Fast Collective Hydrogen-Bond Dynamics in Hexafluoroisopropanol Related to its Chemical Activity

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Abstract

Using fluorinated mono-alcohols, in particular hexafluoro-2-propanol (HFIP), as a solvent can enhance chemical reaction rates in a spectacular manner. Previous work has shown that this enhancement is related to the hydrogen-bond structure of these liquids. Here, we investigate the hydrogen-bond dynamics of HFIP and compare it to the dynamics of its non-fluorinated analog, 2-propanol. Time-resolved and two-dimensional infrared spectroscopy show that the dynamics of single hydrogen-bonds (occurring on a time scale of a few picoseconds) is about twice as slow in HFIP as in 2-propanol. Surprisingly, from dielectric spectroscopy we find

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the opposite behavior for the collective hydrogen-bond dynamics: the time scale for collective hydrogen-bond rearrangements is 3 times faster in HFIP than in 2-propanol, with a characteristic time scale of 140 ps. This difference in time scales indicates that the hydrogen-bonded clusters in HFIP are smaller than in 2-propanol. The smaller cluster size can contribute to the enhanced reaction rates in HFIP by increasing the concentration of reactive, terminal OH groups of the clusters, whereas the fast collective dynamics can increase the rate of formation of hydrogen bonds between reactants and these terminal OH groups. The longer lifetime of the individual hydrogen bonds in HFIP can enhance the stability of the hydrogen-bonded clusters, and so increase the probability of reactant-solvent hydrogen bonding resulting in a reaction.

Fluorinated mono-alcohols, in particular hexafluoro-isopropanol (HFIP), can accelerate chemical reactions in spectacular ways, and many reactions take place only in these solvents.[1–3] A well-known example are metal-catalyzed C−H functionalization reactions, where HFIP has become the most commonly used solvent.[1,2,4] HFIP also effectively stabilizes helical structures in proteins.[2,5] Unraveling the molecular origins of the "booster effect"[6] of fluorinated alcohols is an active field of research. Based on combined calculations and experiments, Berkessel *et al.*[6] have shown convincingly that the hydrogen-bonding properties of HFIP play a crucial role. In particular, aggregation of HFIP molecules into hydrogen-bonded clusters increases the hydrogen-bond donor ability of the terminal hydroxyl proton, and reaction-kinetics experiments show that 2–3 HFIP molecules are involved in the activation of the oxidant.[6] Thus, hydrogen-bonded clusters (rather than monomers) are crucial for the unique catalytic and solvolytic effects of HFIP.

Whereas the hydrogen-bonding structure and energetics of HFIP has been studied experimentally and computationally,[6–11] little is known about the dynamics of the hydrogen bonds in fluorinated alcohols. Yet, the dynamics of the HFIP hydrogen bonds is quintessential to understand activation of reactive intermediates via hydrogen bonding.[12] Here, we investigate the hydrogen-bond dynamics of HFIP and its non-fluorinated counterpart (2-propanol) by combining ultrafast-infrared and GHz-dielectric spectroscopy. These methods provide complementary information on hydrogen-bond dynamics:[13,14] time-resolved infrared spectroscopy probes the random orientational motion of individual OH groups,[15–18] two-dimensional infrared (2D-IR) spectroscopy probes the distribution and fluctuations of the hydrogen-bonds,[18–25] and dielectric spectroscopy can track the dynamics of collective rearrangements, in particular the orientational random motion of hydrogen-bonded aggregates.[26–29] We find that the hydrogen-bond fluctuations and reorientation of individual OH groups (as probed by time-resolved infrared spectroscopy) is slower in HFIP than in isopropanol, but that the collective hydrogen-bond dynamics (probed by dielectric spectroscopy) is significantly faster. Our results show that in HFIP the hydrogen-bonded clusters are smaller and their collective rearrangements occur much faster than in 2-propanol, whereas the individual hydrogen bonds are longer lived. Both these effects can contribute to the enhanced reaction rates observed in HFIP.

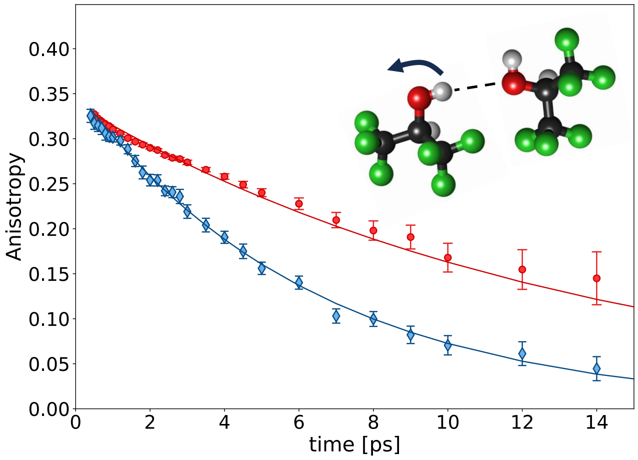

Figure 1: OD-Stretch anisotropy decay of hexafluoro-isopropanol (red circles) and isopropanol (cyan diamonds) measured at 2534 cm^{-1} and 2483 cm^{-1}, respectively. The samples were isotopically diluted (D/H=0.1) to avoid coupling between the molecular oscillators. The solid lines show a least-squares fit of a single exponential decay to the data. The inset shows the single-molecule re-orientation probed in these experiments.

