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Inhomogeneity of the Amorphous Solid Water Dangling Bonds

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Amorphous solid water (ASW) is one of the most widely studied molecular systems because of its importance in the physics and chemistry of the interstellar medium and the upper layers of the Earth's atmosphere. Although the global structure of this material, *i.e.* the bulk and the surface, is well characterised, we are far from having an overall understanding of the changes induced upon chemical or physical perturbation. More specifically, the behaviour of the surface and the immediate sublayers upon mid-infrared irradiation must be understood due to its direct effect on the adsorption capacities of the ASW surface. Small molecules can accrete or form at the surface, adsorbed on the dangling OH groups of surface water molecules. This behaviour allows further reactivity which, in turn, could lead to more complex molecular systems. We have already demonstrated that selective IR irradiations of surface water molecules induce a modification of the surface and the production of a new monomer species which bonds to the surface via its two electronic doublets. However, we did not probe the structure of the dangling bands, namely their homogeneity or inhomogeneity. The structure and orientation of these surface molecules are closely linked to the way the surface can relax its vibrational energy. In this work, we have focussed our attention on the two dH dangling bonds, carrying out a series of selective irradiations which reveal the inhomogeneity of these surface modes. We have also studied the effects of irradiation duration on the surface reorientation, determining that the maximum photoinduced isomerisation yield is $\sim 15\%$.

1 Introduction

Amorphous Solid Water, hereafter referred to as ASW, is a molecular system of great interest, as it is considered to be connected to the origins of life.^{1–5} Infrared spectroscopy revealed the signature of the organisation of the ASW surface: two weak absorption bands, observed at the base of the blue wing of the bulk OH stretching absorption band, were attributed to free OH oscillators “dangling” from the ice surface.^{1,2} In two recent publications we have reported the ability of these dangling bonds at the ASW surface to isomerise towards one unique monomer species upon selective IR irradiation.^{6,7} The monomer interacts with the surface through its two electronic doublets, the OH intensities of both ν_3 and ν_1 modes being magnified by nitrogen complexation on the two OH bonds.⁸ The existence of this type of water monomer has already been postulated: theoretically, in the case of water aggregates⁹ and bulk water,¹⁰ and from combined theoretical and SFG spectroscopic¹¹ or X-ray absorption^{12,13} studies at the liquid/vapour interface. Based on their experimental results, Du *et al*¹¹ determined that at the liquid/vapour interface, approximately 20 % of the water molecules will have one dangling OH (or “single-donor” molecules with a non-

hydrogen bound OH, henceforth “dH”) with a tilt angle of $\leq 38^\circ$ relative to the surface normal. X-ray absorption studies seem to reveal a component in both liquid and ice spectra assigned to symmetrically bound H₂O molecules with two dangling OH bonds,^{12,13} or “acceptor-only” molecules (hereafter, “d2H”). This agrees with the molecular dynamics study of Kuo & Mundy,¹⁰ who calculate that, of the surface water molecules, 19 % are in the d2H orientation, while 66 % are dH. However, Wilson *et al*¹³ conclude that in liquid water, surface molecules exist mainly as single dH because of *cooperative effects*. Molecular dynamics calculations on the surface structure of water clusters⁹ suggest that experimental and theoretical results can be explained by the high lability of surface molecules. The surface is dominated by dH molecules, but such species have orientational freedom and therefore do not exhibit a well defined tilt angle.

Previous work, such as those studies discussed here, has focussed on the dynamics of the liquid/vapour interface, or the spectroscopic characterisation of ASW. They did not, however, address either the vibrational relaxation pathways of the dangling bonds or their homogeneous or inhomogeneous nature directly. In previous selective IR irradiation studies^{6,7} we observed the characteristic isomerisation of dH (and the other surface modes dO and s4) towards a unique monomer species, d2H. We noted that, upon selective irradiation at the absorption band maxima, holes were burnt at frequencies shifted by up to 3 cm^{-1} compared to the irradiation frequency. This re-

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sult implies that only one class of oscillator within the band is able to isomerise. Alternatively, after the initial energy injection, the entire surface is able to reorient into a more organised structure.

In the current study we probe the oscillator classes in the dH modes by selectively irradiating at frequencies across the full width of the OH stretching absorption band associated with the dH modes. We also investigate the effect of irradiation duration on the surface reorganisation. The goal of our experiments was to come closer to understanding the vibrational relaxation pathway(s) leading to isomerisations. We have already reported the saturation of the isomerisation effect upon irradiation of the dH mode maxima^{6,7}. In this study we further probe this phenomenon, in particular the frequency dependence and the saturation kinetics, with a view to developing a fuller understanding of the ASW surface structure and its photoreactivity. It is important to constrain the behaviour of the dH upon irradiation in order to serve as a baseline when investigating their role as adsorption sites for small molecules and the physicochemical processes involved in ASW surface reactivity.

