Large Angular Jump Mechanism Observed for Hydrogen Bond Exchange in Aqueous Perchlorate Solution

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The mechanism for hydrogen bond (H-bond) switching in solution has remained subject to debate despite extensive experimental and theoretical studies. We have applied polarization-selective multidimensional vibrational spectroscopy to investigate the H-bond exchange mechanism in aqueous NaClO₄ solution. The results show that a water molecule shifts its donated H-bonds between water and perchlorate acceptors by means of large, prompt angular rotation. Using a jump-exchange kinetic model, we extracted an average jump angle of 49 ± 4°, in qualitative agreement with the jump angle observed in molecular dynamics simulations of the same aqueous NaClO₄ solution.

Hydrogen bonds (H-bonds) provide the intermolecular adhesion that dictates the unique properties of liquid water and aqueous solutions. Although H-bonds constrain the local ordering and orientation of molecules in solution, these local H-bond networks disband and reform on the picosecond time scale. This structural lability critically influences chemical and biological transformations. Our understanding of the dynamics of hydrogen bond dissociation and reformation has been transformed by the union of ultrafast vibrational spectroscopy and molecular dynamics simulations (1–14), but the detailed mechanism for H-bond switching in aqueous solution remains uncertain. Recent simulation studies of water and aqueous ionic solutions have proposed that H-bond exchange involves large angular jumps of 60° to 70° (1, 5). However, the substantial complexities inherent in simulating the structural and dynamical properties of water highlight the importance of validating this proposal experimentally.

Two-dimensional infrared (2D-IR) spectroscopy provides an excellent opportunity to study this class of ultrafast chemical exchange (15–19). We applied a variation of this technique (Fig. 1) to directly investigate the orientational jump mechanism for H-bond switching in aqueous ionic solutions. The dissolution of NaClO₄ in isotopically mixed water generates two deuterated hydroxyl (OD) stretch frequencies: OD groups associated with these same molecules (21–22); specifically, we address the time-dependent change in orientation of the vibrationally excited hydroxyl groups induced by chemical exchange. The second advance is a modification of the kinetic model (23) used to interpret 2D-IR spectra, so as to include vibrational transition dipole moment reorientation induced by chemical exchange. Previous data analysis assumed H-bond exchange did not induce jump-reorientation (3, 4).

2D-IR spectroscopy monitors equilibrium H-bond switching dynamics on a picosecond time scale (15–19) by labeling molecules through resonant excitation at their OD stretch frequencies and then correlating these initial frequencies (ωₒ) with the (potentially shifted) stretch frequencies (ωₐ) associated with these same molecules after an experimentally controlled waiting time (Tᵳ). Thus, 2D-IR can determine when a vibrationally labeled ODₓ hydroxyl group converts to an ODᵧ configuration during Tᵳ. The cross-peak only reflects H-bond exchange events in which the hydroxy group switches between the ODₓ and ODᵧ configurations. By adding polarization selectivity, we furthermore access the orientational dynamics of water molecules that have switched between ODₓ and ODᵧ configurations. In the polarization-selective 2D-IR measurement, the first two pulses that control the frequency labeling of OD stretches have parallel polarizations that preferentially excite transition dipole moments parallel to the excitation polarization. During the Tᵳ waiting time, the excited molecules randomize their orientation in addition to undergoing H-bond exchange between the ODₓ and ODᵧ configurations (Fig. 1A). If the H-bond exchange only minimally perturbs the orientation of the vibrationally excited hydroxyl group, then both the diagonal and the cross-peak intensities will exhibit similar polarization dependence. However, if the molecules exchange via large angular jumps, the cross-peak signal that results solely from ODₓ-ODᵧ exchanged populations will show distinctly different polarization dependence from the diagonal peaks (Fig. 1B and C).

Figure 2 shows the Tᵳ-dependent polarization-selective 2D-IR spectra for aqueous 6M NaClO₄. The positive peaks shown in red along the diagonal (ωₒ = ωᵣ) result from the fundamental vibrational transition (ω = 0 → 1) within each H-bond configuration. We label the peak volumes Iᵣᵣᵢᵢ for the diagonal (i = j) and the off diagonal (i ≠ j) peaks: i and j refer to the H-bond configurations associated with ωᵣ and ωᵢ, and I and m refer to the laser polarization. The crosspeak at (ωᵢ,ωᵣ) = (2534,2633) cm⁻¹ results from ODₓ switching to ODᵧ, Iₓᵧ. Because this H-bond exchange occurs at equilibrium, the exchange process from ODₓ to ODᵧ will also generate a crosspeak Iᵧₓ at (ωᵣ,ωᵢ) = (2633,2534) cm⁻¹ with fₓᵧ = Iₓᵧ/Ć₀. Experimentally, the u = 1 → 2 excited state absorption of ODᵧ obscures this crosspeak (4), so we use the Iₓᵧ signal to characterize the jump angle. The vibrationally excited molecules that have switched between the ODᵧ and ODₓ configurations project nearly equivalent signal intensities for perpendicular and parallel polarizations. As will be shown, this equivalence reflects the large angular jumps that lead to H-bond switching.

