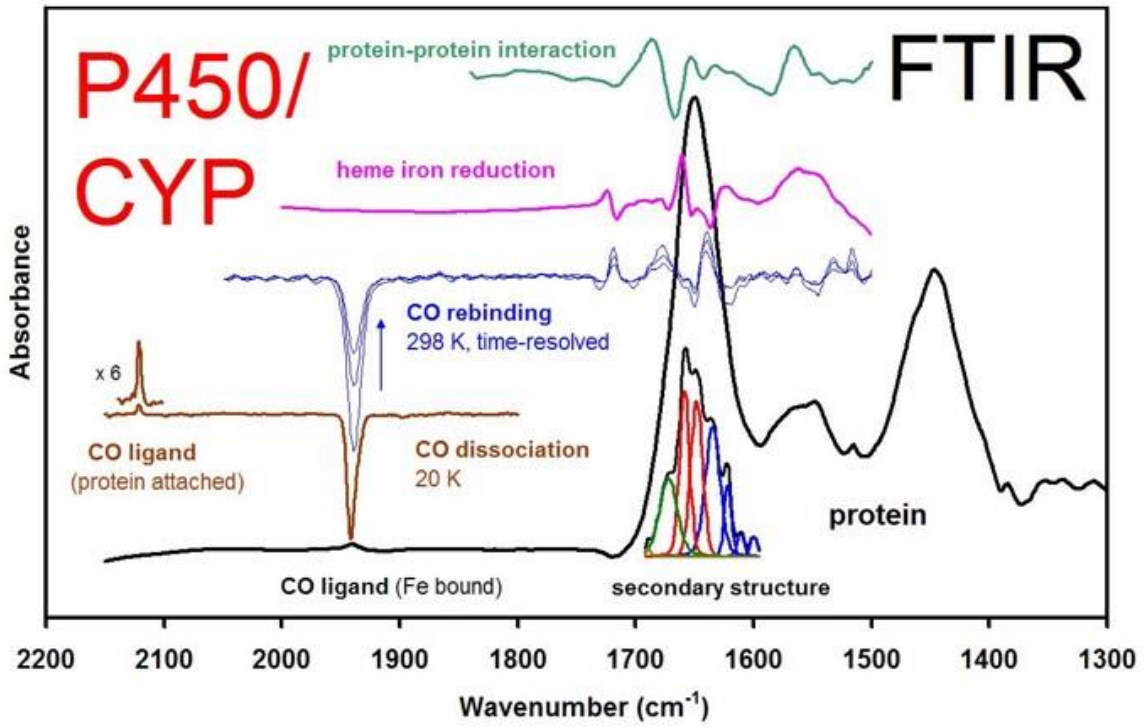
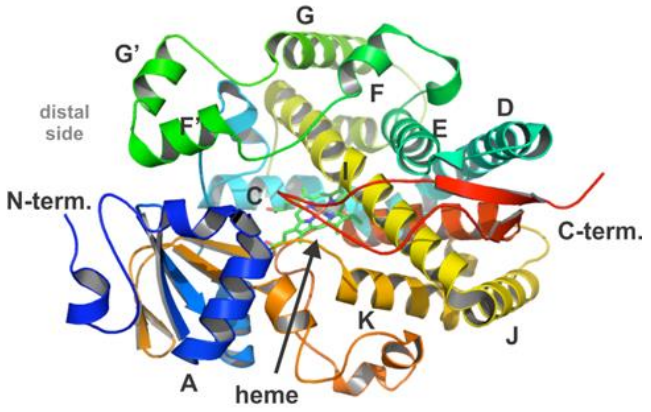
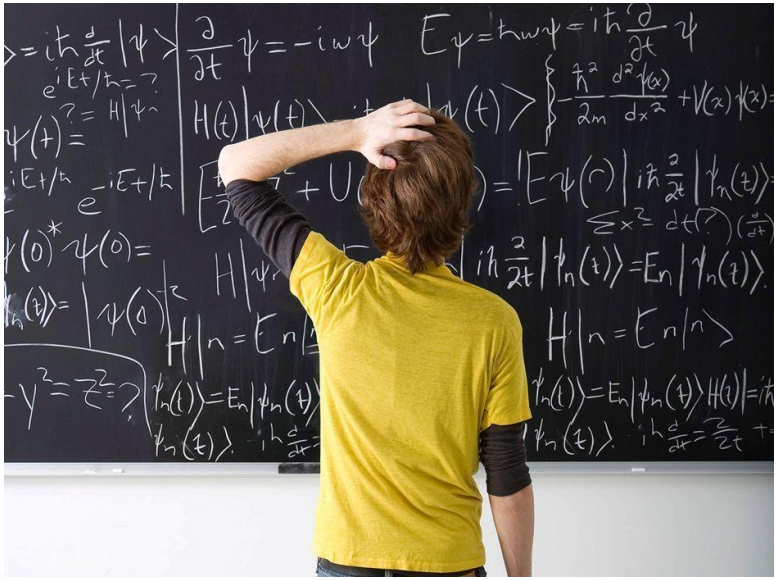
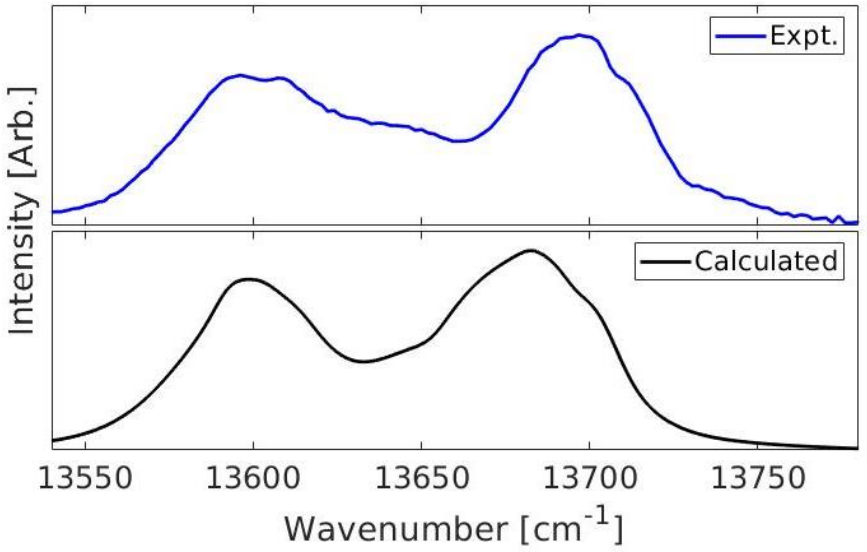