2 Experimental Setup

ASW samples were prepared as follows: deionised water was subjected to multiple freeze-pump-thaw cycles under vacuum to remove dissolved gases. Mixtures of purified H₂O and helium (Air Liquide, $\geq 99.9999\%$) gas were prepared in a ramp with a base pressure of 10^{-4} mbar at a ratio of H₂O/He = 1/25. Ices were produced by flash deposition (in 1 s) of the gas mixture directly onto a gold-plated copper surface, cooled to 3.7 K by a PT-405 Cryomech (0.5 W at 4 K) cryogenic ensemble, inside a chamber of base pressure $\sim 10^{-8}$ mbar at 3.7 K. This temperature was maintained during the whole experiment, apart from a few seconds following deposition, when the temperature briefly rose by 4–5 K. IR spectra were recorded in reflection mode using a Bruker 66/S FTIR spectrometer equipped with a KBr/Ge beamsplitter and a MCT detector (4000–800 cm^{-1}) at 0.5 cm^{-1} resolution. Each spectrum is averaged over 1000 scans. After deposition, ices were subjected to one type of experiment: selective irradiation of the dH surface modes. Irradiations were performed using a tunable IR OPO Laserspec (1.5–4 μm), pumped at 10 Hz by a pulsed Nd:YAG Quantel Brilliant B laser (1064 nm, pulse duration 6 ns). The laser power was ~ 30 mW, with a fwhm ≥ 1.5 cm^{-1} . All the series presented in this article have been carried out at least two times. We have never observed a pressure increase in the chamber upon irradiation, as presented in our recent article.⁷

3 Results and Discussion

3.1 Irradiation series experiments

The dH surface modes exhibit absorption bands, attributed to OH stretching vibrations, at the extremity of the blue wing of the bulk ASW OH stretching absorption band (~ 3300 cm^{-1}). The bulk OH stretch of an ASW sample is shown in the top right-hand panel of Figure 1 (black trace), while the dH absorption bands are magnified in the top left-hand panel (black trace). The two overlapping absorption bands are attributed to 2-coordinate and 3-coordinate H₂O molecules¹, with maximum frequencies at 3720 and 3698 cm^{-1} , respectively. We carried out two types of selective irradiation experiment within the dH mode absorption band frequency range (3725–3680 cm^{-1}).

The first type of experiment was a series of irradiations, each of 30 minute duration, at 5 cm^{-1} steps across the full dH absorption range starting from either 3725 cm^{-1} (“Blue to red”, Figure 1, § 3.1.1) or 3680 cm^{-1} (“Red to blue”, Figure 2, § 3.1.1). The second type of experiment was a series of irradiations, each of 30 minute duration, at irregular frequency jumps within the dH absorption range (Figure 3, § 3.1.2). For ease of comparison, in Figures 1–3, the difference spectra for any irradiation at a given frequency are traced in the same colour (e.g. irradiation at 3670 cm^{-1} is always traced in green).

3.1.1 “Blue to red” and “Red to blue”. The results of the “blue to red” irradiation series (from 3725 to 3680 cm^{-1}) are shown in Figure 1. In this figure we plot both the surface dH dangling region (left-hand side) and that of the bulk OH stretching absorption (right-hand side). We are interested in the bulk OH band as the vibrational relaxation pathways in ASW are likely not restricted to the surface and therefore irradiation could induce changes throughout the ice. In particular, one OH oscillator of each dH molecule always points towards the bulk, and therefore contributes to this band. These oscillators will be referred to as “bulk-facing” hereafter.

The initial irradiation of the ASW sample, at 3725 cm^{-1} , provokes a “hole-burning” at 3727 cm^{-1} accompanied by a broad decrease across both dH modes and a broad decrease in the bulk OH absorption band from 3750–2900 cm^{-1} . Subsequent irradiations at 5 cm^{-1} intervals provoke narrower “hole-burnings” at or near the irradiation frequency, but the broad decrease of the dH bands is not seen again until the last two irradiations at 3685 and 3680 cm^{-1} . This suggests that the broad decrease of the dH bands is associated with irradiation at the red and blue edges of the double-peaked feature. We will further discuss the observed changes in the bulk OH absorption band below.

