

ISOTOPE DEPENDENT, TEMPERATURE REGULATED, ENERGY REPARTITIONING IN A LOW-BARRIER, SHORT-STRONG HYDROGEN BONDED CLUSTER

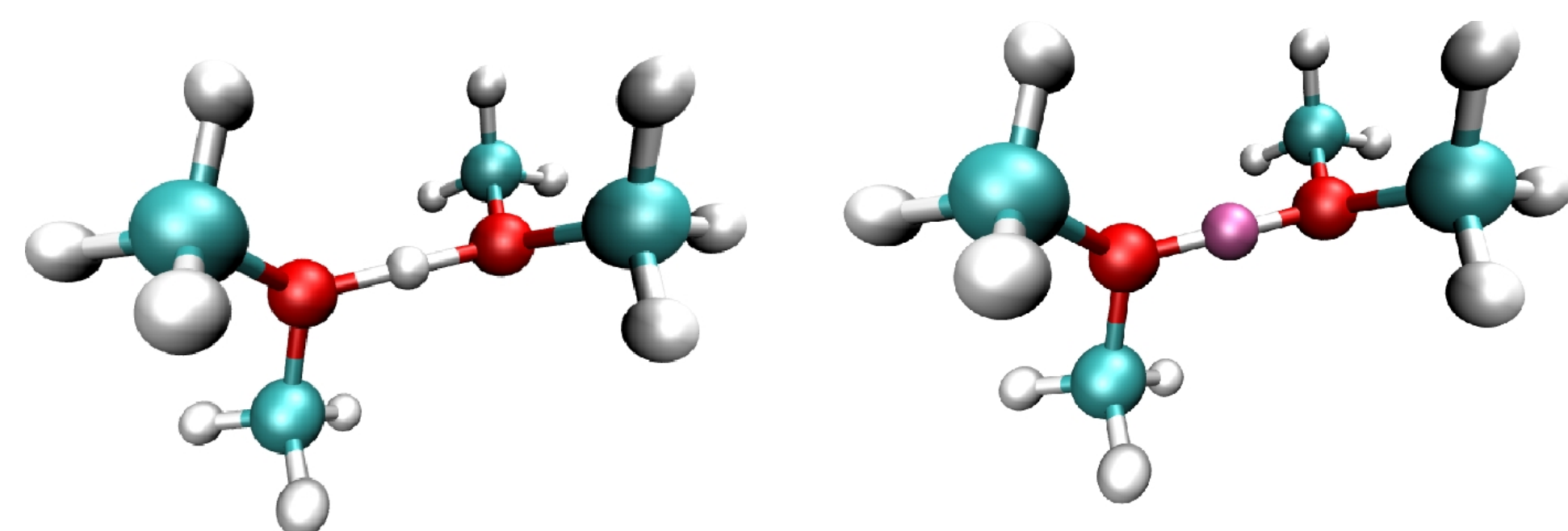
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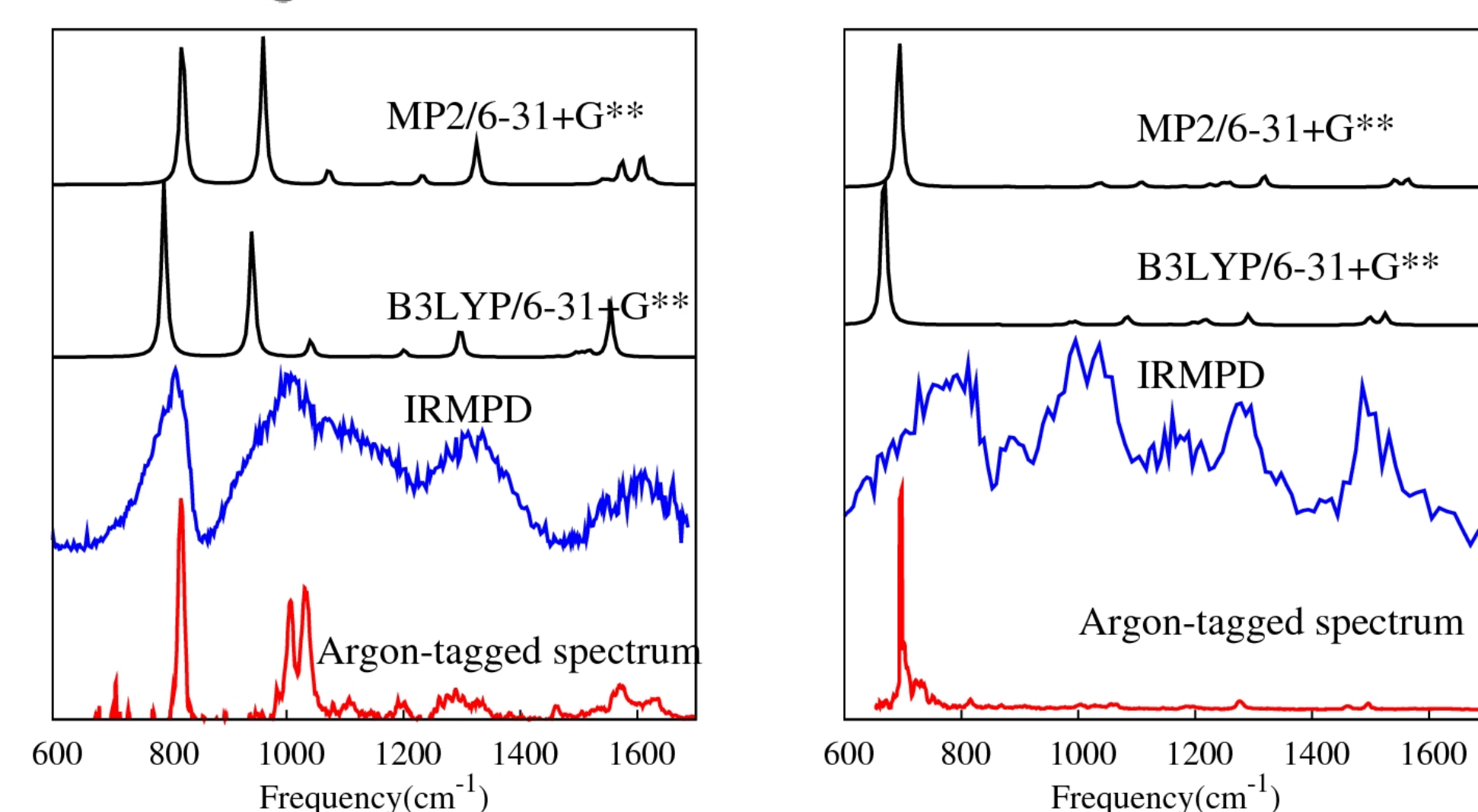
ABSTRACT

