

# Ultrafast Water H-Bond Rearrangement in a Metal–Organic Framework Probed by Femtosecond Time-Resolved Infrared Spectroscopy

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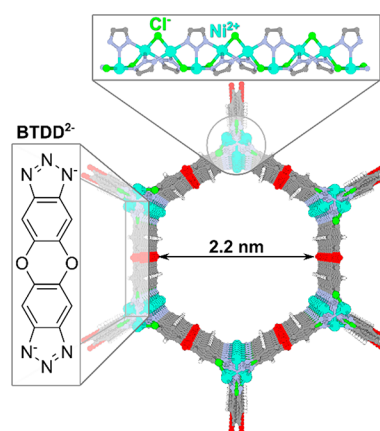
Supporting Information

**ABSTRACT:** We investigated the water H-bond network and its dynamics in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ , a prototypical MOF for atmospheric water harvesting, using linear and ultrafast IR spectroscopy. Utilizing isotopic labeling and infrared spectroscopy, we found that water forms an extensive H-bonding network in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ . Further investigation with ultrafast spectroscopy revealed that water can reorient in a confined cone up to  $\sim 50^\circ$  within 1.3 ps. This large angle reorientation indicates H-bond rearrangement, similar to bulk water. Thus, although the water H-bond network is confined in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ , different from other confined systems, H-bond rearrangement is not hindered. The picosecond H-bond rearrangement in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  corroborates its reversibility with minimal hysteresis in water sorption.

Freshwater scarcity is a growing problem due to pollution, increased urban density, and the exhaustion of freshwater sources. Materials based on metal–organic frameworks (MOFs) have been pursued in water processing and recycling. MOFs are highly porous tunable materials formed through the self-assembly of organic linkers and metal clusters. The resulting well-defined pores, up to several nanometers in diameter, give MOFs the highest surface areas measured to date, making them appealing for water processing.<sup>1</sup> Many MOF-based acquisitions of fresh water<sup>2–7</sup> rely on specific control of MOF–water interactions. Particularly, atmospheric water harvesting (AWH)<sup>8</sup> requires fast and reversible water sorption over a narrow and convenient humidity range (10–30%), which demands exquisite manipulation of water–water and water–framework interactions.<sup>9,10</sup>

Although fundamental physical studies of water in MOF pores have led to the development of more efficient MOFs for AWH,<sup>11–14</sup> there are significant barriers to understanding water H-bond networks and dynamics in MOFs, as water molecules may not behave the same way when confined over nanometer length scales as they do in bulk.<sup>15–20</sup> These challenges are rooted in the characterization methods for MOFs. Diffraction-based methods boast atomic precision but are limited to water that is close to crystalline<sup>11,21,22</sup> and are insensitive to liquid-phase water dynamics. Linear spectroscopy has revealed distributions of water–water H-bonds in MOFs but similarly lacks time resolution.<sup>23,24</sup> MD simulations can provide detailed dynamics, which remain to be verified experimentally. Ultrafast time-resolved spectroscopies are not traditionally applied to powders because of optical scatter. However, methods to overcome this issue have been developed in recent years and it is now possible to optically probe the dynamics of molecules in highly scattering solid samples.<sup>25–28</sup>

Here, we reported water H-bonds and dynamics in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  (BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*][4',5'-*i*])dibenzo[1,4]dioxin) (Figure 1), a promising AWH



