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Water jump reorientation and ultrafast vibrational spectroscopy

Damien Laage [a,*], Guillaume Stirnemann [a], James T. Hynes [a,b,*]

[a] Chemistry Department, Ecole Normale Supérieure, UMR ENS-CNRS-UPMC 8640, 24 rue Lhomond, 75005 Paris, France
[b] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

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ABSTRACT

The reorganization of water's hydrogen-bond (HB) network by breaking and making HBs lies at the heart of many of the pure liquid's special features and many aqueous media phenomena, including chemical reactions, ion transport and protein activity. An essential role in this reorganization is played by water molecule reorientation, long described by very small angular displacement Debye rotational diffusion. A markedly contrasting picture has been recently proposed, based on simulation and analytic modeling: a sudden, large amplitude jump mechanism, in which the reorienting water molecule rapidly exchanges HB partners in an activated process which has all the hallmarks of a chemical reaction. In this contribution, we offer a brief review of the jump mechanism together with a discussion of its application to, and probing by, modern ultrafast infrared spectroscopy experiments. Special emphasis is given to the direct characterization of the jumps via pioneering two-dimensional infrared spectroscopic measurements.

1. Introduction

Liquid water's numerous remarkable features include the great lability of its hydrogen-bond (HB) network. This network constantly rearranges by breaking and forming HBs on a picosecond timescale [1–5]. Further, water's reorganization dynamics plays a key role in a host of fundamental processes, such as S_N2 [6] and proton transfer reactions [7,8], proton transport [9], and protein activity [10]. The HB network rearrangements involve the reorientation of individual water molecules, which has been traditionally viewed as very small step angular Brownian motion of the molecule [10].

In stark contrast with this Debye rotational diffusion picture, two of us recently proposed a very different molecular mechanism, in which water reorientation mainly proceeds through sudden, large amplitude angular jumps [4,11]. In this new picture, which has a robustness vis-à-vis changes in the water force field [11], large jumps occur when a water hydroxyl (OH) group trades HB acceptors, providing the elementary mechanism of HB network rearrangement. Subsequent simulation work depicted these angular jumps as a universal feature of liquid water; they occurred not only in neat water, but also in a broad gamut of aqueous environments, including aqueous solutions of ions [12] and amphiphilic solutes [13,14], confining geometries [15–18] and biomolecular hydration layers [10,19–21].

In this contribution, we initially recount some key aspects of the new picture and its detailed description via molecular dynamics simulation and analytic modeling. We then turn to a focus on experimental probing of the validity of this novel jump picture via ultrafast infrared (IR) spectroscopic measurements, including rotational anisotropy experiments [22] and two-dimensional infrared (2D-IR) spectroscopic experiments [3,23,24]. As will be seen, it is often important to also refer to nuclear magnetic resonance (NMR) spectroscopic experiments [25,26] for a useful comparison for the IR measurements. We will conclude that the jump model provides a predictive theoretical framework to understand not only pure water dynamics but also how a solute alters the surrounding water's dynamics, as illustrated by recent ionic and amphiphilic aqueous solution examples [27]. We do not aim for a complete discussion here, and refer the interested reader to other reviews [10,28] for further details and references.

2. The jump reorientation mechanism: bulk water

As related in Section 1, molecular dynamics (MD) simulations of water indicate the occurrence of large angular jumps when a water OH group trades HB acceptors [4,11]. Fig. 1 depicts this exchange process, which has the essential character of a chemical reaction involving the reactant HB and the final HB. The first step in this mechanism is the initial HB's elongation while a new water oxygen acceptor approaches, in most cases from the second hydration shell of the reorienting water molecule. Once the initial and final oxygen acceptors are equidistant from the rotating water's oxygen, the water OH can suddenly execute a large-amplitude angular jump from one acceptor to another. At the transition state for this HB

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* Corresponding authors. Tel.: +33 1 44322418.
E-mail addresses: damien.laage@ens.fr (D. Laage), hynes@spot.colorado.edu (J.T. Hynes).

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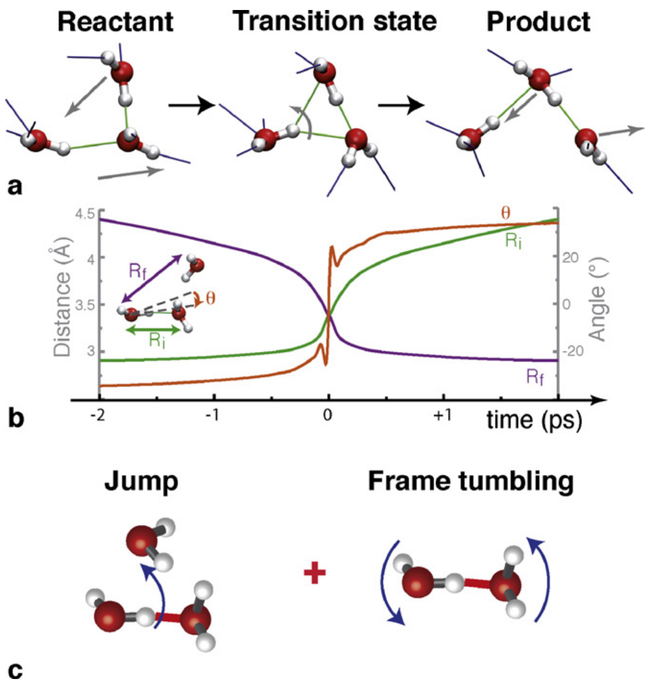