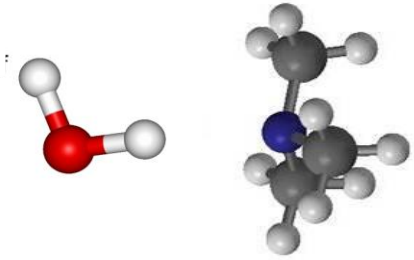


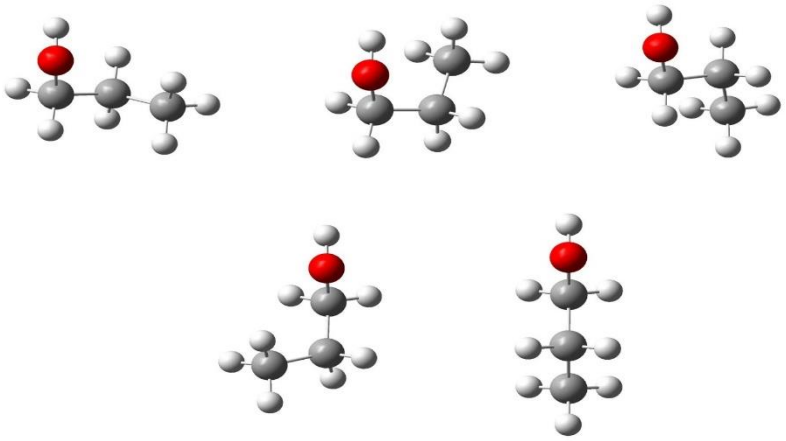


Us (Vibrational Overtones)









$$N_{\text{Complex}} \propto \frac{\text{Measured Intensity}}{\text{Transition Probability}}$$

$$K = \frac{P_{\text{Complex}} \cdot P^{\ominus}}{P_{\text{A}} \cdot P_{\text{B}}}$$

