RADIATION CHEMISTRY

Radical water

Radiation of sufficient energy can knock out a tightly bound core-electron from the inner shell of a water molecule, leaving behind a short-lived, highly excited state. Now, through electron spectroscopy and theoretical simulations, these states have been observed to undergo previously unconsidered proton-mediated processes in solution.

Lars G. M. Pettersson

Ionizing radiation is known to be harmful to living organisms because it creates reactive radicals and charged species. In particular, highly energetic X-rays that ionize by removing one of the innermost (core) electrons of an atom lead to a cascade of events that must be better characterized if we are to fully understand their toxic effects[1]. Writing in *Nature Chemistry*, Petr Slavíček, Bernd Winter and colleagues[2] have now described previously unknown steps within this cascade that involve proton transfer.

Core electrons are considered chemically inert, but they have the important role of screening the electric field of the nucleus — each core electron effectively cancelling the field of one proton. Now consider the absorption of an X-ray photon with enough energy to eject one of the core electrons of an atom, effectively removing one screening charge. If the atom is oxygen, its valence electrons suddenly feel an attraction similar in strength to that generated by a fluorine nucleus, which has one additional proton. If the oxygen is in a water molecule in solution, the core ionization effectively transforms the molecule to H_2F^+ hydrogen-bonded, for example, to water. The H_2F^+ is very acidic, and this strongly favours the transfer of a proton to water to make HF and H_3O^+. But the atom masquerading as a fluorine atom is of course an oxygen atom that is highly excited because of the empty position in its lowest electron level. The lifetime of this excited species is very short, ~4 fs, because the hole can be easily filled by a valence electron. This process releases energy that can be removed either by emission of an X-ray photon or, more commonly, through ejection of another valence electron (this is called Auger decay). The electron can be ejected either from the same molecule or, if there is some orbital overlap, from a different one; both cases lead to a doubly positive final state. Slavíček, Winter and colleagues[2] are now looking to understand the effects of the proton transfer reaction on the electron
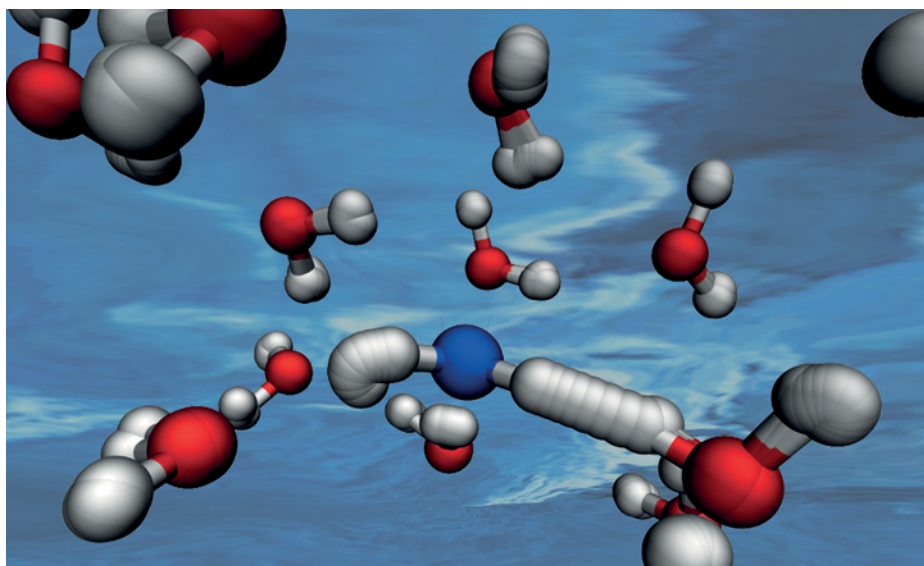

Figure 1 | Superposed atom positions from a 10-fs-long simulation of proton delocalization after creation of a core hole at the central molecule. Oxygens are in red, hydrogens in white, and the oxygen with the core hole is coloured blue. The more strongly hydrogen-bonded hydrogen delocalizes completely along the hydrogen bond on this timescale while the other makes an excursion towards the accepting water and returns.

ejection processes and species produced. And the tool that they use is Auger spectroscopy, which measures the kinetic energy of the ejected electron.

What is unique in hydrogen-bonded systems is the ease with which the protons delocalize between strongly interacting water molecules on core ionization (see Fig. 1); this is due to the release of the substantial zero-point vibrational energy. The heavier deuterium delocalizes less quickly, and it is through this comparison that inferences on the importance of dynamics and proton transfer can be made. By comparing the Auger signal from normal (H_2O) and heavy (D_2O) water, Slavíček, Winter and colleagues have found evidence of proton dynamics affecting the outcome of ionization from the core level[2]. In combination with high-level theoretical simulations, this meant that the details of the process could be deciphered. They

are therefore able to present a new picture of events subsequent to core hole decay in which proton transfer mediates the separation of the final two positive charges, or valence holes.

