東京大学
THE UNIVERSITY OF TOKYO

Daiguji & Hsu Lab
Thermal Engineering
MECH
mechanical engineering

Daiguji and Hsu Lab

第62回 日本伝熱シンポジウム／HTSJ国際伝熱シンポジウム
The 62nd National Heat Transfer Symposium/HTSJ International Heat Transfer Symposium

Alterations in vibrational spectra of adsorbed water

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17th May 2025

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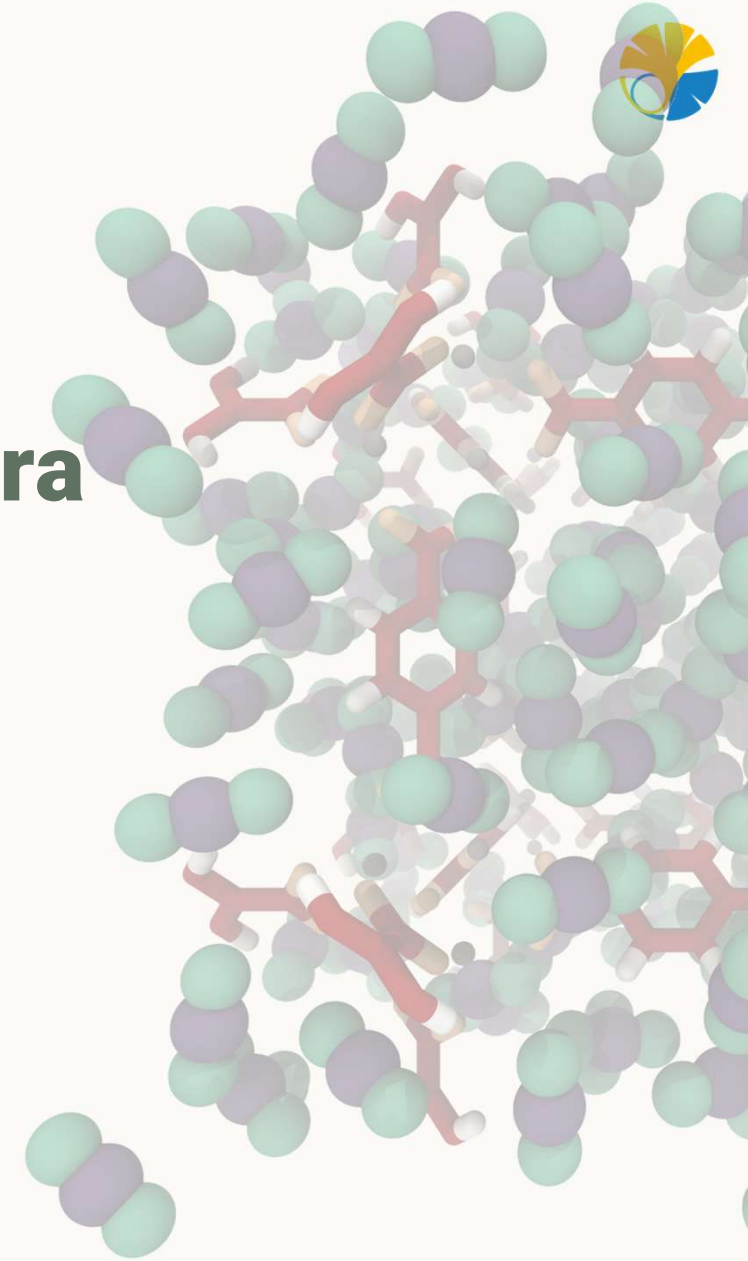
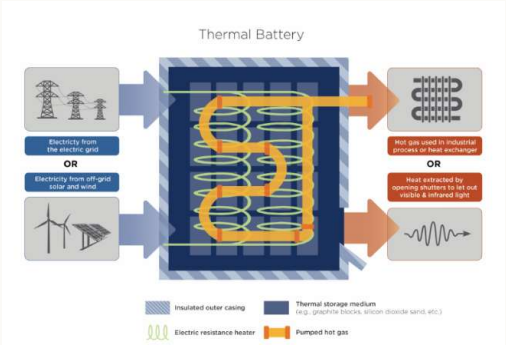


Why water adsorption matters?