Degrees of Freedom Partition

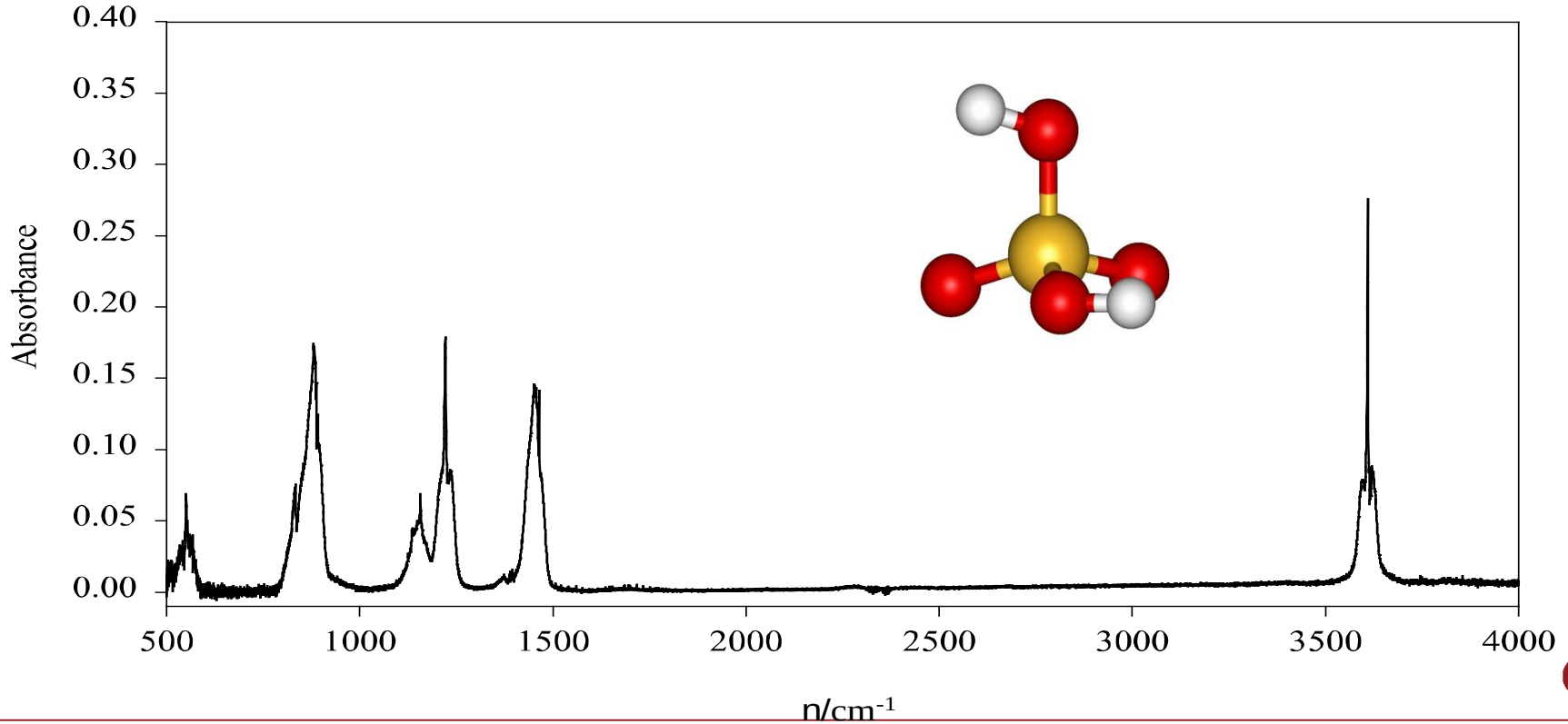
Each particle has 3 degrees of freedom

Each molecule has 3N degrees of freedom; 3 translations, 3 rotations, 3N-6 vibrations

Sulfuric Acid (H2SO4) has 7 atoms, i.e. 15 vibrations

$$E \approx E_e + E_{vib} + E_{rot} + E_{trans}$$

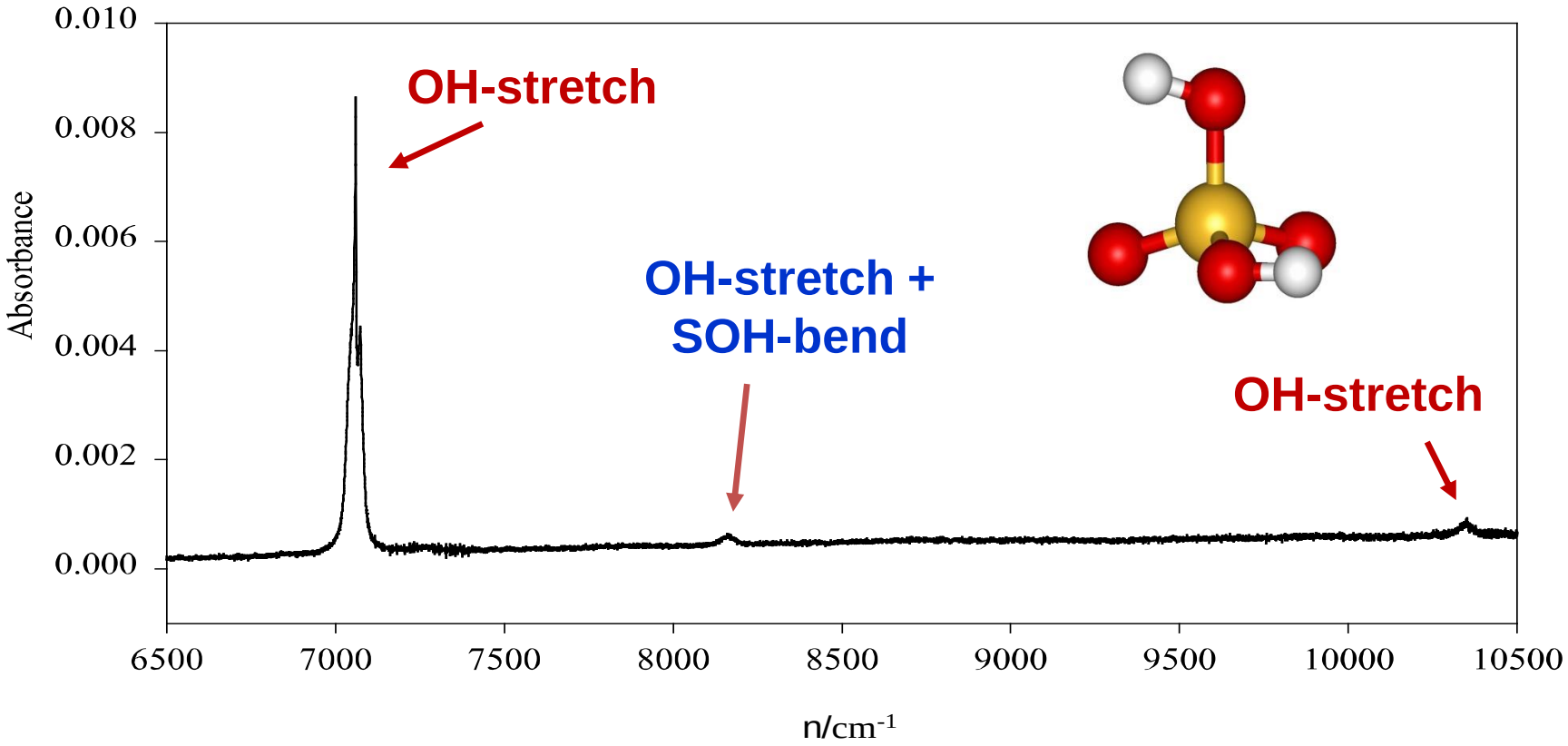
$$3500\ cm^{-1} \rightarrow 2857\ nm$$



Vibrations – Which ones?