At irradiation frequencies close to the maxima of the dH absorption bands (e.g. 3720 (violet), 3700 (green), 3695 (yellow) cm^{-1}) we see the narrowest, deepest “hole-burning” fea-

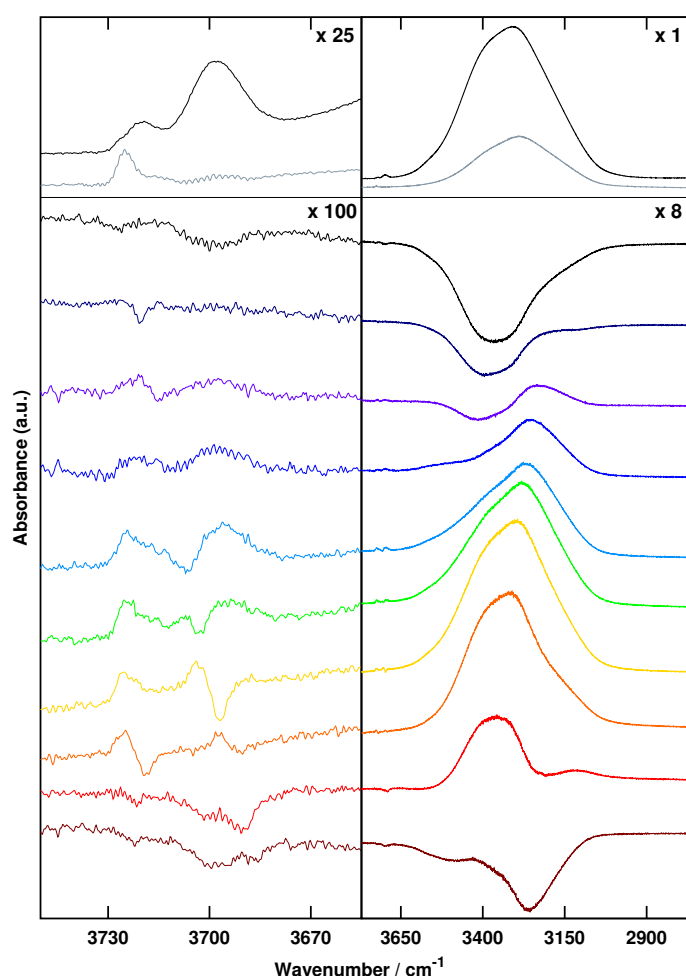


Fig. 1 Series of selective irradiations of the dH bands, from “blue to red”. Upper panels: dH bands (on the left), and bulk component (on the right) of an unirradiated ASW sample (black) and the overall difference spectrum after 10 irradiations (grey). Lower panels: dH bands (left), and bulk component (right) difference spectra after irradiation at the frequency indicated by an arrow (for irradiation $n - (n-1)$). Irradiation duration at each frequency: 30 min. From top to bottom: irradiation at *i.* 3725 cm^{-1} (black, $P_{\text{laser}}=23\text{ mW}$); *ii.* 3720 cm^{-1} (violet, $P_{\text{laser}}=40\text{ mW}$); *iii.* 3715 cm^{-1} (indigo, $P_{\text{laser}}=52\text{ mW}$); *iv.* 3710 cm^{-1} (dark blue, $P_{\text{laser}}=28\text{ mW}$); *v.* 3705 cm^{-1} (light blue, $P_{\text{laser}}=32\text{ mW}$); *vi.* 3700 cm^{-1} (green, $P_{\text{laser}}=28\text{ mW}$); *vii.* 3695 cm^{-1} (yellow, $P_{\text{laser}}=22\text{ mW}$); *viii.* 3690 cm^{-1} (orange, $P_{\text{laser}}=17\text{ mW}$); *ix.* 3685 cm^{-1} (red, $P_{\text{laser}}=13\text{ mW}$); *x.* 3680 cm^{-1} (brown, $P_{\text{laser}}=36\text{ mW}$). Spectra are multiplied by the factor in the top right-hand corner of each panel.

tures, corresponding to loss of oscillators in highly populated orientations. However, at frequencies towards the edges of the absorption band, or intermediate between the two peaks, irradiation provokes “hole-burning” at, or blue-shifted by up to 5 cm^{-1} (although typically $1 - 2\text{ cm}^{-1}$) from, the irradiation

frequency. Thus, these irradiations are provoking isomerisation of molecules at frequencies shifted from the absorption maxima, and therefore the isomerised molecules are drawn from different sub-populations within the dH modes. Thus, we are able to confirm the inhomogeneity of the dH absorption bands.

Irradiations from 3715 to 3685 cm^{-1} provoke the formation of the 3725 cm^{-1} band, indicating the formation of the d2H monomer. That the monomer is not formed upon irradiation at all frequencies, and that the area under the 3725 cm^{-1} peak varies for different irradiations, confirms the assertion that different sub-populations are implicated in the isomerisation process, and that the effect is induced photophysically and not by an annealing process. Additionally, increases in absorbance are observed, centred at the frequency irradiated in the previous step (*e.g.* irradiation at 3715 cm^{-1} provokes an increase in absorbance centred at 3720 cm^{-1}). This suggests that previously depopulated sub-populations are, at least partially, repopulated by subsequent irradiation of neighbouring sub-populations. This effect is most marked for oscillators in the $3700 - 3690\text{ cm}^{-1}$ range *i.e.* near the maximum.