Figure 3 further highlights the polarization-dependent population dynamics by comparing the peak volumes for the isotropic (Iᵣᵣᵢᵢ = Tᵣᵣᵢᵢ + 2Iₓᵧ) and anisotropic (Iᵣᵣᵢᵢ = Tᵣᵣᵢᵢ − Iₓᵧ) signals for a diagonal-peak (ij = PP) and a cross-peak (ij = WP). The Iᵣᵣᵢᵢ signal reflects the population decay of the ODₓ configuration, whereas Iₓᵧ reflects population relaxation and orientational randomization of the ODᵧ configuration. The Iₓᵧ signal rise time reflects the rate of H-bond switching, whereas the decay results primarily from ODᵧ population relaxation. Unlike previous measurements of the H-bond switching time (3, 4), Iᵣᵣᵢᵢ decouples the orientational dynamics from the H-bond configurational switching and so provides a superior measure of the exchange rate. The Iₓᵧ signal clearly shows the very small dependence of

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the cross-peak intensity on the laser polarization. The method used to extract the peak volumes can be found elsewhere (3, 25).

We modeled the polarization-selective 2D-IR spectra using diagrammatic perturbation theory and an angular jump-exchange kinetic model. This provides a framework for interpreting the time ($T_W$) and angle ($\Theta$) dependent excited state population $N_i(T_W)$, orientation, and spectral diffusion dynamics (20, 23, 24). The simplest variant of the angular jump-exchange kinetic model presumes that an orientational jump through angle $\Theta$ accompanies H-bond exchange between the OD$_W$ and OD$_P$ configurations, whereas reorientation of hydroxyl groups occurs diffusively within a particular H-bond configuration. The model requires the angular rate of change during an angle jump to be much larger than the angular rate of change induced by orientational diffusion. As will be discussed, this requirement is consistent with our experimental and simulation results.

The angular jump-exchange kinetic model attributes the dynamics to (i) population decay with decay rates $k_W$ and $k_P$, (ii) orientational diffusion with diffusion constants $D_W$ and $D_P$, and (iii) chemical exchange with rate constants $k_{WP}$ and $k_{PW}$ and a H-bond exchange angle $\Theta$. This model leads to ensemble-averaged populations as a function of $T_W$ and laser polarization. For the $S_{zzz}$ and $S_{zzy}$ geometries, the polarization-dependent populations can be expressed as in Eqs. 1 and 2.

$$\begin{align*}
\frac{N_W(T_W)}{N_P(T_W)}_{zzz} &= \left( e^{+i\Theta} + \frac{4}{3} e^{-i\Theta} \right) \\
&\times \left( \frac{N_W(0)}{N_P(0)} \right) \\
\frac{N_W(T_W)}{N_P(T_W)}_{zzy} &= \left( e^{+i\Theta} - \frac{2}{3} e^{-i\Theta} \right) \\
&\times \left( \frac{N_W(0)}{N_P(0)} \right) \tag{2}
\end{align*}$$

Equations 1 and 2 correspond to matrices that contain all the kinetic coefficients, as well as $\Theta$, $A = \begin{pmatrix} k_w & -k_{PW} \\ -k_{WP} & k_p + k_{WP} \end{pmatrix}$, $B = \begin{pmatrix} k_w + k_{WP} + 6D_w & -(P_2(\cos\Theta))k_{WP} \\ -(P_2(\cos\Theta))k_{WP} & k_p + k_{WP} + 6D_p \end{pmatrix}$, where $P_2(\cos\Theta) = (3\cos^2\Theta - 1)/2$ and $\Theta$ corresponds to an ensemble average. These equations reduce to the exchange kinetic model of Kwak et al. (23) when $\Theta = 0^\circ$ and can be straightforwardly related to the theory of coupled vibrations developed by Golonka and Tokmakoff (21). The $A$ matrix has no orientational dependence and contributes solely to $I_{zzz}^{(0)}$, with dynamics determined by the excited state lifetime and the chemical exchange rate. The $B$ matrix contributes solely to $I_{zzy}^{(0)}$ with dynamics determined by $\Theta$, $D_W$, and $D_P$. As shown in the supporting text, a large jump angle leads to a small $(P_2(\cos\Theta))$ value and the very small cross-peak anisotropy measured experimentally. We have chosen to present the simplest variant of the jump-exchange kinetic model for conceptual clarity, but we have also investigated more sophisticated models. In the supporting text, we discuss three critical aspects of the model and demonstrate that the extracted $\Theta$ value is fundamentally insensitive to the distribution of jump angles, the time evolution of the jump angle, and the detailed dynamics of the orientational randomization for hydroxyl groups that remain in a given H-bond configuration.