$7000\ cm^{-1} \rightarrow 1429\ nm$

$10000\ cm^{-1} \rightarrow 1000\ nm$

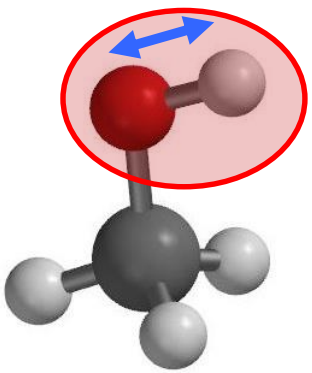


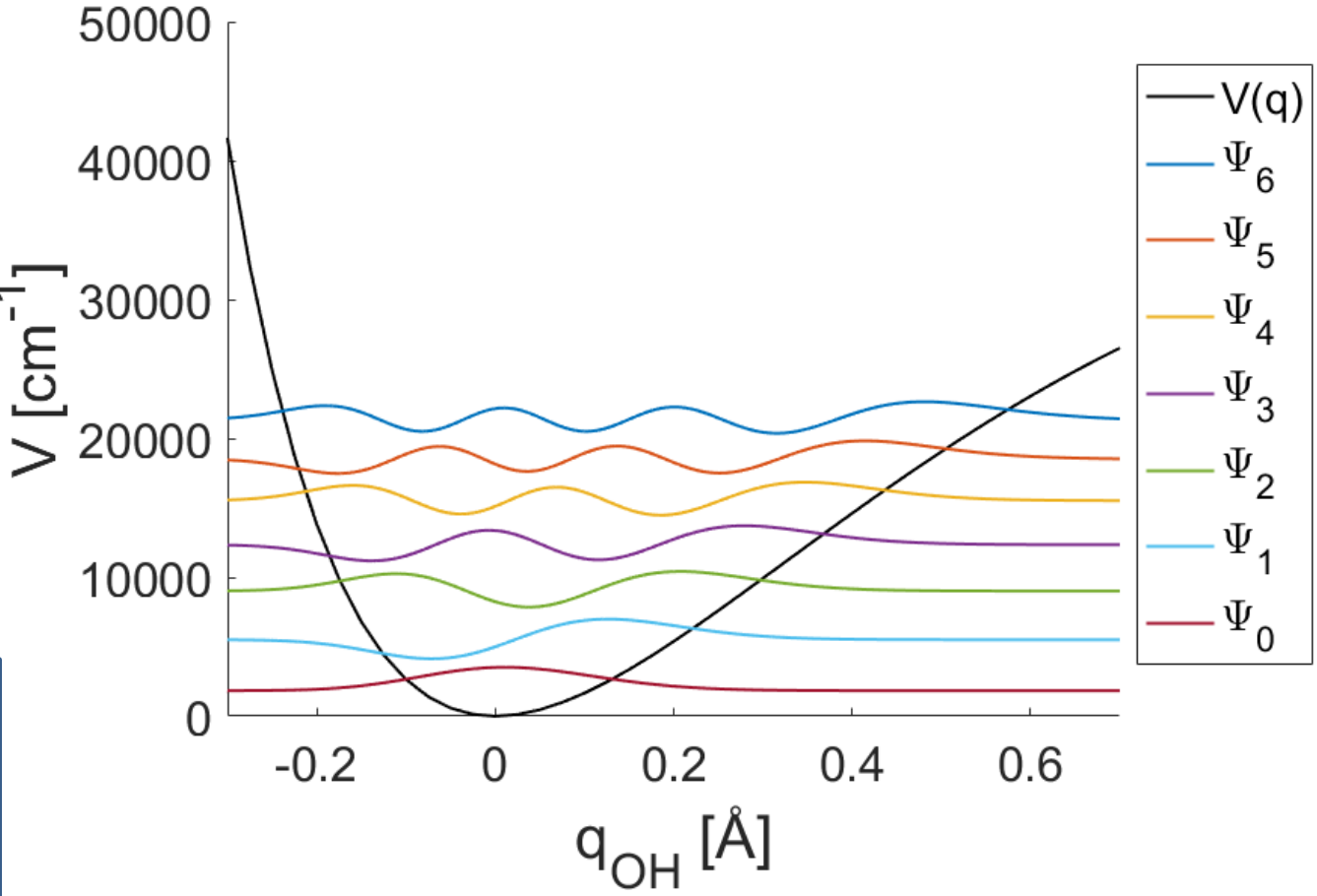
OH vibrations dominate at high energies!

Reduced Dimensionality instead of all 15 vibrations.