Thermal batteries

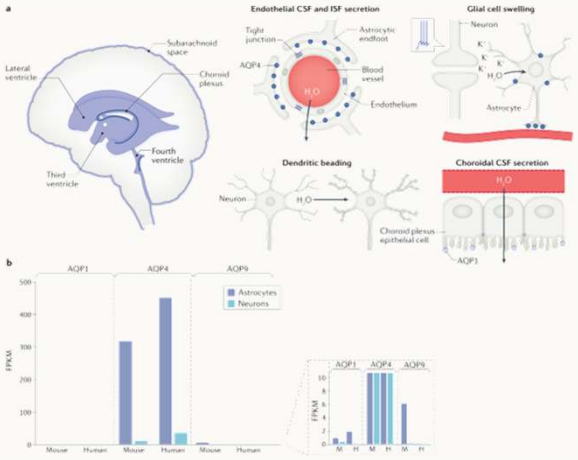


Energy Innovation: Policy and Technology, Forbes, 2023

Dehumidification

ECS, Desiccant Dehumidification, Desiccant wheel

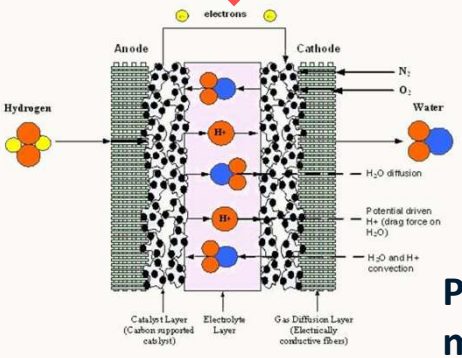
Water adsorption



Drug development/ Brain chemistry

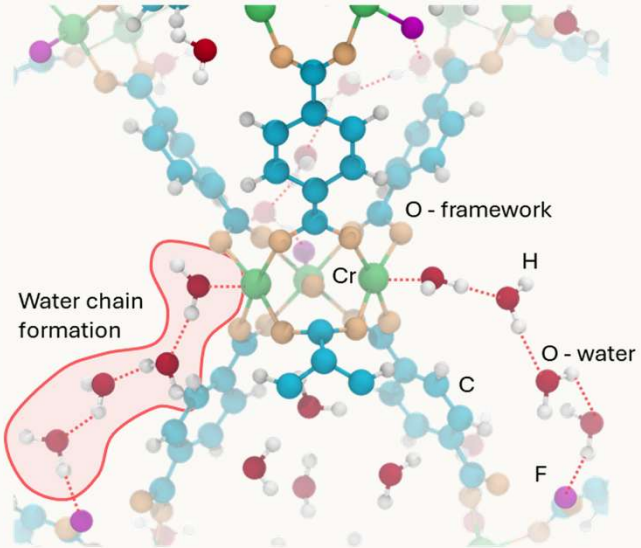
N. MacAulay, Nat. Rev. Neurosci., 2021

Desalination

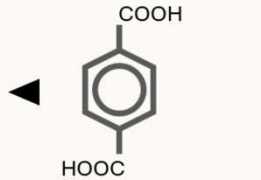


Proton exchange membranes

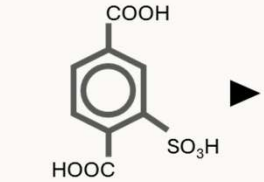
What we studied?



Water adsorption in MIL-101
(650 Pa, 298 K)

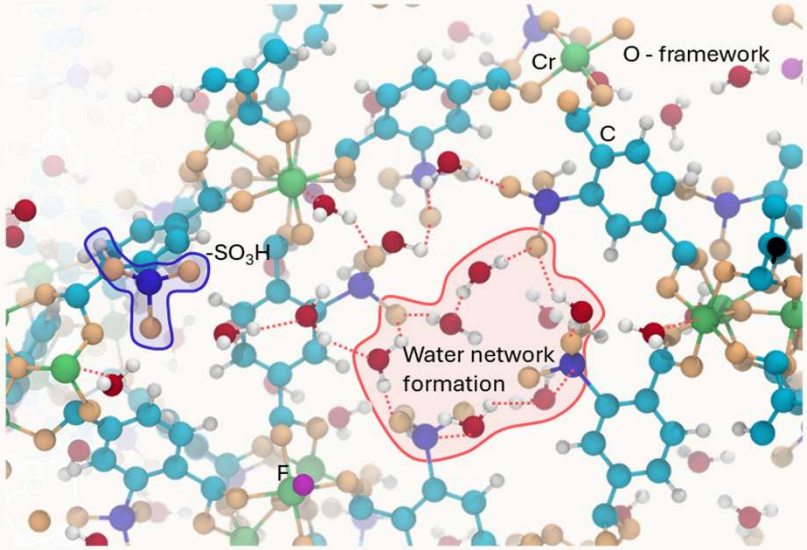


1,4 – benzene-
-dicarboxylate (BDC)