To investigate the dynamics of individual hydrogen-bonds, we track the reorientation of the OD (or OH) groups in HFIP and 2-propanol in real time, using ultrafast infrared spectroscopy on the OH-stretching (or OD-stretching) mode as a probe. To avoid excitonic coupling between the OH- or OD-stretching modes,[30,31] we study isotopically diluted liquids (HFIP-OD in HFIP-OH, or vice versa). In the experiments, a short (∼180 fs) infrared pulse excites (“tags”) the stretching mode of a small fraction of the OH (or OD) bonds of the liquid. The infrared light is polarized, and preferentially excites OH (or OD) bonds that are aligned parallel to the polarization of the excitation pulse. This results in an anisotropic distribution of excited OD (or OH) bonds, which can be characterized by the so-called anisotropy parameter R (defined as $R = (\Delta A_{||} - \Delta A_{\perp})/(\Delta A_{||} + 2\Delta A_{\perp})$, where $\Delta A_{||,\perp}$ are the excitation-induced absorption changes for light polarized parallel and perpendicular to the excitation polarization). The random motion of the OH groups randomizes the anisotropic distribution, leading to a decay of the anisotropy, and the decay of R directly mirrors the correlation function of the OH random orientational motion.[13,14,20] We obtain $R(t)$ from the polarization-dependent absorption changes after correcting the data for a small thermal contribution using a procedure similar to that of ref. 32 (see SI for the details).

Figure 1 shows the anisotropy decay of the OD groups of HFIP (red circles) and 2-propanol (cyan diamonds), as observed in OD/OH dilute isotopic mixtures (see Fig. S1 for the OD-stretch infrared absorption spectra and the frequencies at which the anisotropy decay was measured). The time dependence $R(t)$ can be well described using a single-exponential decay, and we find that the reorientation of the hydroxyl-groups occurs faster in 2-propanol than in HFIP (a similar result is obtained for isotopically diluted HFIP-OH in HFIP-OD, see Fig. S7). This difference in reorientation dynamics is probably due to the difference in density of OH groups in the two liquids:[33,34] full reorientation requires breaking of a hydrogen-bond and formation of a new bond to a neighbouring molecule and therefore the presence of another acceptor OH group. Liquid HFIP has a lower hydroxyl-group density (5.7 OH-groups/nm^3) than 2-propanol (7.9 OH-groups/nm^3) and a less extended hydrogen-bond network, and this probably explains the slower hydrogen-bond dynamics.

We further investigate the dynamics of individual hydrogen bonds using two-dimensional infrared (2D-IR) spectroscopy. In these pump-probe experiments, we vary the infrared exciting and probing frequencies, and measure the absorption change as a function of both these frequencies.[20] The tilt of the contours (the "center line slope" or CLS) in the 2D-IR spectrum (Figure 2a,b; see Fig. S8 for other waiting times) shows to what extent the response depends on the excitation frequency, and the time dependence of this slope (Figure 2c) mirrors the correlation function of

