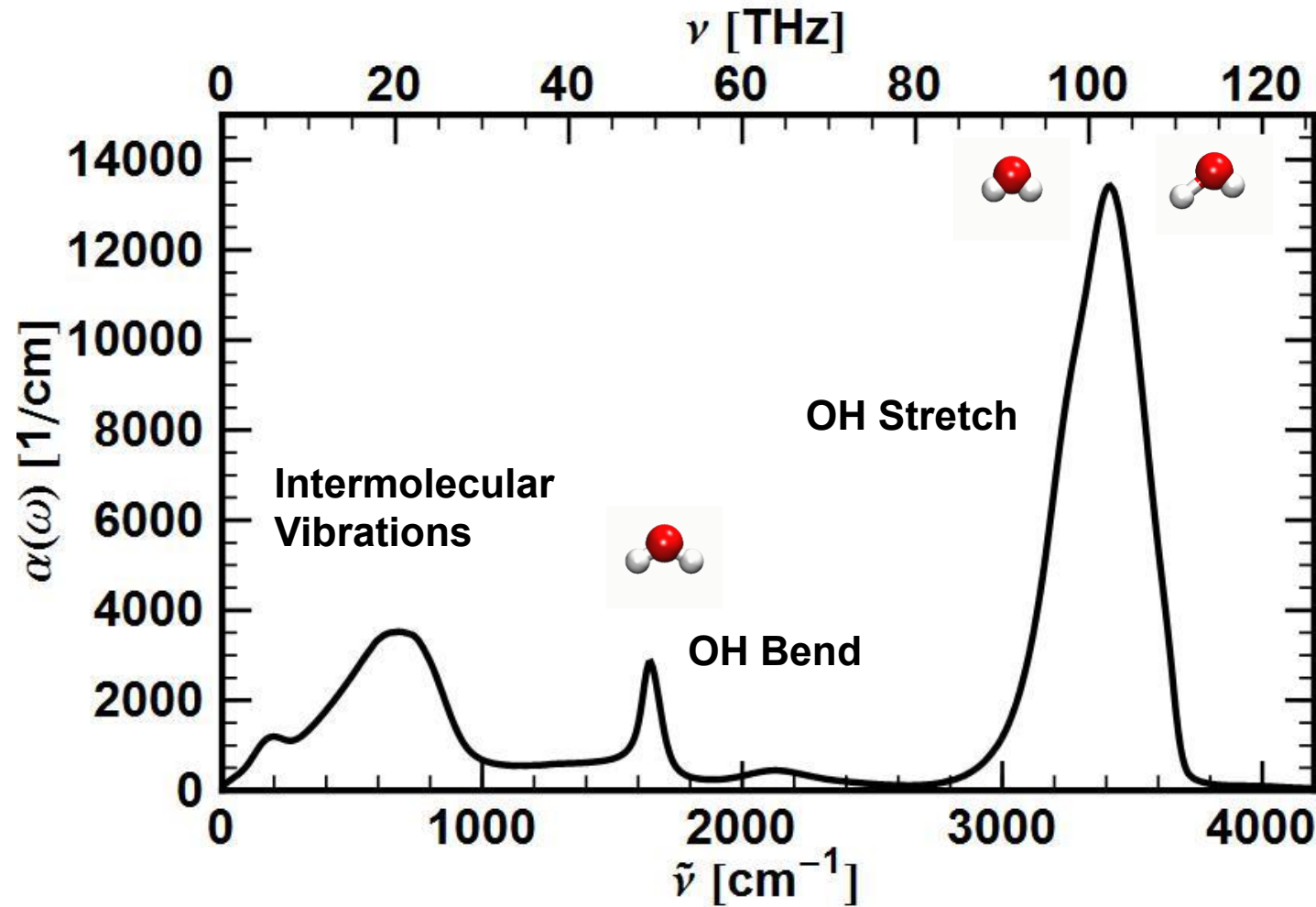# Infrared Absorption Spectrum of Water