The 1D Local Mode Model

q_{OH}





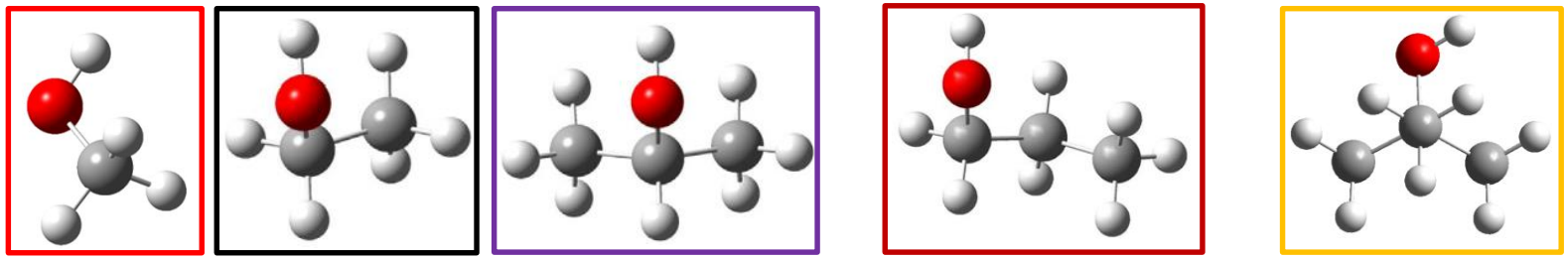
Solved Numerically

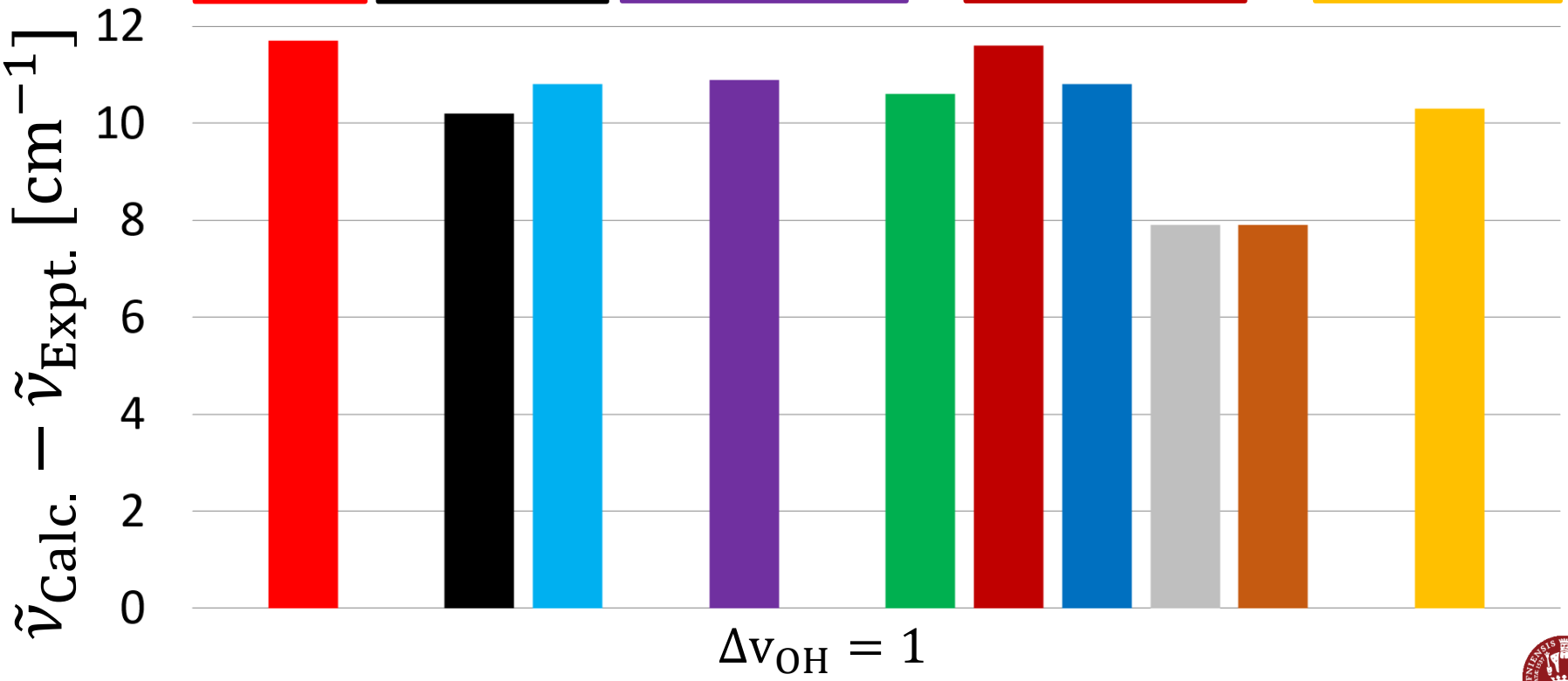
$$\hat{\mathrm{H}} = \frac{\hat{p}_q^2}{2\mu} + \mathrm{V(q)}$$

$$\hat{\mathrm{H}}\psi_i = E_i\psi_i$$

R. Meyer, J. Chem. Phys. 52, 2053, 1970

The 1D Local Mode Model





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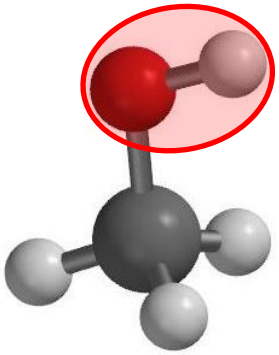
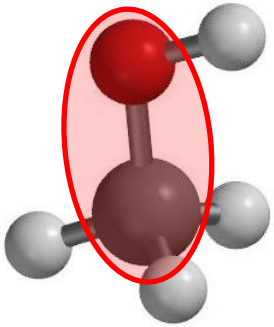
3D LM Model