If we consider the complementary set of selective irradiations, from “red to blue”, as illustrated in Figure 2 we can observe many similarities with the “blue to red” series. The initial irradiation, at 3680 cm^{-1} , provokes a broad decrease across both dH modes accompanied by a broad decrease in the bulk OH absorption band. Subsequent irradiations at 5 cm^{-1} intervals provoke narrower “hole-burnings” at or near the irradiation frequency, but the broad decrease of the dH bands is not seen again until the last two irradiations at 3715 and 3720 cm^{-1} . The formation of the 3725 cm^{-1} band is observed for most “central” frequencies (*i.e.* $3690 - 3715\text{ cm}^{-1}$), as is the repopulation of the previously irradiated frequency. The “hole-burnings” tend to be centred at frequencies blue-shifted by up to 5 cm^{-1} (although typically $2-3\text{ cm}^{-1}$) compared to the irradiation frequency.

For both the “blue to red” and “red to blue” irradiation series, we observe the same overall difference in the ASW after the full irradiation series, as shown by the grey traces in the upper panels of Figures 1 and 2. New bands are formed at 3725 and 3638 (not shown) cm^{-1} , corresponding to the ν_3 and ν_1 stretching vibrations of the d2H monomer.⁶ An overall increase is also observed in the bulk OH signal. All of the irradiation-induced decreases in the dangling bond region are masked by the subsequent repopulation of these oscillator populations, resulting in no “holes” in the overall difference spectra. The similarity between the difference spectra shows that, to a first approximation, the irradiation results of the “blue to red” or “red to blue” series are not affected by the direction of irradiation scanning. This implies that the amorphous ice surface has a high level of organisation with well defined oscillator classes, despite what the term “amorphous”