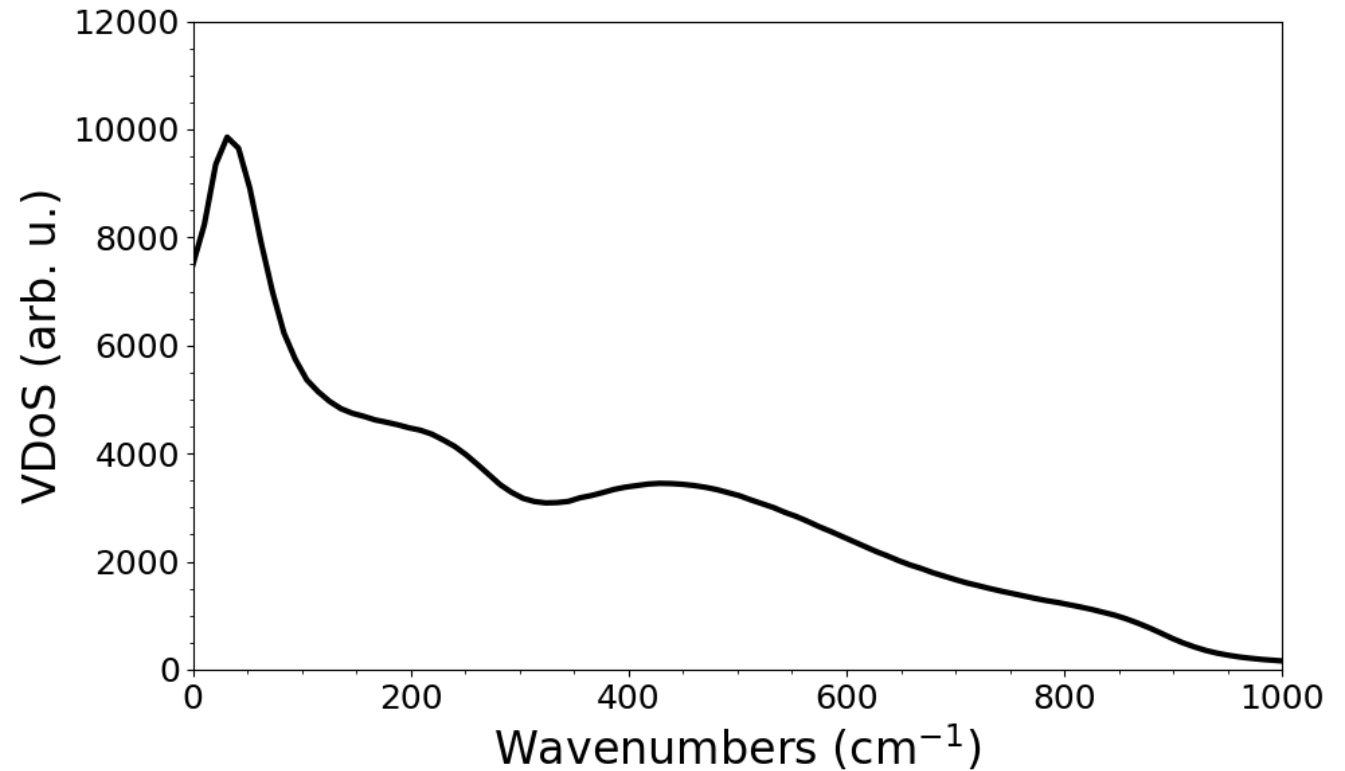
# Vibrational Density of States (VDoS)