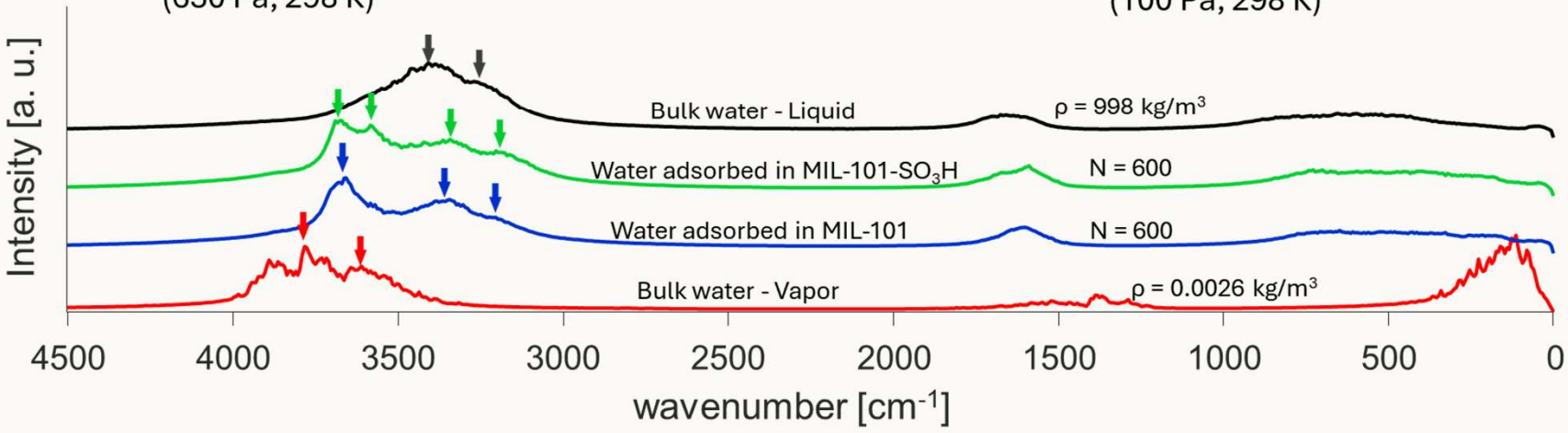


Functionalized
1,4 – BDC

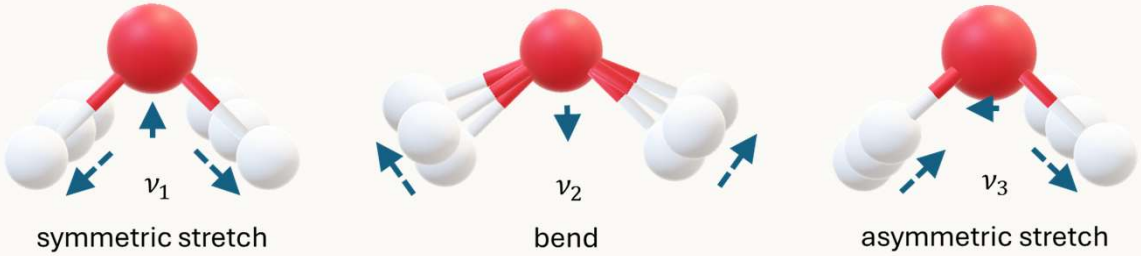
Organic ligands



Water adsorption in MIL-101-SO_3H
(100 Pa, 298 K)