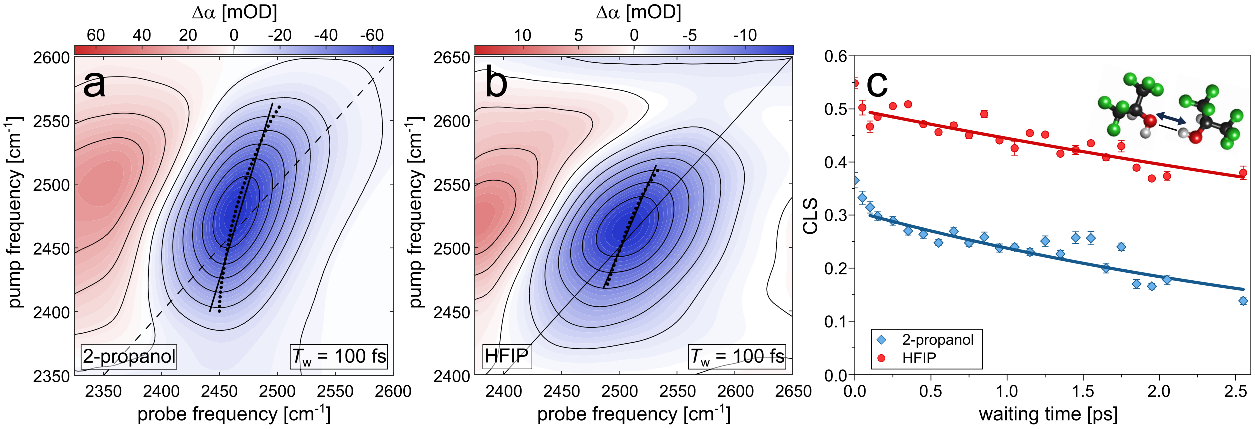

Figure 2: 2D-IR spectra (parallel pulse polarizations) at 100 fs for the OD-stretch band of a) 2-propanol and b) HFIP (D/H=0.1). The dots show the minima (as a function of the probe frequency) at different excitation frequencies, together with the center line (solid). c) Time-dependent center line slope (CLS) for 2-propanol (blue symbols) and HFIP (red symbols) with mono-exponential fits (solid curves). The inset illustrates the hydrogen-bond fluctuations probed by these experiments.

the fluctuations in the OD-stretch frequency,[19,20] and hence of the fluctuations in the hydrogen-bond length.[19] We find that the slope at time zero is smaller in 2-propanol than in HFIP (0.37 vs 0.55), which implies a more heterogeneous hydrogen-bond distribution in HFIP as compared to 2-propanol.[20] The decay of the slope in the two liquids (Figure 2c) shows that the OD-stretch frequency fluctuations are somewhat slower in HFIP than in 2-propanol (see Table 1 for the time constants). These frequency fluctuations are mostly due to breaking and re-formation of hydrogen bonds (required for rotation of the OD bonds probed in the experiment of Fig. 1) and fluctuations in hydrogen-bond length and angle.[18] As such, the CLS and its time dependence demonstrate that individual hydrogen bonds in HFIP are more heterogeneous and less dynamic than in 2-propanol.

To probe the collective dynamics of hydrogen-bonded clusters in HFIP and 2-propanol, we use dielectric spectroscopy, which is sensitive to both single and collective hydrogen-bond dynamics. In the dielectric-loss spectrum $\varepsilon''(\omega)$ of a liquid, the random orientational motions of dipole moments (either of individual molecules or of clusters) give rise to broad peaks, located at frequencies that correspond to the characteristic time scales of these random motions.[35] In mono-alcohols, the dielectric spectra in the MHz to GHz frequency region generally contain three distinct peaks: two peaks at high frequencies predominantly due to the fast rearrangements of individual molecules,[36] and one peak at low frequency that is associated with the slower, collective hydrogen-bond rearrangements.[28,29,37–42]

Figure 3 shows the dielectric spectra of HFIP and 2-propanol. Both spectra can be well described by a combination of three (Debye-type) peaks, and from a least-squares-fit analysis (shown as the curves in Fig. 3; see SI for details) we obtain the time constants and amplitudes associated with each of the three peaks. The time constants are listed in Table 1 (see SI for the amplitudes). The dynamics on fast time scales, characterized by time constants τ_2 and τ_3, show the same trend as we observed in the time-resolved infrared experiments: both these relaxation times are shorter in 2-propanol than in HFIP, indicating that individual hydrogen-bond rearrangements occur slower in HFIP than in 2-propanol. The τ_2 and τ_{or} values are of similar magnitude, which suggests non-diffusive dynamics (in the limit of diffusive reorientational dynamics, the dielectric spectroscopy time should be 3 times slower than the time-resolved infrared time[43]). Such non-diffusive dynamics could arise from restricted dynamics, where the hydrogen-bonded structure imposes constraints on the angular degrees of freedom of the molecules, impeding reorientations with small angular increments.