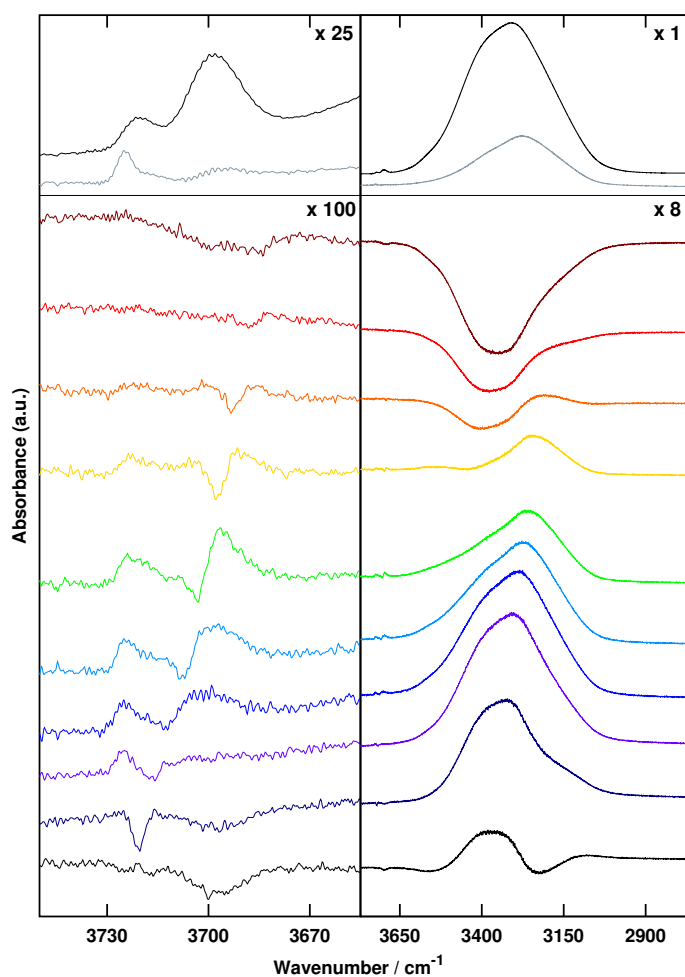


Fig. 2 Series of selective irradiations of the dH bands, from “red to blue”. Upper panels: dH bands (on the left), and bulk component (on the right) of an unirradiated ASW sample (black) and the overall difference spectrum after 10 irradiations (grey). Lower panels: dH bands (left), and bulk component (right) difference spectra after irradiation at the frequency indicated by an arrow (for irradiation $n - (n-1)$). Irradiation duration at each frequency: 30 min. From top to bottom: irradiations at *i.* 3680 cm^{-1} (brown, $P_{\text{laser}}=33\text{ mW}$); *ii.* 3685 cm^{-1} (red, $P_{\text{laser}}=29\text{ mW}$); *iii.* 3690 cm^{-1} (orange, $P_{\text{laser}}=34\text{ mW}$); *iv.* 3695 cm^{-1} (yellow, $P_{\text{laser}}=36\text{ mW}$); *v.* 3700 cm^{-1} (green, $P_{\text{laser}}=36\text{ mW}$); *vi.* 3705 cm^{-1} (light blue, $P_{\text{laser}}=36\text{ mW}$); *vii.* 3710 cm^{-1} (dark blue, $P_{\text{laser}}=29\text{ mW}$); *viii.* 3715 cm^{-1} (indigo, $P_{\text{laser}}=47\text{ mW}$); *ix.* 3720 cm^{-1} (violet, $P_{\text{laser}}=36\text{ mW}$); *x.* 3725 cm^{-1} (black, $P_{\text{laser}}=32\text{ mW}$). Spectra are multiplied by the factor in the top right-hand corner of each panel.

intuitively suggests. These oscillator classes differ in orientation and are able to reorganise upon IR irradiation. Some of the subpopulations of OH oscillator contributing to the dH absorption bands may be unreactive to selective IR irradiation. Additionally, almost all of the irradiations produce the d2H

monomer, suggesting a well-defined energy relaxation pathway within the surface molecules. A similar effect, the reorientation of two H-bonded partners with respect to the H-bond upon IR selective irradiation, has previously been observed in the case of ethanol dimers trapped in cryogenic nitrogen matrices.¹⁴

Finally, we discuss the effects observed in the bulk OH region from $\sim 3750 - 2900\text{ cm}^{-1}$. Surprisingly, whether we consider the series “blue to red” or “red to blue” we observe almost identical behaviour, namely an initial decrease in absorbance across the full absorption band (irradiations *i. - ii.*), followed by a red-shift (irradiation *iii.*), and finally an increase in absorbance across the full absorption band (irradiations *iv. - ix.*). This behaviour is independent of the irradiation frequency, as it is reproduced in almost identical fashion in Figures 1 and 2. It appears, rather, to have a dependence on the irradiation time (*i.e.* the total number of incident photons). We attribute the observed differences in the bulk OH region to one of two explanations: either (*a*) a surface-specific reorientation of the “bulk-facing” OH oscillators of the dH H₂O surface molecules, or (*b*) a more widespread reorganisation of the immediate subsurface layers of the ASW H-bonded network.

Upon irradiation of the dH modes we observe the formation of the d2H monomer; the simplest way to achieve this is the direct isomerisation of a dH, *i.e.* for each new d2H we add a dangling OH oscillator and remove a “bulk-facing” OH oscillator. Thus we expect to observe a new band at 3725 cm^{-1} (and the smaller ν_1 at 3638 cm^{-1}) but a decrease in the bulk OH band, corresponding to the conversion of the “bulk-facing” OH oscillators into dangling OH oscillators. This was the case upon an initial irradiation of an ASW sample at the dH band maxima (3720 or 3698 cm^{-1} , 60 minutes),⁶ where we systematically observed a net loss in the bulk OH absorption band due to formation of d2H. For irradiations *i.* and *ii.* we observe a decrease in the bulk OH band, and thus could consider that a surface-specific reorientation was responsible. As described in our recent study,⁷ we observe no H₂O desorption upon irradiation (within experimental sensitivity limits), therefore the decrease in dH and bulk OH bands does not necessarily imply a loss of material. The difference in area under the bulk OH absorption band after irradiations *i.* and *ii.* is approximately one tenth of the area before irradiation, and therefore we can assume that the majority of OH oscillators, *i.e.* those in the tetrahedrally H-bonded ice bulk, are unaffected by these irradiations. However, subsequent irradiations provoke an increase in the area under the bulk OH absorption band, with the overall difference in area after 10 irradiations corresponding to approximately one third of the area of the original ASW bulk OH absorption band. Thus, the simple surface-specific conversion of dH to d2H does not seem to be applicable. Can such differences be explained by a surface-only energy relax-

ation channel involving the dH, dO, and s4 surface modes, or is a wider reorganisation in the subsurface layers of the ice necessary?

Although ultimately the response to this question is beyond the scope of the current study, as it requires modelling of the energy relaxation pathways in the surface, (subsurface) and bulk regions of ASW, several points should be taken into consideration. The peak of the bulk OH absorbance increases is redwards of the original bulk OH absorption band maximum. A redshift in the bulk OH band is traditionally interpreted as being the result of a greater degree of organisation within the amorphous ice (*i.e.* the formation of a fully tetrahedrally-bound bulk network with fewer defects than in the fully amorphous case). A redshift is observed, for example, during crystallisation of an ASW sample upon annealing.¹⁵ Such an interpretation clearly invokes reorganisation in the subsurface layers (and perhaps the bulk) of the ice.