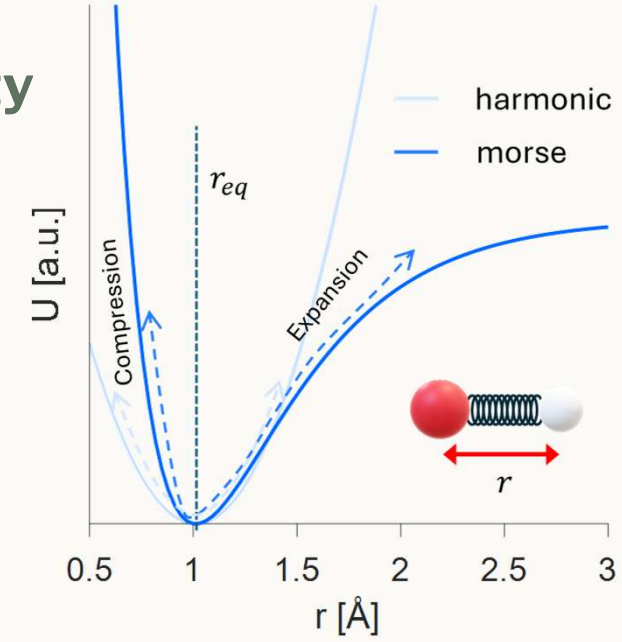


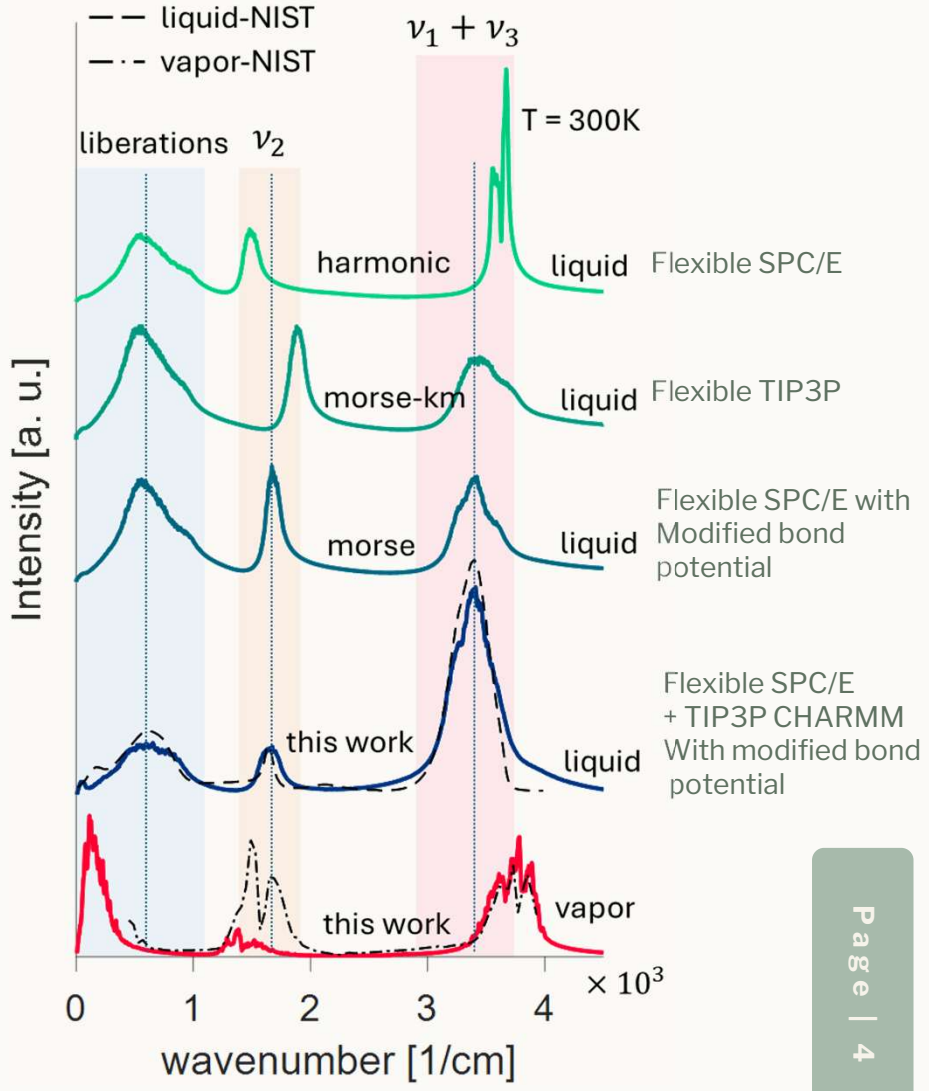
Challenges in simulating water



Anharmonicity

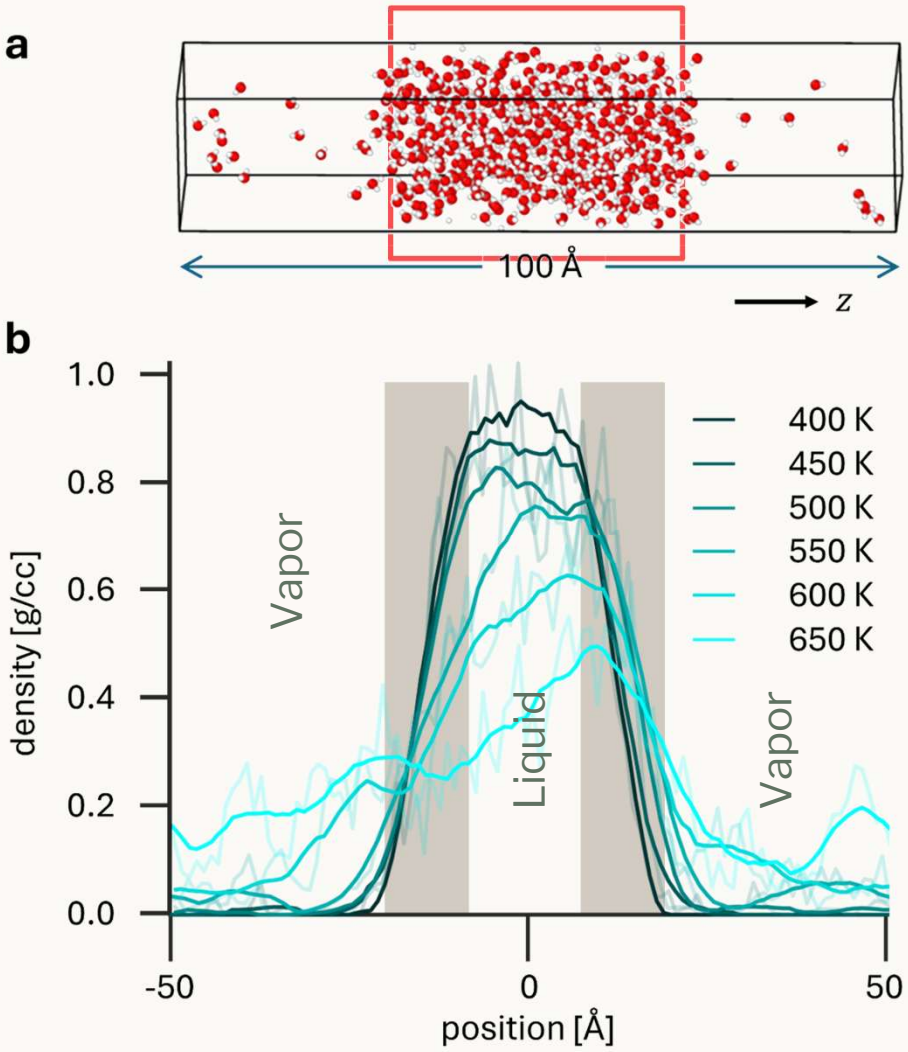
O-H bond easier to stretch than compress