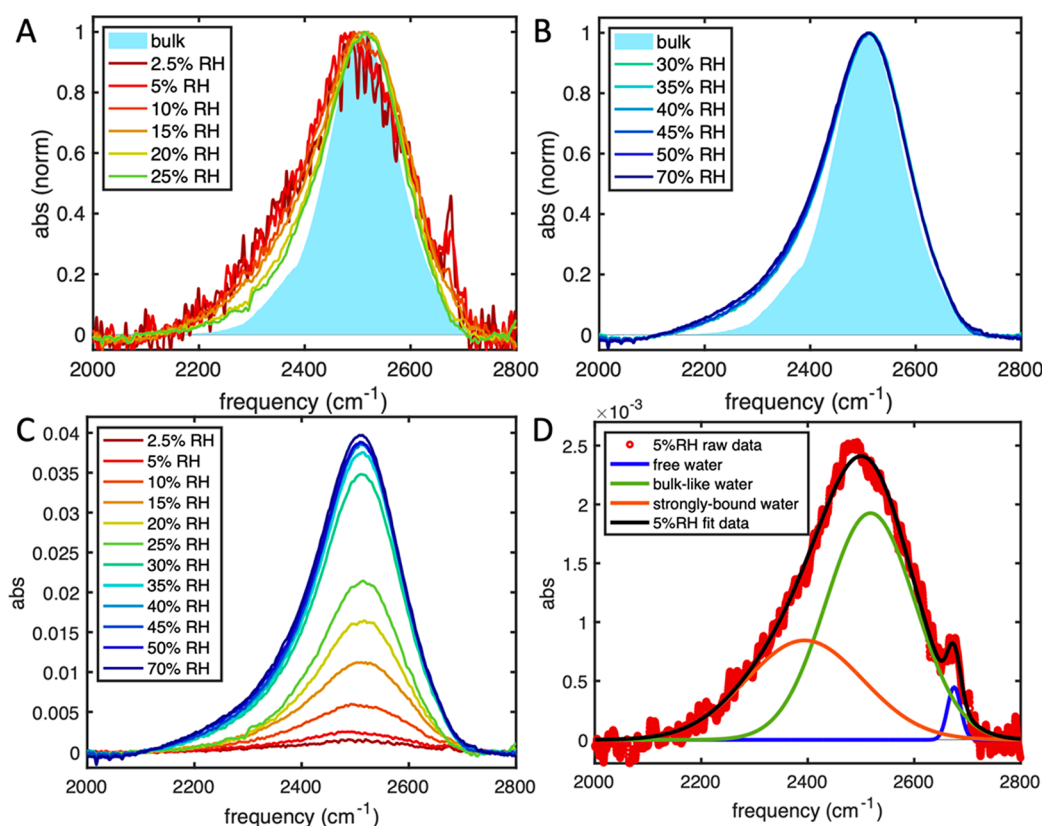
**Figure 1.**  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  structure with H-bond acceptors (N, O, and  $\text{Cl}^-$ ) and open metal sites ( $\text{Ni}^{2+}$ ).

MOF,<sup>29,30</sup> using a suite of linear and nonlinear infrared spectroscopies.  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  boasts a series of linear hexagonal channels with a pore diameter of 2.2 nm, near the “critical diameter” for water adsorption, which allows for high-capacity reversible water uptake over a narrow pore-filling step.

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**Figure 2.** FTIR spectra of HOD in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ . Normalized background-subtracted spectra of HOD in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  compared to HOD in bulk water (solid filled area) at humidities (A) from 2.5% to 25% RH and (B) from 30% to 70% RH. (C) Raw background-subtracted spectra of HOD in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  at humidities from 2.5% to 70% RH. (D) Fitted background-subtracted spectra of HOD in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  at 5% RH.

We found a similar but stronger H-bond network in the MOF pores than in bulk water. Ultrafast measurements showed that the water network dynamics in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  are intermediate between dynamics in bulk water and in other confined systems.<sup>31</sup> Water in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  exhibited an inertial libration that is too fast to be resolved, just like bulk water systems, and constrained slow rotations beyond the lifetime of OD modes, similar to other confined systems. However, water in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  displays a picosecond rotation that is constrained in an  $\sim 50^\circ$  angle. The large angle indicates H-bond rearrangement, highlighting its easiness in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ , a key difference from other confined systems.