The presence of a subsurface structure intermediate between the bulk ice structure and the surface structure in nanocrystalline ice was widely investigated in the studies of Devlin and Buch.^{3,16} However, it seems that the H-bond network surrounding the “bulk-facing” OH oscillators reorganises in a specific, reproducible manner upon irradiation of the dH modes, and that this reorganisation is largely independent of the surface OH oscillators (as it is independent of frequency). As such, the changes that we observe in the bulk OH band could also be a sum of different processes in different oscillator classes, each with its own oscillator strength. In this case, populations with higher oscillator strengths would tend to overpower the others, and the global changes would represent the balance between different reorientation processes. Such processes could be confined to the surface layer, or may extend into the subsurface.

A detailed discussion of these processes would require further study, but some insight can be gained by considering the work of Laage and Thompson¹⁷ on the effect of nanoconfinement on the reorientation dynamics of water. The authors conclude that this reorientation is dramatically affected by the size of the hydrophilic pores, and that the longest time for this effect is 2.6 ps in bulk liquid. Ramasesha *et al.*¹⁸ report on the ultrafast (fs) 2D IR spectroscopy of HOD/D₂O mixtures, studying the effects of H-bond strength on the ability of water to reorient and concluding that dH do not persist in liquid water, where the most important water coordination structure is tetrahedral. A surprising picture of ASW is revealed by Schober *et al.*¹⁹ who claim that ices behave in a “crystal-like” manner because there is a “considerable reduction in the number of decay channels to sound-like excitations”. This is attributed to a low local disorder in ASW, which is also the conclusion of this work and our two previous publications.^{6,7} As can be seen from these three highlighted studies (among thousands), the dynamics of the vibrational relaxation in the

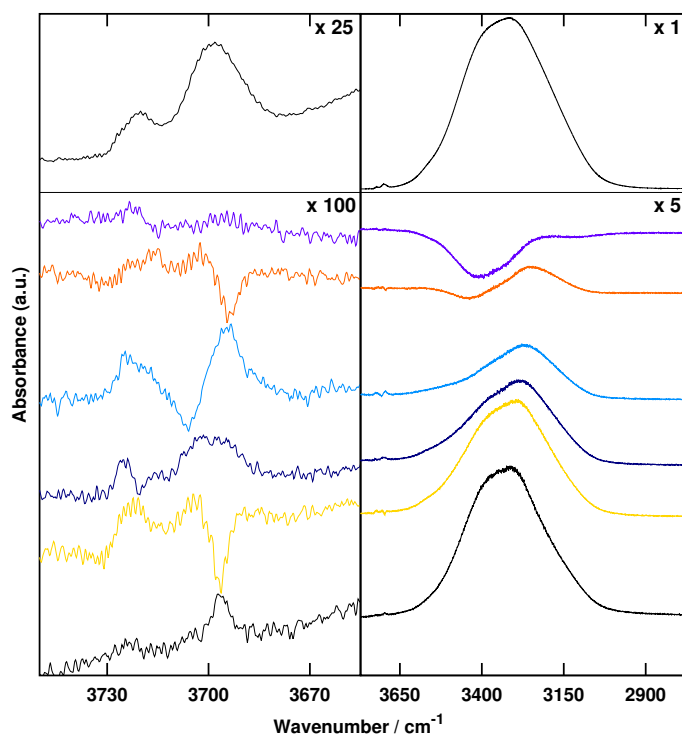


Fig. 3 Selective irradiations at irregular frequency “jumps” within the dH bands. Upper panels: dH bands (on the left), and bulk component (on the right) of an unirradiated ASW sample. Lower panels: dH bands (left), and bulk component (right) difference spectra after irradiation at the frequency indicated by an arrow (for irradiation $n - (n-1)$). Irradiation duration at each frequency: 30 min. From top to bottom: irradiation at *i.* 3715 cm^{-1} (indigo, $P_{\text{laser}}=37$ mW); *ii.* 3690 cm^{-1} (orange, $P_{\text{laser}}=42$ mW); *iii.* 3705 cm^{-1} (light blue, $P_{\text{laser}}=35$ mW); *iv.* 3720 cm^{-1} (violet, $P_{\text{laser}}=22$ mW); *v.* 3695 cm^{-1} (yellow, $P_{\text{laser}}=47$ mW); *vi.* 3725 cm^{-1} (black, $P_{\text{laser}}=22$ mW). Spectra are multiplied by the factor in the top right-hand corner of each panel.

surface and immediate sublayers of ASW is a very complex subject and a full understanding can only be attained by dedicated theoretical modelling.

3.1.2 Irregular frequency jumps. To further investigate the behaviour of surface H₂O molecules upon selective irradiation of the dH modes, we performed a series of irradiations at irregular frequencies across the dH absorption feature, as illustrated in Figure 3.