If the Auger decay occurs very quickly, a highly unstable, doubly positive, single water molecule is generated that dissociates into atomic oxygen and two protons: the latter become associated with water molecules as acidic H_3O^+. Another possible mechanism in this case is intermolecular Coulombic decay[3], which involves electronic coupling to neighbouring water molecules through hydrogen bonding. In this mechanism the Auger electron is ejected from a neighbouring water instead of from the one with the core hole. The result is a pair of neighbouring water molecules with single positive charges that repel each other in this charge-separated state. In the gas phase this process has

previously been studied for water dimers in which the two ionized species are seen to separate rapidly[4]. In the liquid phase the molecules cannot move freely, but proton transport along hydrogen bonds is very efficient, so the positive charges can still separate quickly. Left behind are two highly reactive OH radicals, which can cause damage to biomolecules or react with each other to form hydrogen peroxide, H_2O_2, which is more stable but also a strong oxidant. Slavíček, Winter and colleagues now propose a different and more efficient path to this charge-separated state, which is based on core-hole-induced proton delocalization along a hydrogen bond.

As discussed above, the core hole modifies the potential energy surface (along the proton-transfer reaction coordinate) such that the minimum is found at the molecule accepting the hydrogen bond. The proton then delocalizes in this potential forming a highly vibrationally excited, Zundel-like state in which it is shared more equally between the two waters[5]. The Auger transition now occurs with the proton more loosely connected to the remaining OH, which becomes OH^+ through the decay. There are then two possibilities, one of which sees the proton transfer completely, resulting in OH^+ and H_3O^+; the other involves the transfer of an electron from the accepting water to the elongated

$[OH\text{---}H]^{2+}$. In the latter case the proton is restored to the original molecule, resulting again in two neighbouring ionized water molecules from which the repelling charges quickly migrate away through proton transport as above. The process is thus similar to intermolecular Coulombic decay but made significantly more efficient by being strongly mediated by the proton.

Core-hole-induced proton transfer, or rather delocalization, is not new but has been demonstrated to affect the X-ray emission spectra of water through similar comparisons of isotope effects[6,7]. X-ray emission after a core hole has been created is a minority channel for water, where the focus has been more on what can be concluded about the structure of the hydrogen-bonding network in water, in spite of these dynamical effects[8]. The study by Slavíček, Winter and colleagues puts the focus on the important field of radiation-induced chemistry, where effects become more severe through the appearance of doubly charged species after the Auger process, compared with the singly charged result of X-ray emission. Both processes occur in parallel, however, and important unanswered questions concern the lifetimes of these reactive species in various solutions and at relevant interfaces, such as encountered inside a living cell.

A remaining uncertainty is the timescale of recombination and neutralization of

the generated electrons and protons. Considering the femtosecond to picosecond timescale of these decay processes, it is an open question as to what extent the decay products themselves affect spectrum measurements. As Slavíček, Winter and colleagues suggest[2], determining the timescales should be the target for future studies using recently available free-electron lasers and high-harmonics sources that can provide the required temporal and elemental resolution. But identifying the major initial products following core ionization provides an important starting point, in particular for dynamical simulations that can provide additional insight into these processes. ❑

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REACTION METHODOLOGY

Speed dating for reactions

A simple method to investigate the functional group compatibility and scope of new reaction methodology could improve the speed with which it is adopted by end-users, and have benefits in many related areas of chemical research.

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Chemoselectivity — the art of persuading one functional group of a molecule to react in preference to others — has long been a challenge to chemists involved in the development of synthetic methodology or in target-oriented total synthesis[1]. Designing a reactant system or catalyst that interacts avidly with the desired reactive centre while sparing other functionality in the substrates is not straightforward. Such is the difficulty of the challenge that an entire field of protecting group chemistry has been developed to overcome the issue.

Given the endless range of substrates and conditions under which a chemist may

wish to apply new methodology, how best to assess and optimize the chemoselectivity of new reactions is an important question. Writing in *Nature Chemistry*, Karl Collins and Frank Glorius present a possible solution[2]. Their simple and practical method for assessing chemoselectivity can be applied to any reaction: by carrying out the reaction in the presence of a range of additives containing functionality commonly encountered in potential substrates, moieties that affect the outcome of the reaction are highlighted. By monitoring the yield of desired product, recovered starting material and recovered additive, the method can also

tease out the root of any problems, thereby helping to inform strategies to overcome the issues. In some cases, improvements in reaction performance may even be serendipitously discovered.

The additives cannot, of course, be representative of the steric and electronic properties of every potential substrate, so are not completely predictive. They do, however, provide a useful guide — Collins and Glorius provide a series of validation experiments conducted for a Hartwig-type amination reaction. They also argue that, in some cases, use of an additive containing a particular functional group may be