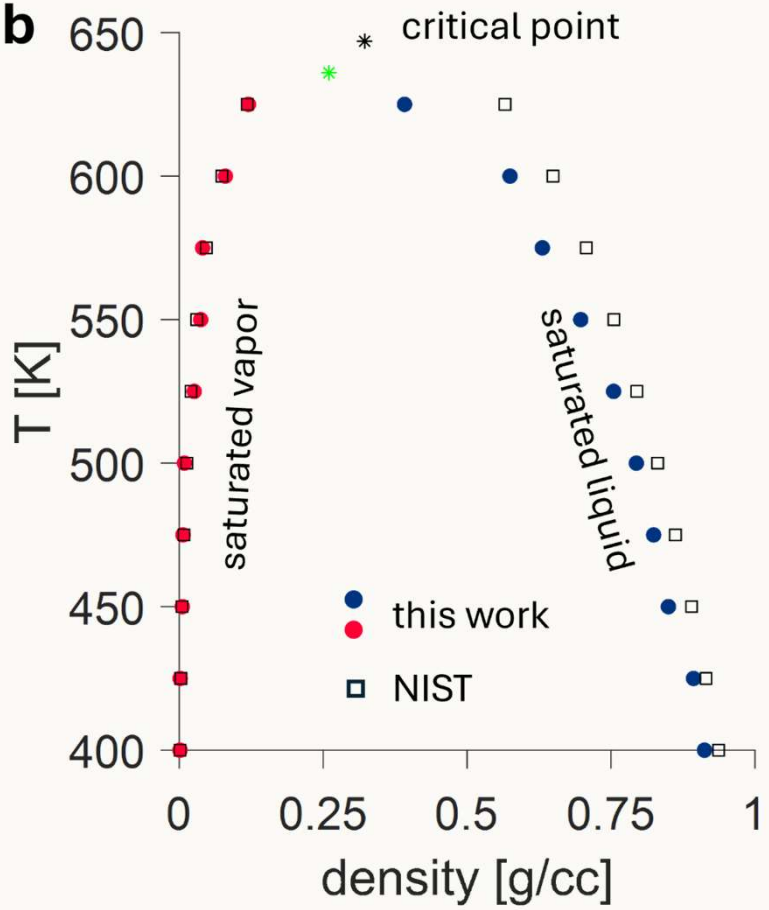




[Accepted] Auti, G. et al. Physical Chemistry Chemical Physics, 2025

Validating the water model



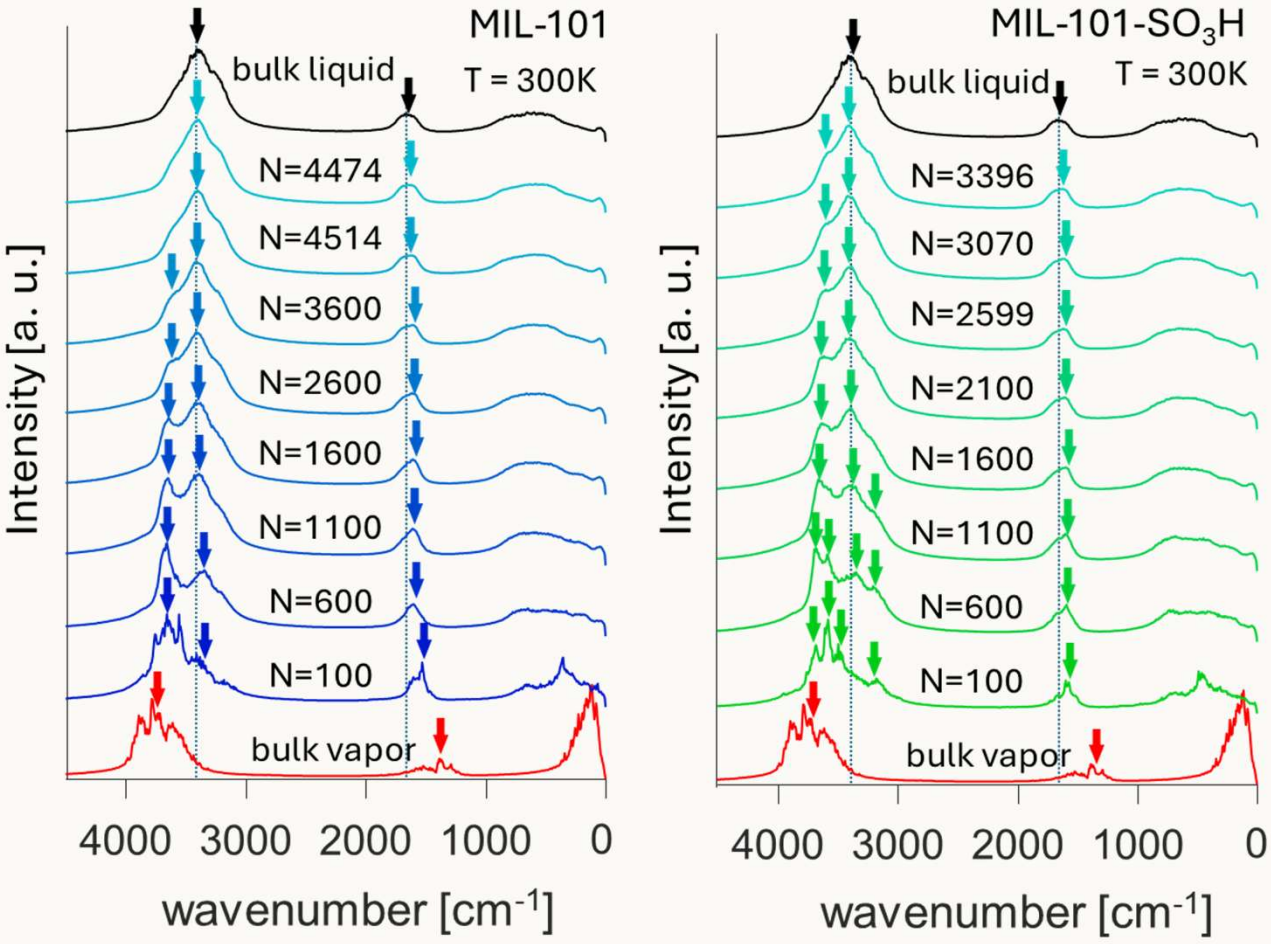


Spectra of adsorbed water