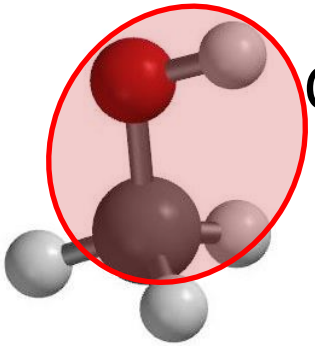
OH-stretch

q_{OH}



CO-stretch

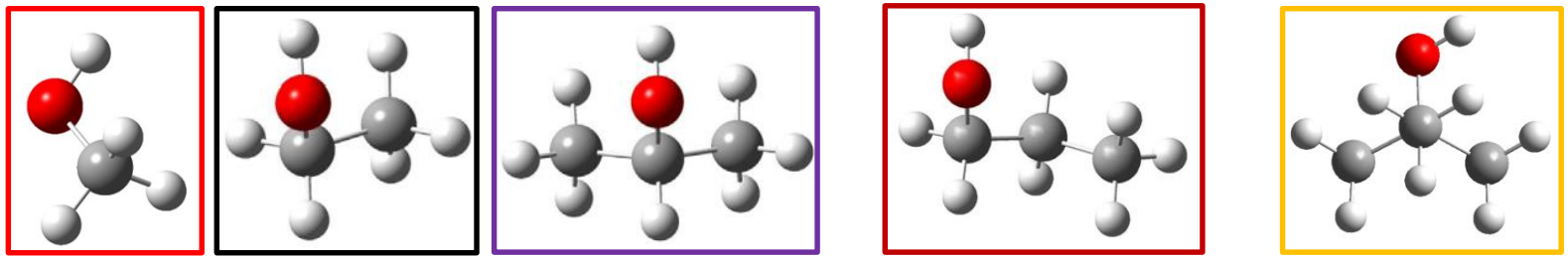
q_{CO}

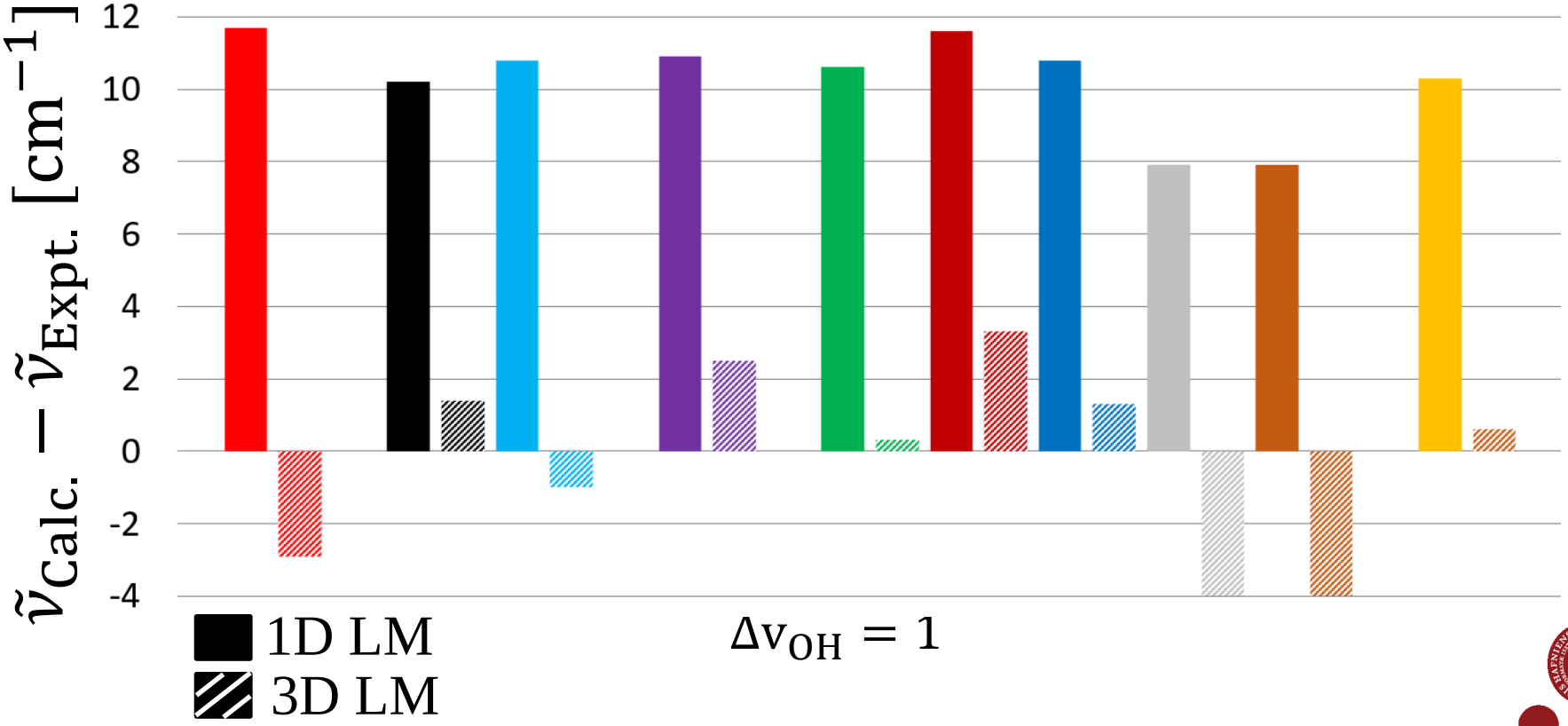


COH-bend

q_{COH}

3D LM Model





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CCSD(T)-F12a/VDZ-F12

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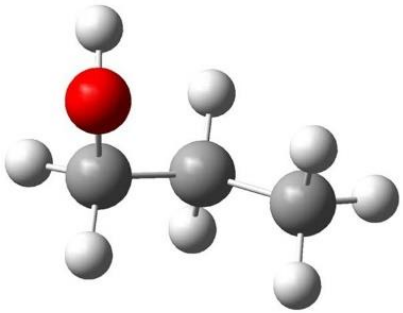
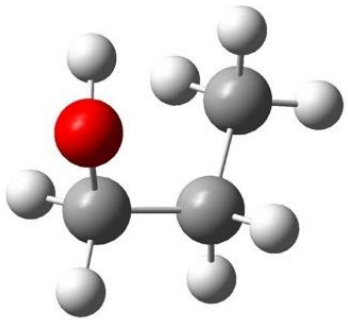
1-Propanol Conformers (T = 298 K)