We used numerical response function calculations based on the above model to analyze the experimental data. The calculated anisotropic spectra appear in Fig. 2D. We used standard methods to obtain starting values for the vibrational relaxation, orientational diffusion, and frequency-frequency correlation function parameters (4, 23). The fitting of the polarization-selective 2D-IR spectra allow the extraction of the H-bond exchange rate $k_{WP}$ and jump angle $\Theta$. The analysis uses global fitting of the polarization-selective 2D-IR spectra for $T_W$ times of 0.2, 1, 2, 3, 4, 5, and 7 ps. Fitting results give $\Theta = 49 \pm 4^\circ$, $(6D_W)^{-1} = 5 \pm 0.5$ ps, $(6D_P)^{-1} = 4.6 \pm 0.5$ ps, $(k_{WP})^{-1} = 9 \pm 1$ ps, $(k_{WP})^{-1} = 18 \pm 2$ ps, and a total exchange rate of $\tau_W = (k_{WP} + k_{WP})^{-1} = 6 \pm 1$ ps, consistent with our previous result (4). We also fit the $T_W$-dependent $I_{zzz}^{(0)}$ and $I_{zzy}^{(0)}$ peak volumes, as shown in Fig. 3. These fitting results agree with the response function global fitting, within experimental error. Within the angular jump-exchange kinetic model, only large values of $\Theta, D_W$, and $D_P$ could lead to the very small anisotropy of the cross-peak $I_{zzy}^{(0)}$, but the anisotropy of the diagonal peaks greatly constrains $D_W$ and $D_P$. These constraints, as well as the high sensitivity of the cross-peak anisotropy to small changes in the jump angle around $49^\circ$, render the $\Theta$ value extracted from the measurements robust.  

![Fig. 1. Interpretation of polarization-selective 2D-IR signals.](link-to-figure)
jump angle of 49° occurring with a 50-fs time constant. By simulating the same solution as that used previously (Fig. 3 S8), which has been accurately modeled with an impulsive angular jump and conforms to the predominantly subpicosecond angular dynamics observed in the simulation. Whether the lack of quantitative agreement between experiment and simulation reflects limitations in the CPMD simulation or the modeling of the experimental data awaits further investigation.

Fig. 2. Normalized polarization-selective 2D-IR spectra at \( T_w = 0.2, 3, \) and 7 ps. (A) Parallel polarization spectra (\( S_{zzzz} \)), (B) perpendicular polarization spectra (\( S_{zyzy} \)), and (C) anisotropic spectra, \( S_{aniso} = S_{zzzz} - S_{zyzy} \). Peak assignments can be found in the text. The cross-peaks show very little anisotropy compared with the diagonal peaks (C), clearly indicating that large-angle rotation of hydroxyl groups accompanies H-bond switching. (D) Calculated anisotropic spectra based on Eqs. 1 and 2.

Fig. 3. Logarithmic plot of the polarization-selective peak volumes for the isotropic, \( I_i^{(1)} = I_{zzz}^{(1)} + 2I_{zyy}^{(1)} \), and anisotropic, \( I_i^{(aniso)} = I_{zzz}^{(aniso)} + I_{zyy}^{(aniso)} \), signals for the \( ij = PP \) diagonal-peak and the \( ij = WP \) cross-peak. The solid lines give the kinetic model fit to the data with a H-bond exchange rate of 6 ± 1 ps and a jump angle of 49 ± 4°.

Fig. 4. CPMD simulation of the jump angle for H-bond switching between the OD\(_2\) and the OD\(_\alpha\) configurations for aqueous 6 M NaClO\(_4\) solution. The data have been fit with a sum of two error functions (solid line). Results show the change in angle proceeding with two time constants, 50 fs for an initial 40° angular jump and 1 ps for a slower 27° angular rotation.

We also performed Car-Parrinello molecular dynamics (CPMD) simulations (25) of aqueous 6 M NaClO\(_4\) to complement our experimental studies (20). The CPMD methodology differs substantially from that used previously (1, 5, 14) to study H-bond switching, yet as shown in Fig. 4, very similar angular jump dynamics emerge in the CPMD simulations of H-bond switching between OD\(_2\) and OD\(_\alpha\) configurations (1, 5). Analysis of the mean trajectory indicates that the orientation changes on two time scales, with a 40° jump occurring with a 50-fs time constant and a 27° reorientation occurring with a 1-ps time constant. By simulating the same solution as that studied experimentally, we can make a direct comparison between experiment and simulation. The results of the simulation qualitatively agree with our experimental results, validating the angular jump mechanism for H-bond switching in aqueous NaClO\(_4\) solutions. The time constant for the fast component resembles the period of a water librational motion, consistent with the assessment that the orientational jump reflects a primarily concerted rotational motion. The 1-ps process occurs too slowly to be viewed as concerted, but our experiment cannot accurately measure the detailed time evolution of the angular jump because the cross-peak intensity grows in with \( \tau_w = 6 \) ps. Nonetheless, for \( T_w < 2 \) ps, the cross-peak shows a very small anisotropy (Fig. S8), which has been accurately modeled with an impulsive angular jump and conforms to the predominantly subpicosecond angular dynamics observed in the simulation. Whether the lack of quantitative agreement between experiment and simulation reflects limitations in the CPMD simulation or the modeling of the experimental data awaits further investigation.

References and Notes
20. Methods are detailed in supporting online material at Science Online.
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Supporting Online Material
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Materials and Methods
Figs. S1 to S11
Table S1
References
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