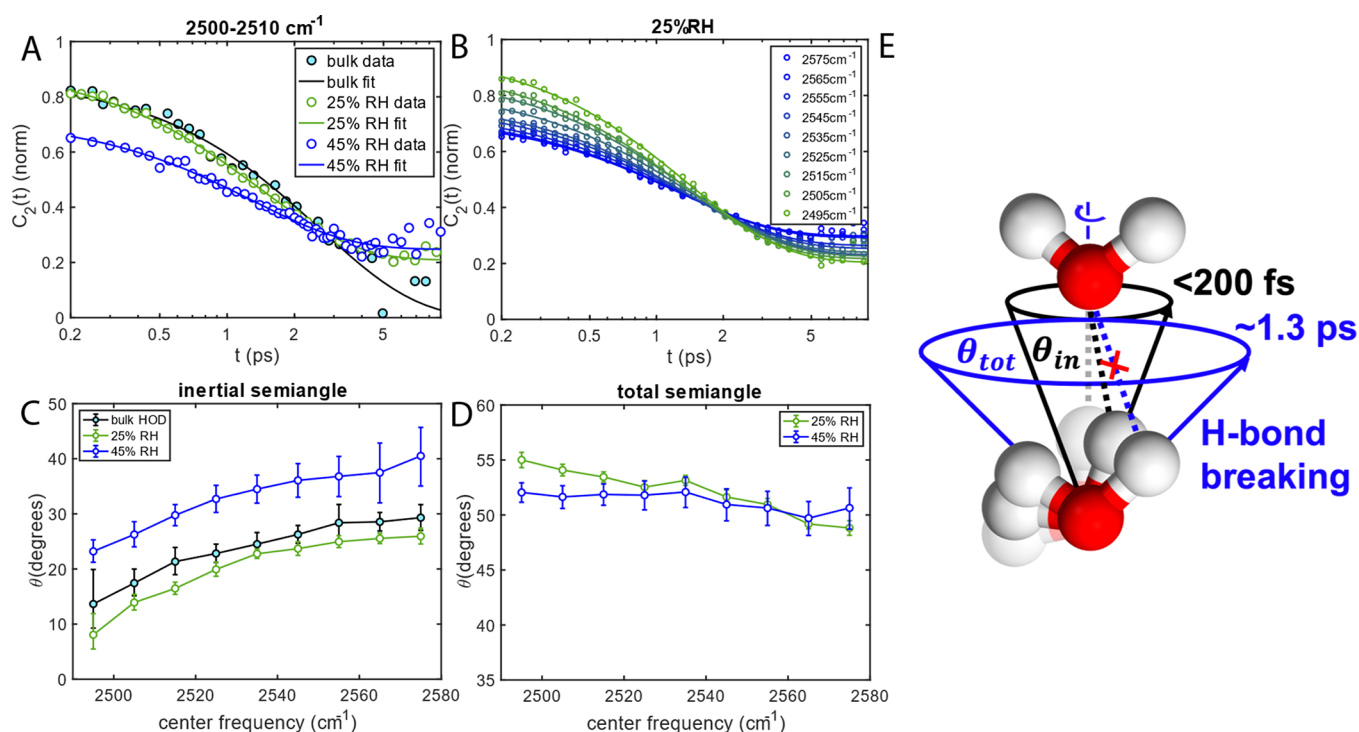
Insights into water adsorption in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  have already been made using infrared spectroscopy.<sup>12</sup> However, to obtain further details, it is necessary to reduce spectral congestion, as  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  and water both have complicated IR spectra. This was accomplished through a combination of isotopic labeling and background subtraction. We mixed  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  to obtain a 10% HOD in  $\text{H}_2\text{O}$  solution. The OD stretch of HOD molecules in  $\text{H}_2\text{O}$  removes the effects of symmetric and antisymmetric modes and reduces the effects of delocalization and Fermi resonances<sup>32</sup> that complicate  $\text{H}_2\text{O}$  spectra.<sup>33</sup> Subtracting  $\text{H}_2\text{O}/\text{Ni}_2\text{Cl}_2\text{BTDD}$  peaks further simplified the spectra (see Figures S7–S8 in the Supporting Information).

After subtraction, we can detect three separate peaks.<sup>12</sup> First, there is a sharp high-frequency peak near  $2650\text{ cm}^{-1}$ , which is a “free water” peak corresponding to OD stretches with no H-bonds<sup>34</sup> (Figure 2A). Second, there is a main peak around  $2500\text{ cm}^{-1}$  that is overlapped with the OD stretches of bulk water. We refer to this central peak as “bulk-like”. Finally, we

observed a broad low-frequency shoulder (“strongly bound water”) around  $2400\text{ cm}^{-1}$ . The “strongly bound water” describes water with high H-bond donor characteristics<sup>35</sup> (Figure 2D). The Fermi resonance peak<sup>12</sup> at even lower frequencies disappears in HOD spectra (see Figure S10 in the Supporting Information).