$$C(\tau) = m\langle v(t) \cdot v(t + \tau)\rangle_t$$

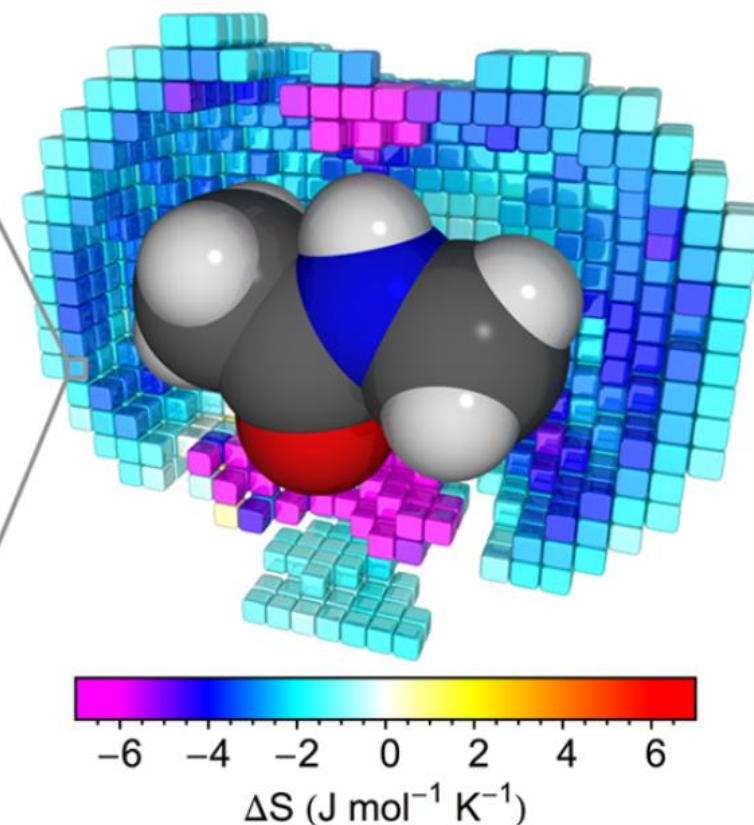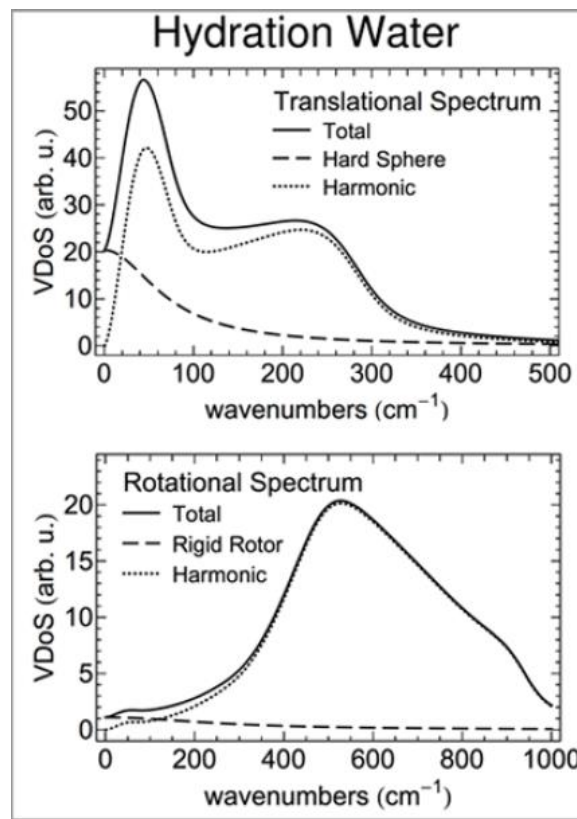$$VDoS(\omega) = \frac{2}{k_b T}\left[\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega\tau}C(\tau)d\tau\right]$$

$$\int_0^{\infty} VDoS(\omega)\, d\omega = 3N - N_{constraints}$$

# 2-Phase Thermodynamics (2PT)

Lin, Blanco, Goddard III, *JCP* 119, 11792 (2003).
Lin, Maiti, Goddard III, *JPCB* 114, 8191-8198 (2010).