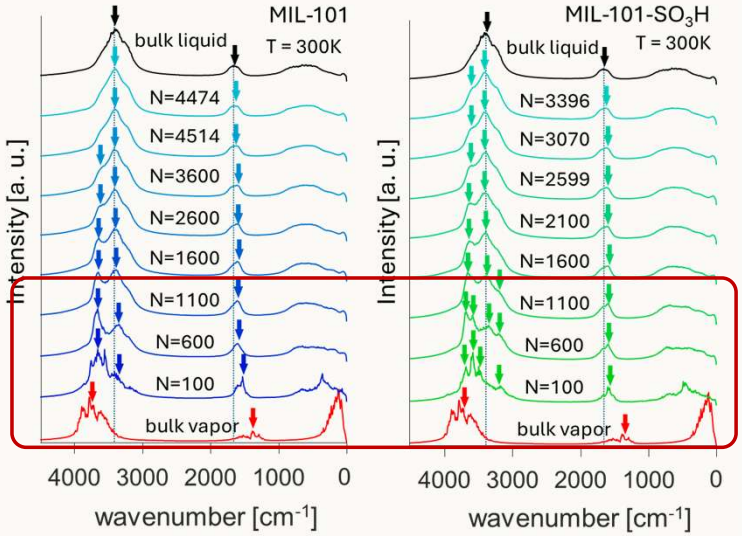
$$I(\omega) = \int_{-\infty}^{\infty} C_{vv}(t) e^{i\omega t} dt$$

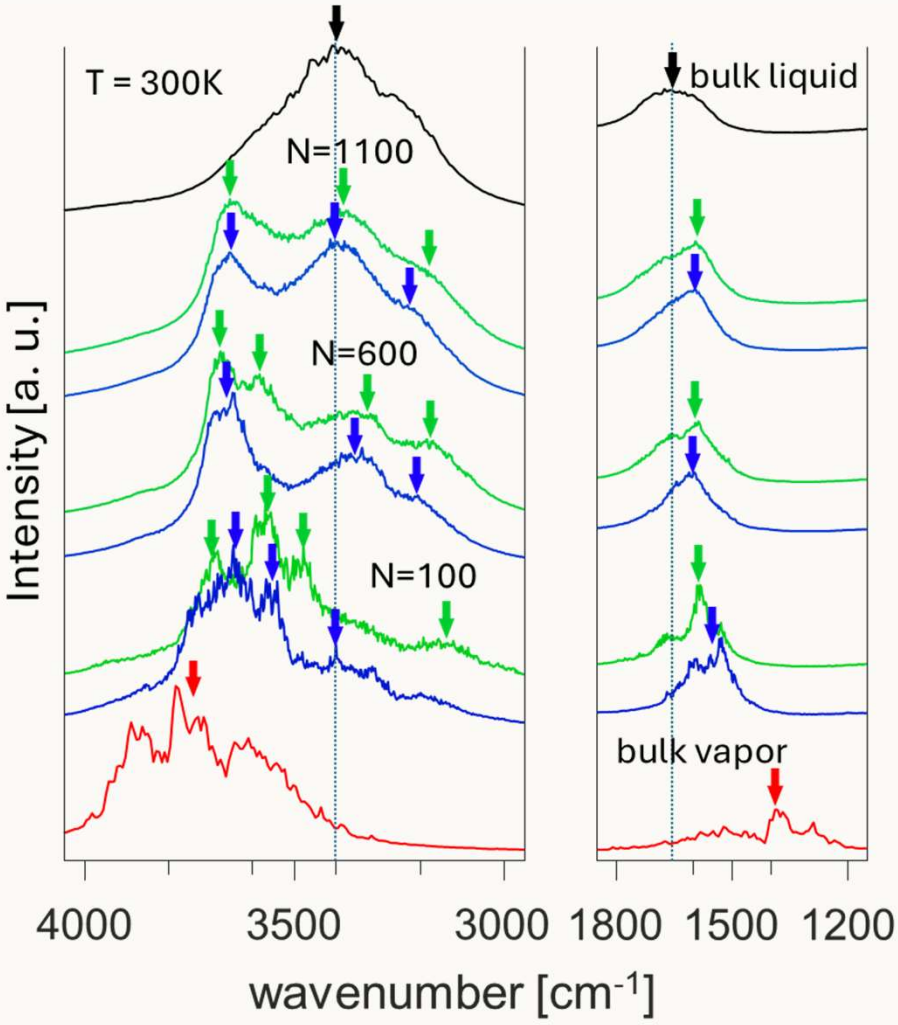
$$C_{vv}(t) = \frac{1}{N} \sum_{i=1}^{N} \vec{v}_i(t) \cdot \vec{v}_i(0)$$