The free, bulk-like, and strongly bound water peaks show dramatic changes in the early stages of pore filling (Figure 2A). The free water peak is only significant below 15% RH, indicating that all water molecules experience H-bonds when the pores are partially or completely filled. This contrasts with FTIR results of some other MOFs, which continue to exhibit the free water peak even when the pores are full.<sup>21,23,36,37</sup>

The strongly bound peak and bulk-like peak, in contrast, remain significant at all water loadings. We assign the strongly bound peak at low water loadings to waters with strong interactions to the framework triazolates and open metal sites. This assignment follows theoretical predictions<sup>31</sup> and is further supported by the spectra in the fingerprint region, which indicates that the environment around the triazolate group changes most significantly at the lowest water loadings (Figure S9.1). The detailed description of the strongly bound peak at low water loadings is only possible due to the removal of Fermi resonance.<sup>12,36</sup> The low-frequency end of the OD band decreases in relative intensity as water loading increases, but its absolute absorbance increases with water loading (Figure 2C) and never becomes negligible like the free water peak, which is clear when comparing the MOF HOD spectra to bulk HOD (Figure 2B).



**Figure 3.** PSPP measurements. (A) Anisotropy dynamics taken from 2500 to 2510  $\text{cm}^{-1}$  and (B) anisotropy dynamics at 25% RH taken at each frequency region from 2495 to 2575  $\text{cm}^{-1}$ . (C) Inertial and (D) total cone semiangles as a function of frequency. Error bars show 95% confidence from fitting. (E) Schemes of the wobbling-in-a-cone model. Before wobbling, the hydroxyl group points to the acceptor oxygen with H-bond (gray dashed line). Within  $<200$  fs, the hydroxyl group wobbles within inertial cone semiangle  $\theta_{in}$  (black cone) along the O–O axis which does not have a large angle to break H-bonds (black dashed line). Within  $\sim 1.3$  ps, the hydroxyl group wobbles within the total cone semiangle  $\theta_{tot}$  (blue cone), large enough to break H-bonds (blue dashed line).

These trends indicate the following filling mechanism: initial water binding occurs at the highly charged open metal and triazolate sites shown in Figure 1. Evidence for this initial binding site is found in large shifts to the triazolate band, which may be due to either direct water–triazolate interactions or changes in the ligand–metal interactions that result from water binding.<sup>38,39</sup> Additional water molecules then bind to the waters at these charged sites, forming H-bond chains that include most of the pore water at humidities above 15%. The fact that the absorbance of the strongly bound peak increases with water loading indicates strong water–water H-bonds as well. This observation agrees with the water sorption mechanism previously proposed for  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ .<sup>12,31</sup> However, FTIR alone reveals few differences between the pore water corresponding to the bulk-like peak and actual bulk water. For a more detailed view of the bulk-like peak, we investigated the ultrafast dynamics of the water molecules.

We collected polarization-selective pump–probe spectroscopy (PSPP) for HOD in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  at 25% and 45% RH, below and above the pore-filling step, respectively. The ultrafast laser pulses are tuned specifically centered at the bulk-like peak position, to reveal its dynamics. In PSPP, parallel and perpendicular pump–probe signals are collected as a function of delay time and used to calculate the rotational anisotropy, or Legendre second-order orientational correlation function ( $C_2(t)$ ), which quantifies how fast molecules lose their correlation to original orientations (Figure S11 in the Supporting Information).