We investigate and analyze the vibrational properties, including H/D isotope effects, in a fundamental organic hydrogen bonded system using multiple experimental (infrared multiple photon dissociation and argon-tagged action spectroscopy) and computational techniques. The differences between simulated cluster spectroscopy of the isotopically labeled systems were analyzed from a system-bath coupling perspective. We have found that the energy repartitioning between modes leads to a complex spectral evolution as a function of temperature.

PROBLEM



- System: H/D bound dimethyl ether dimer
- Left Figure $[\text{Me}_2\text{O-H-OMe}_2]^+$
- Right Figure $[\text{Me}_2\text{O-D-OMe}_2]^+$
- A prototype of low-barrier, short-strong hydrogen bonding systems seen in biological, material and condensed phase chemistry.



- ### Experiments
- Argon-tagged Vibrational Spectroscopy
 - Infrared Multi-photon Dissociation (IRMPD)
- ### Observations
- Experiments at different conditions show different spectra, especially for the deuterium species.
 - IRMPD is roughly a broadened version of argon-tagged for H-spectra, but additional peak shift is seen in D-spectra.

METHODOLOGY

Simulations

- Ab initio molecular dynamics: Born-Oppenheimer and atom-centered density matrix propagation (ADMP).

Spectroscopy

- Fourier transform of both velocity and dipole auto-correlation functions. (FT-VAC and FT-DAC)

$$I_V(\omega) = \int dt \exp(-i\omega t) \langle \mathbf{V}(\mathbf{0}) \cdot \mathbf{V}(t) \rangle$$

$$\alpha_\mu^{QC}(\omega) \propto \omega^2 \left\{ \int dt \exp(-i\omega t) \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \right\}$$

Analysis of spectroscopy

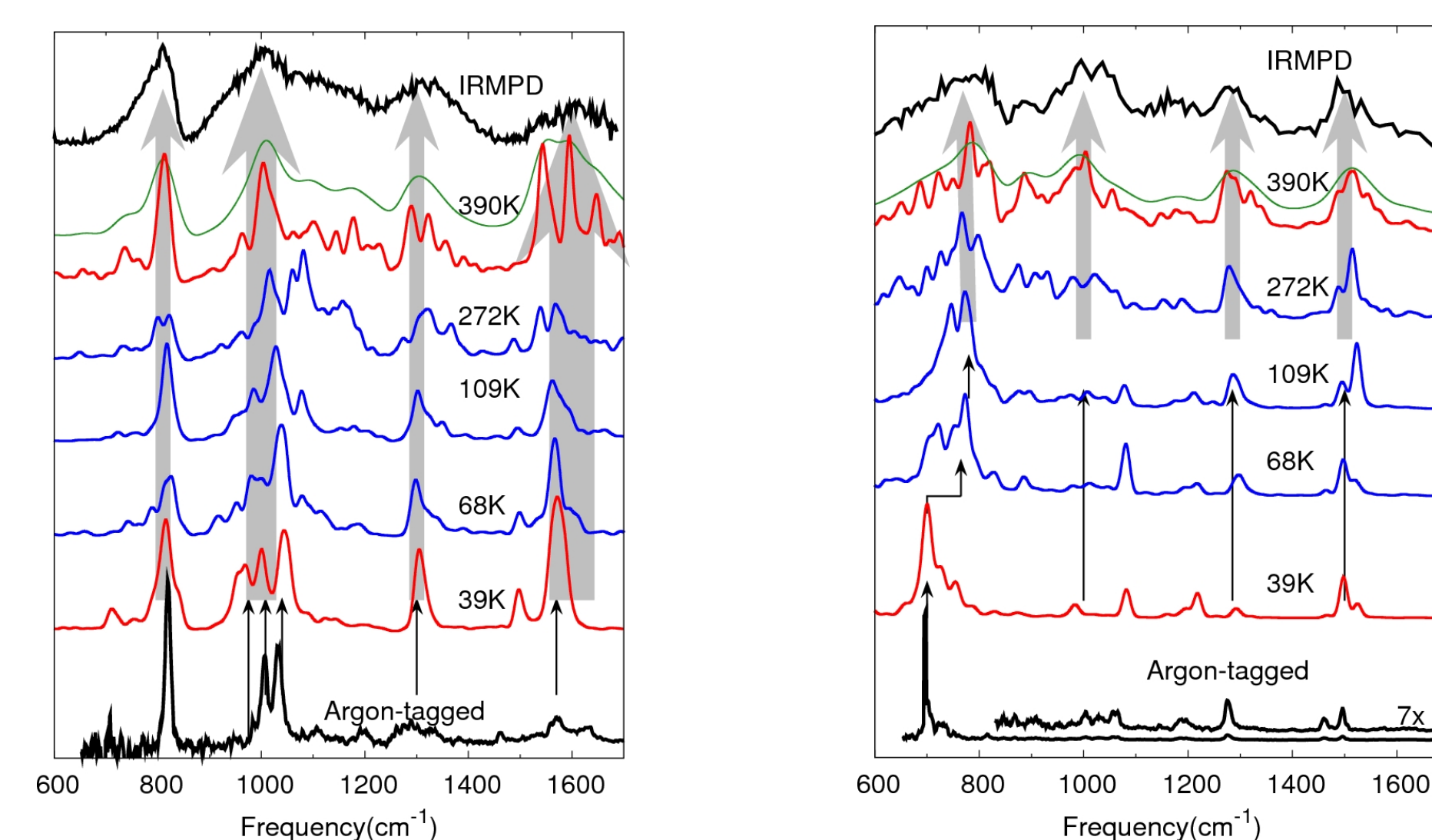
- Decomposition of vibrational density states to local modes \Rightarrow energy repartitioning