Velocity autocorrelation function



Spectra of adsorbed water





Normal mode analysis

$$\vec{F} = -\frac{dV}{dx} = -kx \quad \& \quad -kx = -m\frac{d^2x}{dt^2}$$

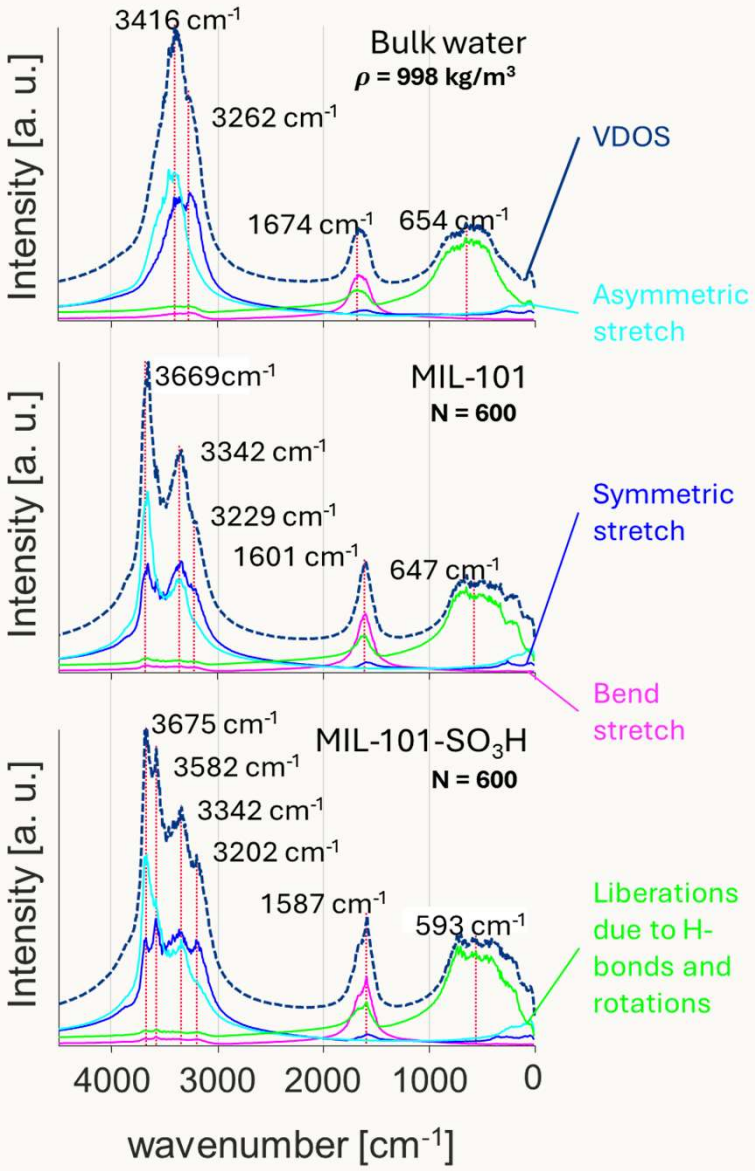
$$-kx = -4\pi^2\nu^2 mx$$

In three dimensions and for a set of N atoms,

$$\boldsymbol{HX} = 4\pi^2\nu^2\boldsymbol{X}$$

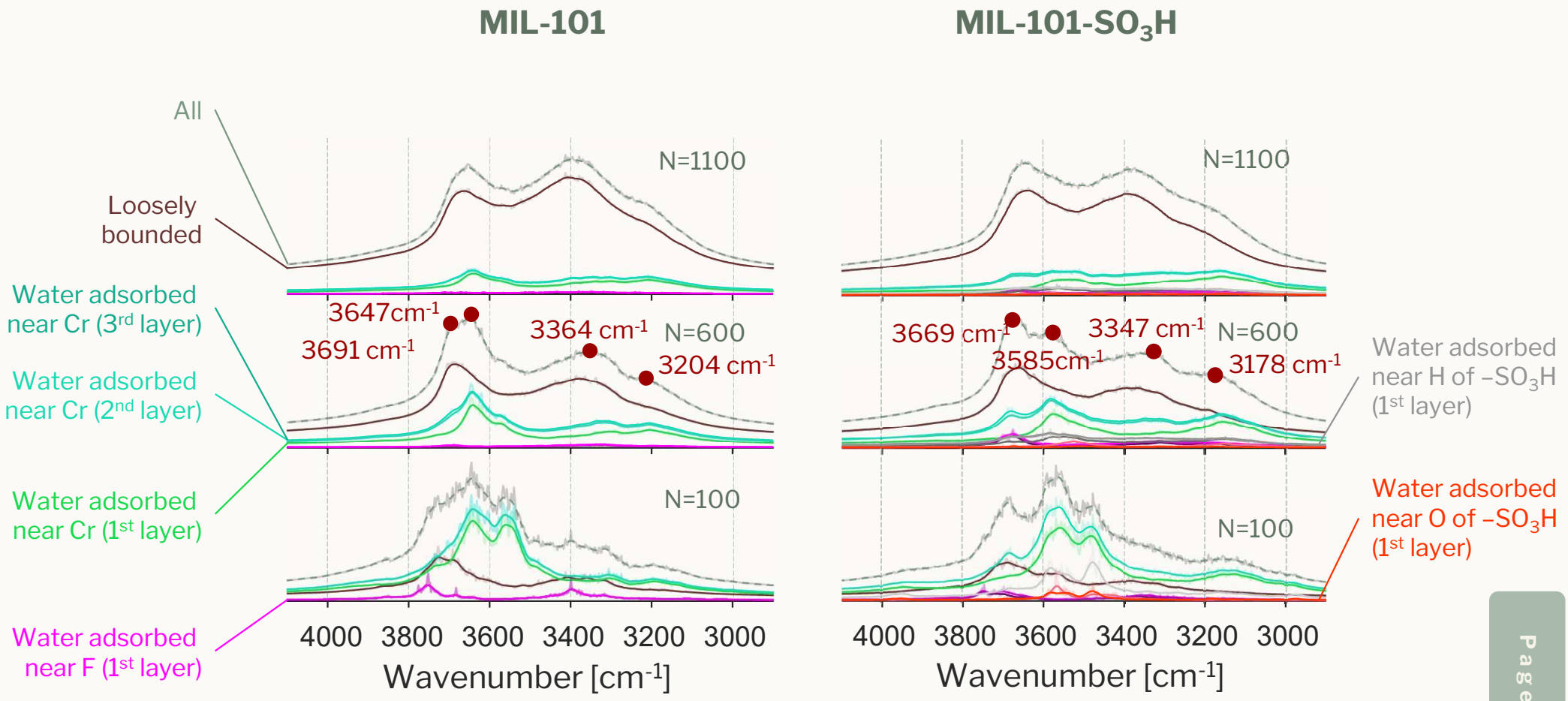
$$\boldsymbol{H} = \begin{bmatrix} \boldsymbol{H_{11}} & \cdots & \boldsymbol{H_{1N}} \\ \vdots & \ddots & \vdots \\ \boldsymbol{H_{N1}} & \cdots & \boldsymbol{H_{NN}} \end{bmatrix}, \boldsymbol{H_{ij}} = \begin{bmatrix} \frac{\partial^2 U}{\partial X_i \partial X_j} & \frac{\partial^2 U}{\partial X_i \partial Y_j} & \frac{\partial^2 U}{\partial X_i \partial Z_j} \\ \frac{\partial^2 U}{\partial Y_i \partial X_j} & \frac{\partial^2 U}{\partial Y_i \partial Y_j} & \frac{\partial^2 U}{\partial Y_i \partial Z_j} \\ \frac{\partial^2 U}{\partial Z_i \partial X_j} & \frac{\partial^2 U}{\partial Z_i \partial Y_j} & \frac{\partial^2 U}{\partial Z_i \partial Z_j} \end{bmatrix}$$