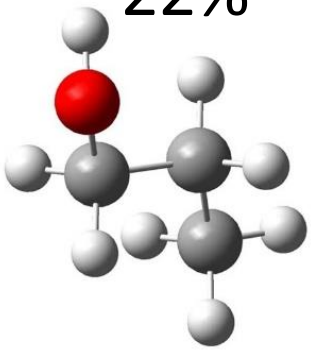
20%



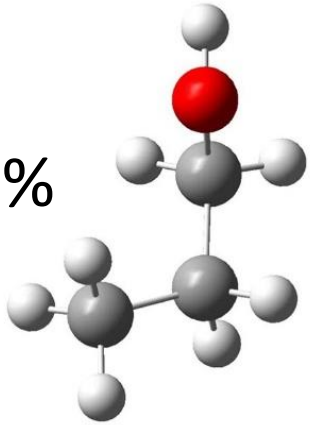
20%

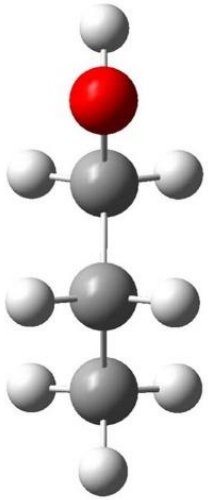


22%



26%





12%

Opt: CCSD(T)/aug-cc-pVTZ
Thermal: B3LYP/aug-cc-pVTZ

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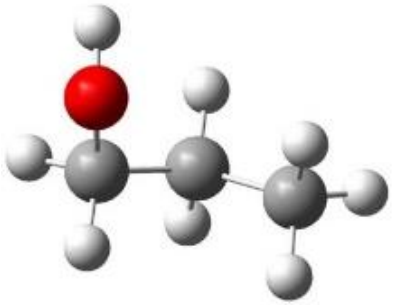
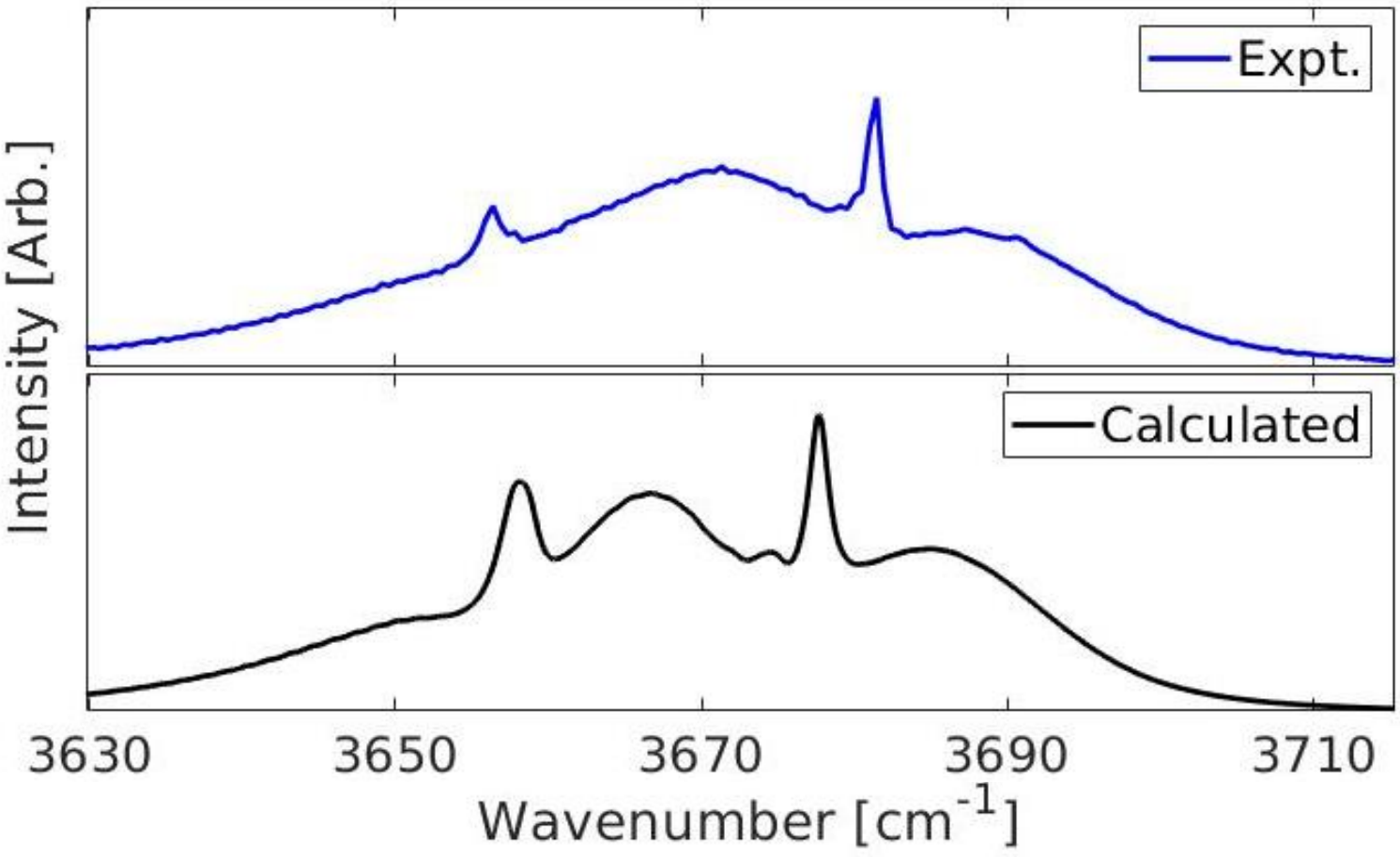
v=1, OH-Stretch 1-Propanol