$$\mathcal{V}_{i,j}(\omega) = \int dt \exp(-i\omega t) \tilde{V}_{i,j}(t)$$

$$\tilde{V}(\omega) = \sum_i C_i(\omega) * \tilde{H}_i$$

- $C_i(\omega)$ —energy content in the i -th mode.
- Evolution of $C_i(\omega)$ as function of temperature enable us to probe the energy repartitioning.

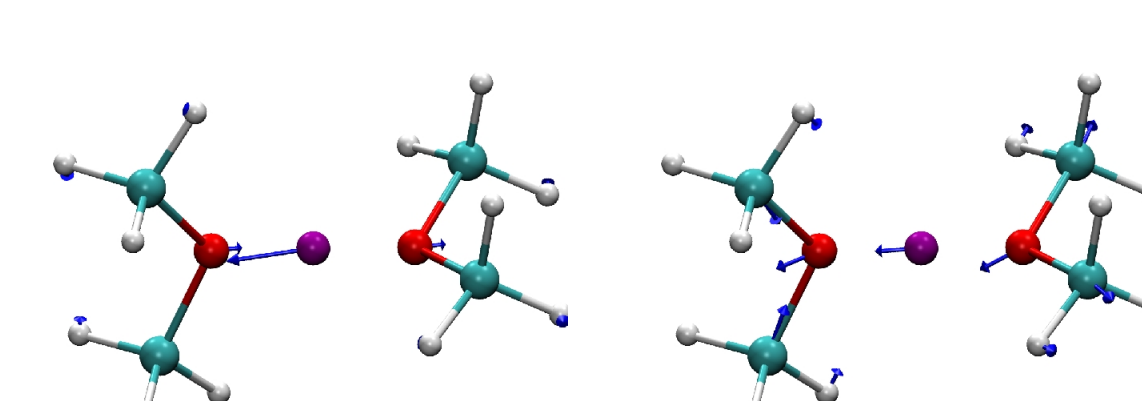
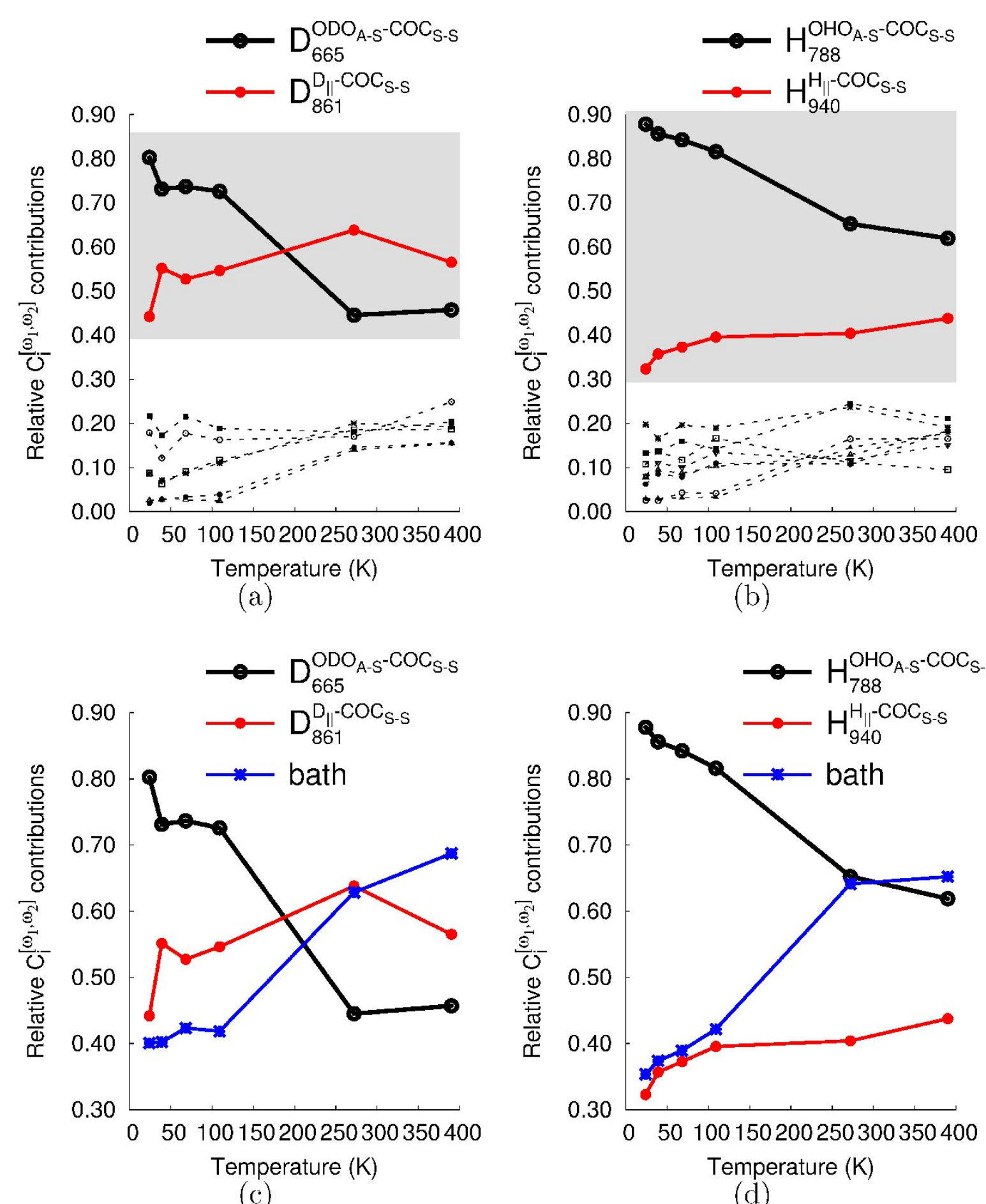
RESULTS



