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
The Physical Chemistry (IR Spectroscopy) Community

- **Density**: Sucrose
- **P450/CYP**
  - Protein-protein interaction
  - Heme iron reduction
  - CO rebinding (298 K, time-resolved)
  - CO dissociation (20 K)
- **Absorbance**
- **FTIR**
- **Wavenumber (cm⁻¹)**: 2200 to 1300
- **Secondary structure**: CO ligand (Fe bound), CO ligand (protein attached), protein
Us (Vibrational Overtones)

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

\[ K = \frac{P_{\text{Complex}} \cdot P^\Theta}{P_A \cdot P_B} \]
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

\[ E \approx E_e + E_{vib} + E_{rot} + E_{trans} \]

\[ 3500 \text{ cm}^{-1} \rightarrow 2857 \text{ nm} \]
Vibrations – Which ones?

7000 cm\(^{-1}\) → 1429 nm

10000 cm\(^{-1}\) → 1000 nm

OH vibrations dominate at high energies!

Reduced Dimensionality instead of all 15 vibrations.
The 1D Local Mode Model

\[ q_{OH} \]

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

Solved Numerically

\[ \hat{H}\psi_i = E_i\psi_i \]

The 1D Local Mode Model

\[ \hat{\nu}_{\text{Calc.}} - \hat{\nu}_{\text{Expt.}} [\text{cm}^{-1}] \]

\[ \Delta \nu_{\text{OH}} = 1 \]

Vogt, Bertran Valls, and Kjaergaard, JPCA 2020
3D LM Model

OH-stretch $q_{OH}$

CO-stretch $q_{CO}$

COH-bend $q_{COH}$
3D LM Model

\[ \tilde{\nu}_{\text{Calc.}} - \tilde{\nu}_{\text{Expt.}} \text{ [cm}^{-1}\text{]} \]

- 1D LM
- 3D LM

\[ \Delta \nu_{\text{OH}} = 1 \]

Calc., Expt.

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CCSD(T)-F12a/VDZ-F12

Wallberg, et al. SAA 2019
1-Propanol Conformers (T = 298 K)

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

Wallberg, et al. SAA 2019
\( v=1, \text{OH-Stretch 1-Propanol} \)

- Vogt, Bertran Valls, and Kjaergaard, *JPCA* 2020
- Wallberg, et al. *SAA* 2019
$v=4$, OH-stretch 1-Propanol

Vogt, Bertran Valls, and Kjaergaard, JPCA 2020

Wallberg, et al. SAA 2019