- Quantify thermodynamic properties of **liquid**

- The VDoS of liquid is represented as a superposition of two analytical models
  - Hard sphere fluid ("gas-like")
  - Harmonic oscillator ("solid-like")



Hydration Water

Translational Spectrum — Total, Hard Sphere, Harmonic

Rotational Spectrum — Total, Rigid Rotor, Harmonic
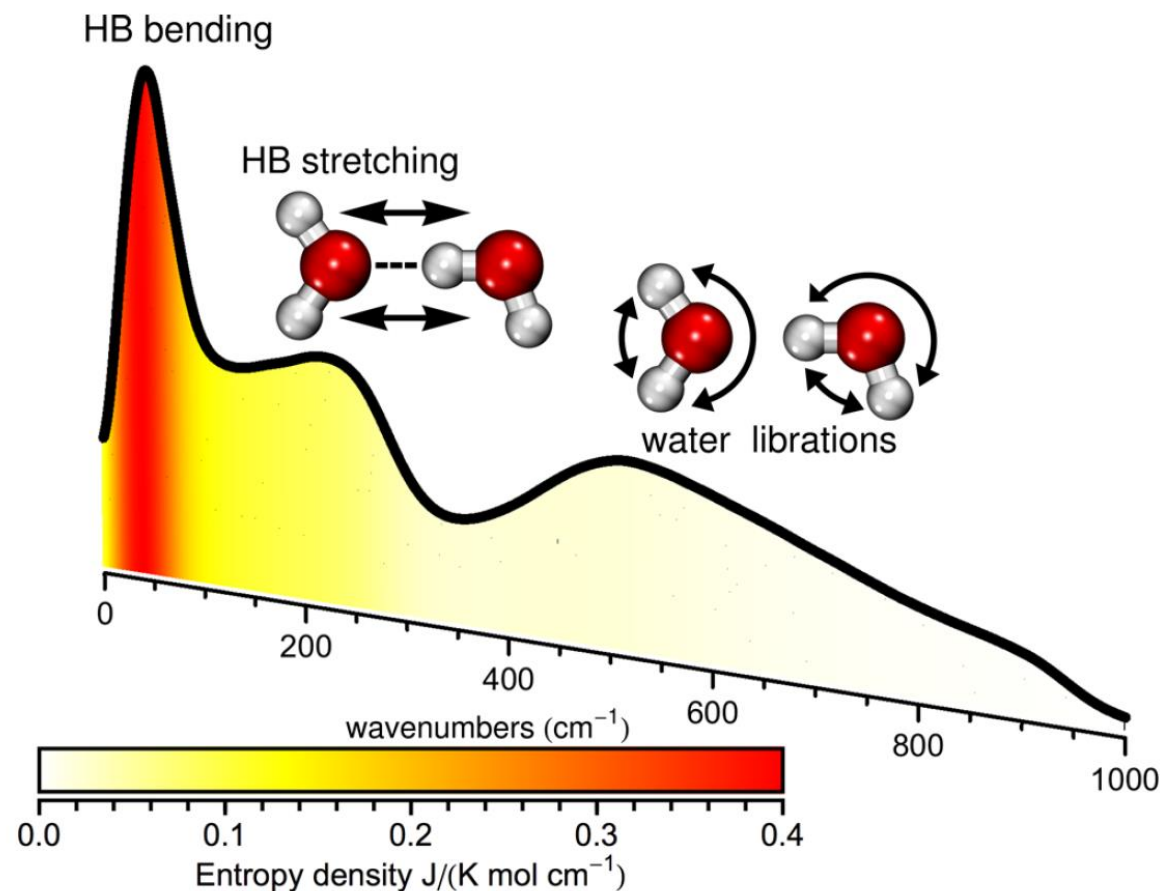
$\Delta S$ (J mol$^{-1}$ K$^{-1}$)

Rasmus A. X. Persson, Viren Pattni, Anurag Singh, Stefan M. Kast, and Matthias Heyden. *Journal of Chemical Theory and Computation.* **2017.** *13* (9), 4467-4481. DOI: 10.1021/acs.jctc.7b00184

# 2-Phase Thermodynamics (2PT)

- Decompose VDoS of liquid into **gas-like phase** and **solid-like phase**

- Describe entropy of both phases → Entropy of liquid

- **3D-2PT**