$[\text{Me}_2\text{O-H-OMe}_2]^+$

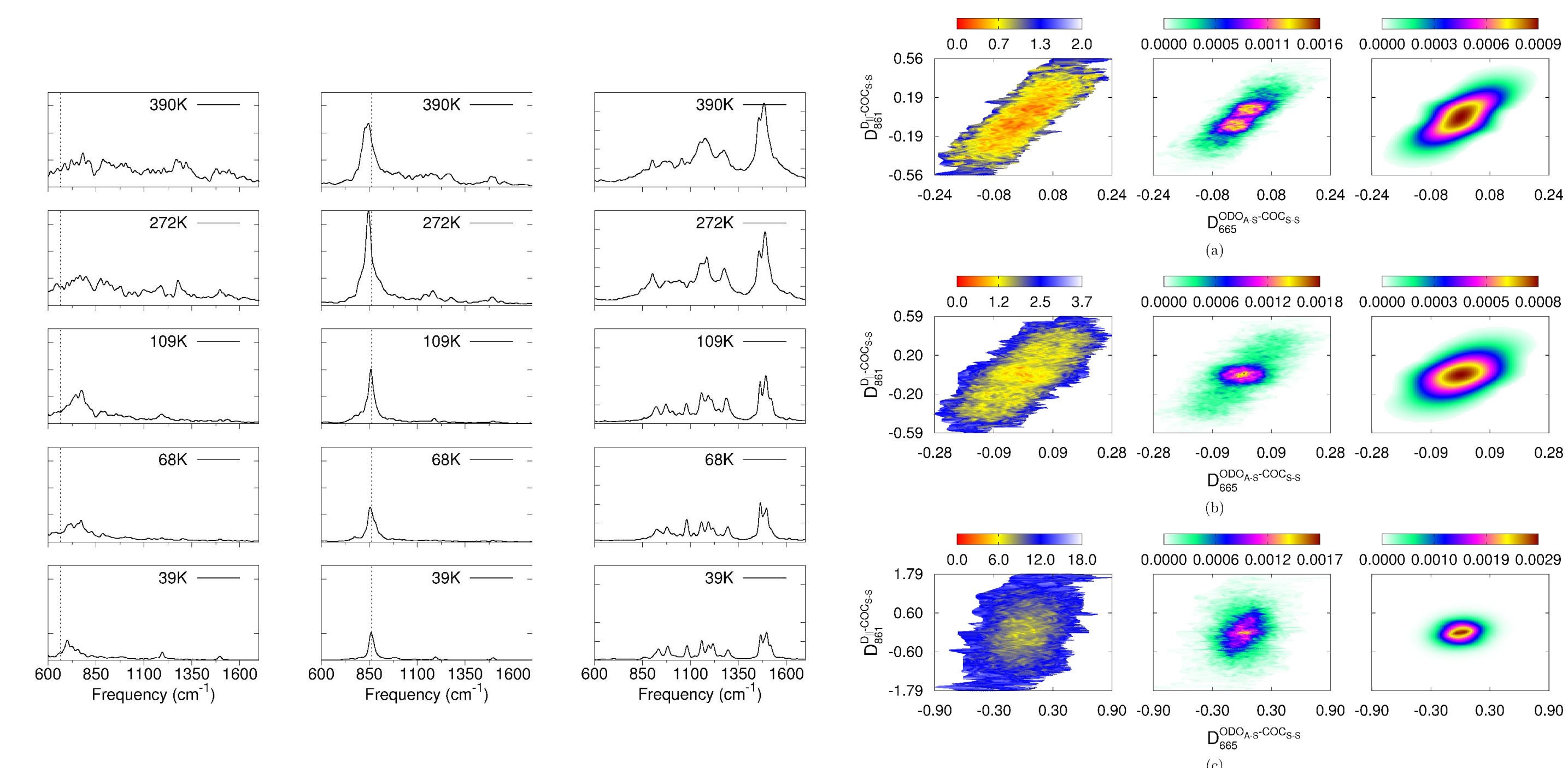
$[\text{Me}_2\text{O-D-OMe}_2]^+$

- We reproduced argon-tagged and IRMPD results at low and high temperature. Intermediate simulated spectra show smooth progression between two experimental results.
- Blue shift of the peak $\approx 700 \text{ cm}^{-1}$ from low to high temperature for deuterium spectra, but absent in that of hydrogen.



- Two dominant modes involving OHO stretch, COC stretch and methyl wag dominated energy in $600 \sim 860 \text{ cm}^{-1}$ (blue shift region for D-spectra)

- Weaker system-bath coupling in deuterium causes efficient energy between the two system modes, which causes the blue-shift in D spectra.



- $C(\omega)$: deuterium spectra is determined by the energy content inside the light mode $\text{D}_{665}^{\text{ODO}_{\text{A-S}}-\text{COC}_{\text{S-S}}}$
- Temperature regulates coupling between modes through sampling of anharmonicity in potential surface.
- Quantum and classical distributions are similar in the right two panel of the right figure.

CONCLUSIONS

- We obtained measured spectra consistent with experiments at different conditions using single potential surface, with temperature as the only independent parameter.
- A weaker system-bath coupling in D systems causes a blue-shift in spectrum, whereas a strong system-bath coupling leads energy from system modes to dissipate into bath modes.

ACKNOWLEDGMENT

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Reference

Xiaohu Li, et. al. *J. Chem. Phys.*, In Press, Xiaohu Li, et. al. *J. Chem. Phys.*, **128**, 184308 (2008), D. T. Moore, et. al. *ChemPhysChem*, **5**, 740 (2004), J. R. Roscioli, et. al. *Science*, **316**, 249 (2007)