Unlike the two irradiation series presented above, the initial irradiation (*i.*) does not produce an overall decrease in the dH absorbance, and the decrease in the bulk OH band is less marked. In this series, a decrease in the bulk OH band is only observed for irradiation *i.* and seems less symmetrical than that observed for irradiations *i.* and *ii.* in the other series. However, we observe a “hole-burning” at the irradiation

frequency and the production of a band at 3725 cm^{-1} corresponding to the d2H monomer. Thus, in this case the decrease in the bulk OH absorption band can be directly attributed to the loss of the “bulk-facing” oscillator upon isomerisation to the d2H mode.

In common with the systematic irradiation series presented in § 3.1.1, each irradiation in our irregular irradiation series produces a “hole-burning” at the irradiation frequency and the repopulation of the previously irradiated oscillator class. This confirms the inhomogeneity of the oscillators contributing to the dH absorption bands. All irradiation frequencies correspond to “central”, rather than band edge frequencies, and thus we expect to see formation of the d2H monomer upon each irradiation. This is indeed the case, except for the final irradiation at 3725 cm^{-1} . We have previously demonstrated the irreversibility of the isomerisation to d2H;⁷ no “hole-burning” is observed upon irradiation of the newly-formed 3725 cm^{-1} band.

Although the pattern of “hole-burning” is identical between all three series (Figures 1 – 3), it is important to note that the other changes observed in the dH absorption feature depend on the prior irradiation history of the ice. We systematically observe repopulation of the oscillator class at the previously irradiated frequency. An example of this is the irradiations performed at 3695 cm^{-1} (traced in yellow): we always observe a “hole-burning” at 3697 cm^{-1} and the d2H absorption band at 3725 cm^{-1} , but the other peak in the difference spectrum appears at different frequencies (3703 cm^{-1} in Figure 1, 3691 cm^{-1} in Figure 2, and 3722 cm^{-1} in Figure 3) which correspond to the position of the previous depopulation of oscillators. We performed a series of irradiations at the frequencies $3705\text{--}3710\text{--}3715\text{--}3710\text{--}3705\text{ cm}^{-1}$, *i.e.* “red to blue to red”, and observed the same results as for all other irradiation series presented here: dH isomerised to d2H and the surface reorganised. Again, however, we do not observe exactly the same behaviour upon each irradiation, as the ice irradiation history is different from one series to another.

To summarise the results of our irradiation series experiments, the observed irradiation effects can be divided into two categories: firstly, the isomerisation of dH molecules to the d2H monomer and reorientation of dH to repopulate previously irradiated oscillator classes; and secondly, the concurrent changes to the bulk OH absorption feature. Selective irradiation at frequencies across the double-peaked dH absorption band provokes the formation of narrow holes ($\sim 5\text{ cm}^{-1}$), revealing the presence of different classes of dH oscillator and demonstrating the inhomogeneity of the 3720 and 3698 cm^{-1} bands. It also reveals the interconvertibility between the different oscillator populations, affirming the lability of dH molecules, as suggested by theoretical studies.⁹ Additionally, irradiation of the surface dH modes results in changes in the bulk OH absorption band indicating a link with the bulk ice. It

is unclear whether these differences can be entirely attributed to the reorientation of “bulk-facing” OH oscillators of surface molecules, or whether a more global reorganisation of the sub-surface, or even the bulk ice, is involved.

3.2 Effect of irradiation time

The second aspect of our study concerns the influence of irradiation time upon the surface reorganisation of ASW. The results of experiments upon the irradiation time are presented in Figure 4. A series of short irradiations was performed at 3698 cm^{-1} on a single ASW sample in order to investigate the kinetics of the “hole-burning” process. The area under the dH absorption band was calculated after each irradiation, and is plotted in the right-hand panel of Figure 4 in the form of the percentage decrease in dH band area compared to the initial ASW sample (as blue points, linked with a dotted line to indicate the series, rather than a fit). We observe an initial rapid increase in the hole area, followed by a plateau after ~ 50 minutes, indicating a saturation of the “hole-burning” effect. In addition to the irradiation series (in blue), four individual irradiations were performed for 7, 30, 60, and 90 minutes on four ASW samples, and the decrease in dH band area of these experiments is plotted as individual red circles. We see that the percentage decrease for an irradiation of a given length of time is constant, regardless of whether the irradiation was a single “long” irradiation, or a series of shorter irradiations. In both cases, the main effect of the irradiation *i.e.* an approximately 15 % decrease in the area of the dH absorption feature, is achieved after ~ 50 minutes. This shows that only a small proportion of surface molecules is able to isomerise.