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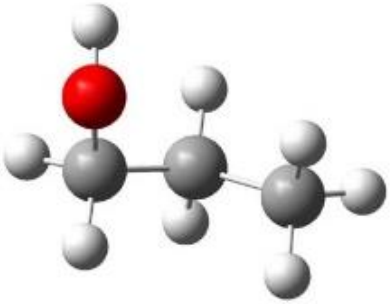
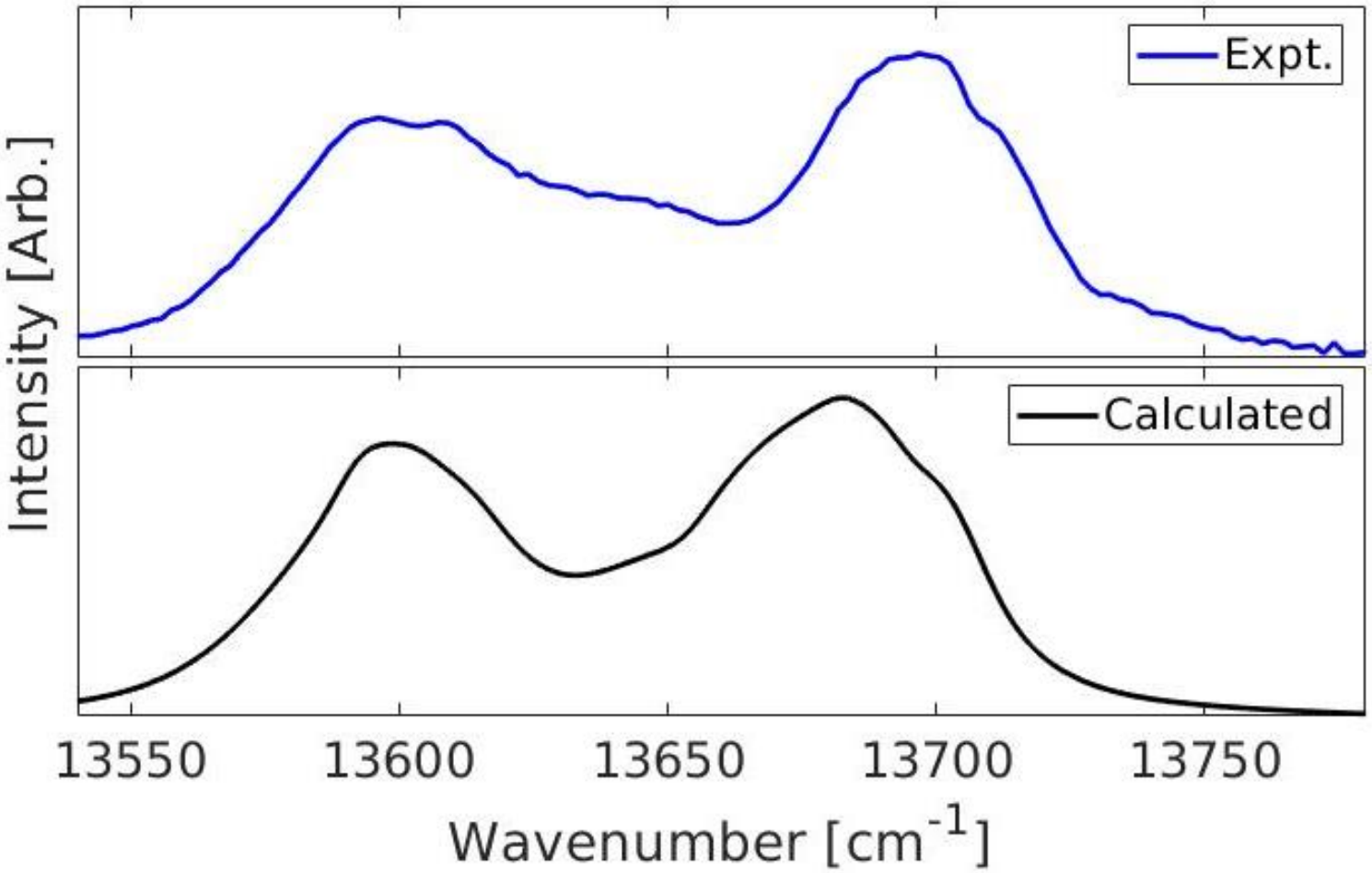
v=4, OH-stretch 1-Propanol





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