The  $C_2(t)$  dynamics of bulk water and water networks in MOFs show similarities and differences. They decay on similar time scales, but notably, that water dynamics in MOFs decay

to an offset, while bulk water relaxes to zero (Figure 3A). Another similarity is that the initial  $C_2(t)$  of all systems shows a frequency dependence (Figure 3B for 25% RH MOFs, and Figures S13.1 and S13.2 for others). These results are qualitatively similar to previous simulated rotational dynamics of water in  $\text{Co}_2\text{Cl}_2\text{BTDD}$ .<sup>31</sup> To extract quantitative information, we fitted the data using the wobbling-in-a-cone model.<sup>40</sup> The rotational dynamics of wobbling-in-a-cone is described by an initial fast reorientation ( $<200$  fs) constrained within the cone with a semiangle  $\theta_{in}$ , which determines the  $C_2(t)$  at  $t = 0$  (Figure 3E), followed by the molecules rotating in a larger cone leading to a semiangle  $\theta_{tot}$  (Figure 3E).

For bulk water, the second rotation is unconstrained ( $\theta_{tot} = 90^\circ$ ) and thus is fitted to a single exponential. The result indicates water fully reoriented with  $\sim 2.4$  ps regardless of H-bond intensity (i.e.,  $\omega_{OH}$ ) while  $\theta_{in}$  is frequency dependent (Figure 3D). This result agrees with the literature as the strong H-bond leads to tight initial rotations, while the picosecond reorientation describes H-bond rearrangement that only depends on the H-bond acceptor availabilities.<sup>41</sup>

For water H-bond networks in MOFs, at both RHs, their  $C_2(t)$  values are fitted with a single exponential and a constant, indicating after the initial rotation, there is another constrained reorientation, followed by a slow rotation beyond the OD stretch lifetime. The initial rotation  $\theta_{in}$  exhibits a frequency dependence similar to that of bulk water, thus depending on H-bond strength (Figure 3C). However, after that, OD wobbles in a confined cone in  $\sim 1.3$  ps, different from the unconstrained rotation of bulk water. Similar wobbling-in-a-cone motions have been observed for water in other confined environments.<sup>40,42</sup> However, at both RHs,  $\theta_{tot}$  is  $\sim 50^\circ$ , which

is much larger than the  $\theta_{\text{tot}}$  reported in other confined environments, including porous silica and reverse micelles.<sup>40,42</sup> Indeed, the  $50^\circ$   $\theta_{\text{tot}}$  is larger than the typical cutoff angle for H-bond definition ( $\sim 30^\circ$ ).<sup>43–45</sup> Thus, it suggests water H-bonds need to rearrange to accommodate this wobbling motion. It is interesting to notice that the wobbling relaxation rate is not quite sensitive to OD frequency, indicating the H-bond network rearrangement does not depend on H-bond strength, similar to bulk water. However, it is less random than bulk water, as it preserves some initial orientational memory. At 25%, the  $\theta_{\text{tot}}$  becomes smaller at higher OH frequency, suggesting a more confined rotation with fewer H-bonds.<sup>35,46–48</sup> This could suggest a layered structure prior to pore filling, agreeing with prior simulations that predicted  $C_2(t)$  for water near the pore wall, which is mostly hydrophobic, would have a higher offset than  $C_2(t)$  for water near the core.<sup>31</sup> However, after pore filling,  $\theta_{\text{tot}}$  becomes less frequency dependent.

The origin of the picosecond dynamics and cone angle may indicate extra H-bond acceptors in  $\text{Ni}_2\text{Cl}_2\text{BTDD}$ . Theoretical studies suggested that H-bond rearrangements were limited by the availability of new acceptors.<sup>49</sup> Chloride ions, the ether, and the triazolate groups could serve as additional acceptors, and FTIR spectra of the strongly bound water peak indicate water with more H-bond interactions.<sup>35</sup> This mechanism remains to be verified by additional simulations. The fact that the water H-bond network can rearrange on a picosecond time scale in a confined geometry distinguishes  $\text{Ni}_2\text{Cl}_2\text{BTDD}$  from other confined systems that hinder H-bond rearrangements. The similar rearrangement time scale to bulk water indicates that even after water molecules are trapped inside of these MOFs, it does not cost extra energy to break H-bonds, making reversible desorption feasible.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c01728>.

Methods, PXRD data, nitrogen isotherm data, FTIR spectra and processing, and PSPP data processing (PDF)

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### Author Contributions

#M.L.V. and G.Y. contributed equally.

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### Notes

The authors declare no competing financial interest.

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