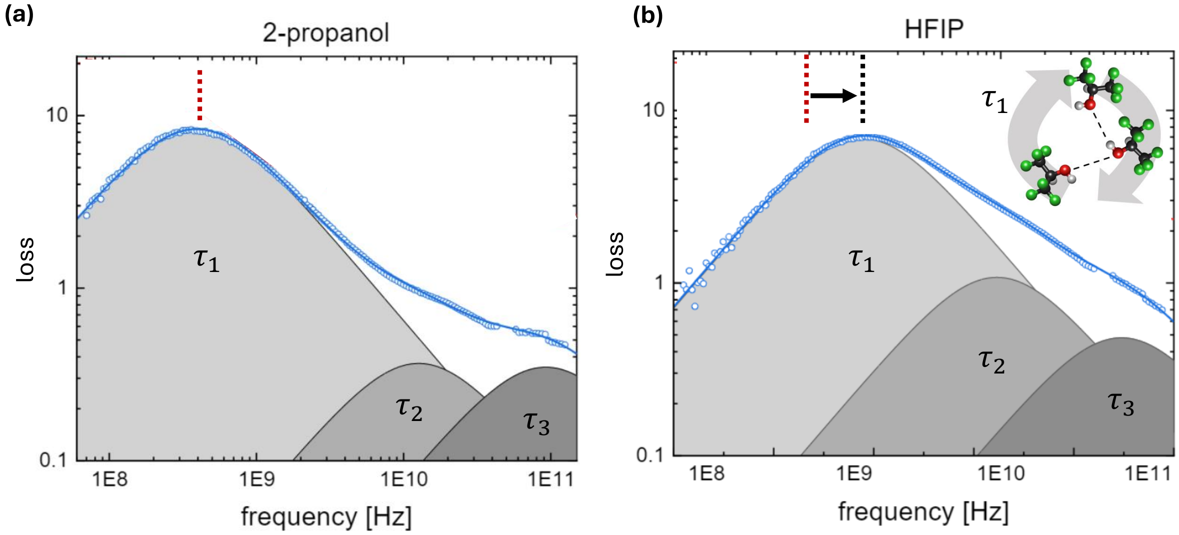

Figure 3: Dielectric-loss spectra of (a) 2-propanol and (b) HFIP. Symbols show experimental data, solid lines show fits of a combination of three Debye peaks to the data (see SI for details). Shaded areas show the contributions of the individual Debye peaks to the spectrum. The inset schematically illustrates the type of process probed by the low-frequency peak in these experiments.

Whereas the time-resolved infrared and dielectric-spectroscopy experiments both show that individual hydrogen-bond rearrangements are slower in HFIP than in 2-propanol, we find the opposite behavior for the dynamics of hydrogen-bonded clusters: the most intense, low-frequency peak in the dielectric spectrum, which is associated with collective hydrogen-bond dynamics, is at a much higher frequency for HFIP than for 2-propanol (light-grey peak in Fig. 3), and the associated time constant τ_1 is nearly three times shorter for HFIP (Table 1). This shows that the collective hydrogen-bond rearrangements occur much faster in HFIP than in 2-propanol. The shorter τ_1 time, combined with the slower individual hydrogen-bond dynamics in HFIP as compared to 2-propanol, implies that the hydrogen-bonded aggregates are significantly smaller in HFIP than in 2-propanol. This size difference is confirmed by the larger spectral heterogeneity of the OD-stretch mode in the 2D-IR experiments (small aggregates have a larger proportion of terminal hydrogen bonds, which differ in strength from the hydrogen bonds in the interior of the aggregate, and this translates into a broader distribution of OD-stretch frequencies),[18,44,45] by the broader distribution of vibrational lifetimes (Fig. S9),[45] and by the smaller amplitude of the τ_1 peak in HFIP as compared to 2-propanol.

The small hydrogen-bonded cluster size and fast collective hydrogen-bond dynamics in HFIP can both contribute to its chemical activity. Berkessel *et al.* have shown that the catalytic activity of HFIP is caused by hydrogen-bonded clusters in this solvent. Interestingly, their calculations show that the hydrogen-bond donor capacity of a terminal HFIP molecule in a hydrogen-bonded cluster increases with cluster size, but that this effect already levels off at a cluster size of 3; and their chemical-kinetics experiments show that aggregates of only 2–3 monomers are responsible for the activation of the oxidant.[6] Our results imply that the cluster size in HFIP is smaller than in

Table 1: Relaxation times τ_j obtained from least-squares fits to the time-resolved infrared, center line slopes, and dielectric-spectroscopy data. See SI for details of the data analysis.

	TRIR	2D-IR	Dielectric spectroscopy		
	τ_{or}/ps	τ_{CLS}/ps	τ_1 / ps	τ_2 / ps	τ_3 / ps
2-propanol	7 ± 1	3.9 ± 0.4	408 ± 5	12.6 ± 0.8	1.7 ± 0.2
HFIP	14 ± 1	8.6 ± 0.7	140 ± 11	17.5 ± 2.7	2.4 ± 0.3

2-propanol. As a consequence, (1) the concentration of terminal (i.e., reactive hydrogen-bond donating[6]) OH groups is larger in HFIP than in 2-propanol; (2) due to the faster collective hydrogen-bond dynamics, these reactive terminal OH groups have a higher frequency of encounters with the reactant molecules; (3) individual OH-groups reorient more slowly and the hydrogen-bonds fluctuate less. Hence if a hydrogen bond is formed it has a longer lifetime, and longer-lived hydrogen bonds to reactants might enhance the reaction. These three effects can give rise to a dynamical contribution to the "booster effect" of HFIP, complementing the structural booster effects reported by Berkessel *et al.*[6] and others.

Acknowledgement

The authors thank Martina Knecht for recording the dielectric spectra. F.C. is a Chargé de Research of the Fonds de la recherche scientifique-FNRS.

Supporting Information Available

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