Does this correspond to a 15:85 vibrational relaxation branching ratio between isomerisation at the surface and relaxation through the bulk? This would not be a surprising result, as similar branching ratios have previously been observed for molecular species trapped in cryogenic matrices *e.g.* ethanol dimers in argon or nitrogen matrices.¹⁴ When the photoequilibrium is reached, not all of the selectively-irradiated band has vanished and thus a non-negligible proportion of the original population of oscillators remains. This could be due to slightly differing orientations of the two partners with respect to the H-bond, favouring a relaxation through the matricial phonons, or a rapid reverse isomerisation process. Such differences can be very subtle, as in the case of CO in an argon matrix.²⁰ In the case of ASW, one of the most salient physical parameters is the *cooperative effect* between the H_2O molecules.²¹ In fact, not only the cooperative effects, but also the anti-cooperativity between OH groups must be considered; anti-cooperativity could also arise from polarisation by the closest H-bonds,²¹ depending on the basic or acidic behaviour of the nearest neighbouring H_2O molecules. The cooperative and anti-cooperative effects could explain the fact that some

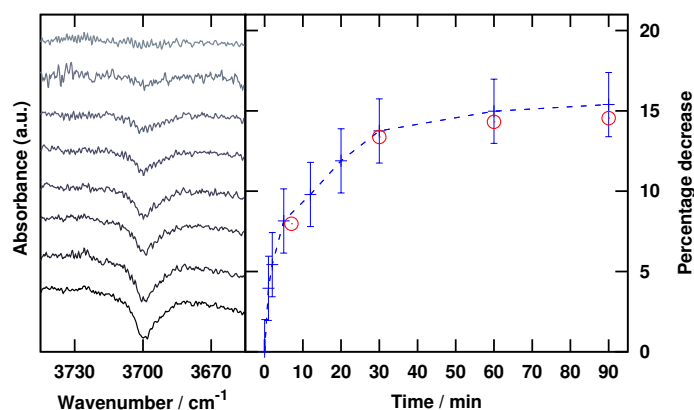


Fig. 4 Effect of irradiation time on dH absorption band. Left-hand panel: difference spectra for irradiations of an ASW sample at 3698 cm^{-1} (average power $\sim 30\text{ mW}$) for cumulative durations of (top to bottom) 1, 2, 5, 10, 20, 30, 60, and 90 minutes. Right-hand panel: Average percentage decrease in dH absorption band area calculated from the difference spectra of three irradiation experiments (blue). The bars upon the data points represent the dispersion between the experiments. The results of individual irradiations of 7, 30, 60, and 90 minutes duration (at the same frequency and power) are displayed as red circles.

weaker H-bonds are broken upon irradiation while others reinforced by cooperative effects are not. As a result, the effects we observe are most likely due to a subtle equilibrium between cooperative/anti-cooperative effects and other means of vibrational relaxation such as the reorientation of neighbouring oscillators, whose vibrational frequency range overlaps with the main irradiated population, and are thus also irradiated. The final balance of these competing influences results in a 15:85 branching ratio. We performed an experiment to probe the effect of ice thickness on the saturation of the photophysical restructuring of the ASW surface. For an ice approximately four times thicker than those normally deposited, we observe the same overall effects on the dH region *i.e.* saturation of the “hole-burning” at approximately 15 % of the dH absorption band area.

3.3 Conclusion

In this work we have provided experimental evidence for the inhomogeneous broadening of the two dH bands due to the presence of multiple oscillator populations. IR selective irradiation at multiple frequencies, whether sequential or irregular, within the double-peaked dH absorption feature, leads to the reorganisation and reorientation of surface molecules and the isomerisation of dH molecules to the d2H species: an unusual water monomer interacting with the surface through its two electronic doublets. Surprisingly, it seems that the H-bond network between surface molecules and the bulk ice, *i.e.*

that of the surface water molecules whose OH bonds point toward the bulk, reorganises in a really specific way upon irradiation, independent of the reorientation of the free OH oscillators. Although it will not change the fact that dH molecules isomerise to d2H molecules or that reorientations and reorganisations occur at the surface, it could become relevant if molecules adsorbed at the surface are more sensitive to one dH orientation. We also observed saturation of the “hole-burning” phenomenon for irradiations at 3698 cm^{-1} ; a 15:85 branching ratio has been found between molecules in the dH bands that photoisomerise and those that are unreactive at this irradiation frequency. This illustrates that only a restricted quantity of dH oscillators are photo-sensitive, and can be understood if photoisomerisation is only a minor vibrational relaxation channel in competition with energy relaxation through the bulk ice.

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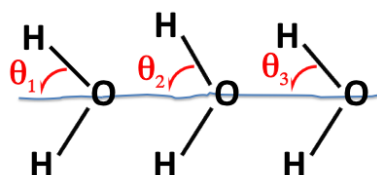


Fig. 5 Table of Contents Graphic. In this work we have selectively irradiated the dangling bonds at the surface of amorphous solid water, revealing their inhomogeneity.