Fig. 1. (a) Schematic representation of typical reactant, transition state and product configurations for the jump mechanism, (b) Average time evolution of three key quantities during a jump: distance R_i to the initial HB acceptor, distance R_f to the final HB acceptor and (signed) angle θ between the reorienting OH and the bisector plane of the angle between the initial HB axis and the final HB axis. The origin of the time axis is set to the crossing of the transition state. (c) Schematic representation of the dominant jump motion and of the slower diffusive tumbling of the HB axis leading to a reorientation of the local frame.

exchange reaction, the rotating water forms a symmetric bifurcated HB with its initial and final water acceptors [4,11]; this concerted feature of the reaction avoids the cost of completely breaking the initial HB to form a "dangling" OH, since the new HB is partially formed while the original one is being broken [11]. The HB with the new partner eventually stabilizes, while the initial partner leaves. As is implied by the concerted character just noted, the jump mechanism's free energy barrier originates not only from the initial HB's elongation, but also from the new partner's penetration into the first shell (additional smaller contributions arise from HB fluctuations and from the OH angular motion) [11,29,30].

The mechanism displayed in Fig. 1 should clearly be understood as an average, simplified, but nonetheless representative mechanism. The actual exchange paths are distributed around this typical mechanism, an aspect illustrated by the wide jump angle distribution found around the average amplitude of 68° [11].

Since the jumps discussed above result in the reorientation of water molecules, their signature can be sought in the time-correlation function (tcf) of the molecular orientation. These dynamics can be probed by ultrafast IR spectroscopy [22], as well as more traditional NMR methods [25,26]. For a given body-fixed vector such as the water OH bond, this function reveals the rate of the loss of the memory of the initial orientation. Its definition is

$$C_n(t) = \langle P_n[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle,$$

with P_n the nth order Legendre polynomial and $\mathbf{u}(t)$ the molecular orientation at time t. Ultrafast polarized pump-probe infrared spectroscopy experiments measure the anisotropy decay, which is approximately proportional to $C_2(t)$ [22,31]. Beyond an initial time interval (<200 fs) where water molecules partially reorient via fast librational motions, i.e. rotations hindered by the HB network-imposed restoring torques, $C_2(t)$ decays exponentially with a characteristic time τ_2.

The characteristic reorientation time resulting from a reorientation through large jumps can be determined through the jump model developed by Ivanov [32], which generalizes the diffusive angular Brownian motion picture to finite amplitude jumps [4,11]. With the assumptions that the jumps have a constant amplitude $\Delta\theta$, are uncorrelated, and occur with a frequency of $1/\tau_{jump}$ around axes distributed isotropically, the (second-order) reorientation time is

$$\tau_2 = \tau_{jump} \left\{ 1 - \frac{1}{5} \frac{\sin(5\Delta\theta/2)}{\sin(\Delta\theta/2)} \right\}^{-1}$$

Simulations can provide the two features of the jumps, their amplitude $\Delta\theta$ and their frequency $1/\tau_{jump}$ (from SPC/E water simulations at 300 K, $\Delta\theta = 68^\circ$ and $\tau_{jump} = 3.3$ ps [11]). A key point is that the jump frequency $1/\tau_{jump}$ is now identified as the forward rate constant for the reaction which breaks an initial stable HB to form a new different stable HB [4,11].

However, this simple model incorrectly assumes fixed molecular orientation between jumps, and thus requires extension. In particular, this assumption implies that while a water OH bond retains the same HB acceptor, the OH direction remains frozen. But this is not the case, due to the intact HB axis reorientation through a tumbling motion of the local molecular frame of the hydrogen-bonded pair, which needs to be included (see Fig. 1c). The jump contribution can be combined with the frame component to produce the extended jump model (EJM) [4,11], which gives an overall EJM reorientation time

$$\frac{1}{\tau_2^{\mathrm{EJM}}} = \frac{1}{\tau_2^{jump}} + \frac{1}{\tau_2^{frame}}$$

The structure of this result indicates that the faster of the two contributions will dominate the overall time; this will typically be the jump time, although on occasion the frame time can become important [19,33,34].

The EJM provides an excellent description of the τ_2 reorientation times measured by both pump-probe IR anisotropy and NMR spectroscopies and calculated from simulations [4,11]. However, a diffusive model could still give rise to the experimental data. The measured smooth exponential decay of $C_2(t)$ could either result from sharp large amplitude jumps averaged over a great number of water molecules jumping at different times, or rather from infinitesimal reorientations for each water molecule. The ratio of the second-order time τ_2 with the first- or third-order times would be needed to furnish the distinction between pictures [4,11], but these latter times are currently not experimentally accessible. We note here that while the Debye dielectric relaxation time is a first-order reorientation time, it pertains to the *collective* reorientation of the total dipole, and due to strong correlations between individual water molecules, it is significantly longer than the first-order single-molecule reorientation time of interest here [11]. Other direct and incisive experimental evidence is thus necessary to determine unambiguously the reorientation mechanism.

Some first experimental support of the jump model came from the analysis of quasi-elastic neutron scattering spectra (QENS), discussed elsewhere [35]. But among the many experimental techniques probing water HB dynamics, including QENS [35], NMR spectroscopy [26] and ultrafast pump-probe IR spectroscopy [22], the most recent – and arguably most powerful – has been 2D-IR spectroscopy, which accounts for its special emphasis here. Numerous discussions of 2D-IR are available [23,36–38]; our present discussion addresses only the key relevant aspects necessary for water HB dynamics [3,36,39–41]. This technique follows the time-fluctuations of vibrational frequencies and yields the correlation between the frequencies at two instants separated by a given time delay. Its application to water [31] provides