Eigenvalues of this **H correspond to the normal modes of vibration**

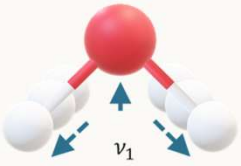


C. Atilgan et al, Ann. Rev. Biophysics, 2012

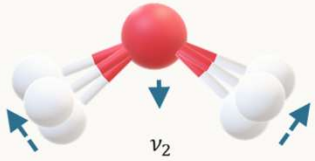
Site specific adsorption



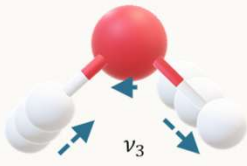
Summary



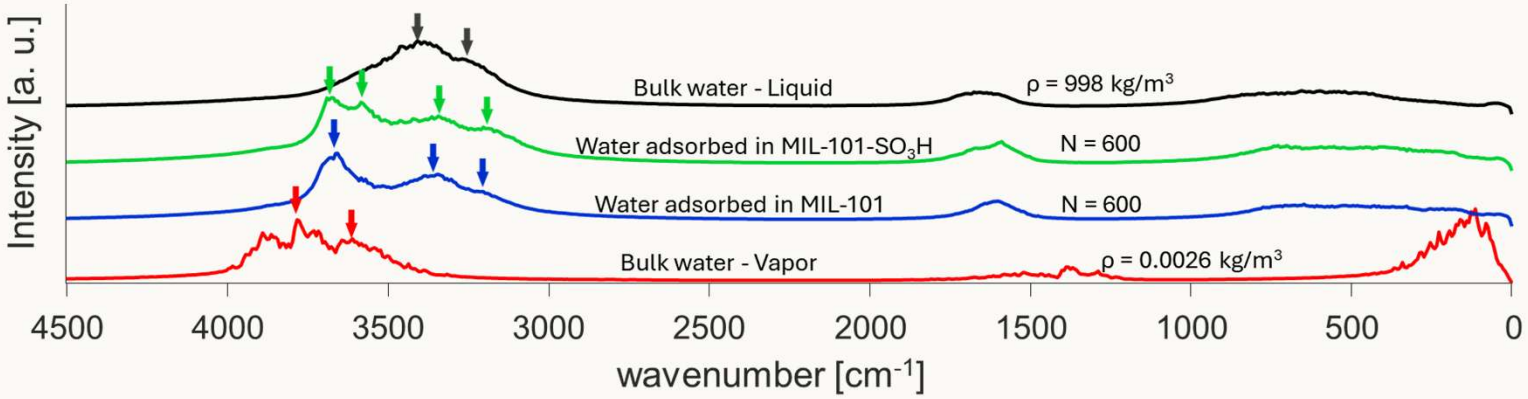
symmetric stretch



bend



asymmetric stretch



G. Auti, H. Jiang, J.-J. Delaunay, and H. Daiguji, Phys. Chem. Chem. Phys., 2025 (accepted)

Graduate student: **Jiang Hao**

DAIKIN

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Core Research for Evolutionary Science and Technology
JST, CREST Grant No. JPMJCR17I3

Thank you!