Enhanced Biological Damage through Water Ionization

ONDŘEJ SVOBODA[1], DANIEL HOLLAS[1], MILAN ONČÁK[1] AND PETR SLAVÍČEK[1,2]

[1]*Department of Physical Chemistry, Institute of Chemical Technology, Prague, Technická 5, Prague 6, Czech Republic*
ondrej.svoboda@vscht.cz

[2]*J. Heyrovský Institute of Physical Chemistry, Academy of Sience of the Czech Republic, v.v.i., Prague 8, Czech Republic*
petr.slavicek@vscht.cz

The radiative damage to living cells can proceed either directly or indirectly through the interaction with water. It is generally agreed that indirect damage is more harmful to the living cells. However, its mechanism is still only partially understood. The simulations we have performed [1] on the water dimer system provide further insight into the mechanism in question.

The valence photoelectron spectrum of water comprises four characteristic peaks centered at approximately 12 eV ($1b_1$), 15 eV ($3a_1$), 18 eV ($1b_2$) and 32 eV ($2a_1$). We have carried out molecular dynamics simulations following the electron ejection from the first three molecular orbitals (so called inner-valence MOs). Moreover water dimer being constituted of hydrogen bond donor and hydrogen bond acceptor moieties, we have investigated the donor and acceptor sites separately. In our molecular dynamics simulations we have been using the semiclassical surface-hopping algorithm together with the complete active space self consistent field (CASSCF) method for the description of electronic structure.

The molecular dynamics simulations suggest the final products are state-dependent. The ionization from the highest occupied molecular orbital leads unequivocally to the formation of H_3O^+ and $OH^\bullet$ species. When higher energy is available, we have observed also the dissociation into $H_2O^{\bullet+}$ and H_2O fragments. Finally if an electron is ejected from the $1b_2$ molecular orbital the atomic hydrogen ($H^\bullet$) is formed together with $H_2O^{\bullet+}$ and $OH^\bullet$ radicals. In an environment containing multiple water molecules, the $H_2O^{\bullet+}$ radical-cation would immediately react with another water molecule yielding H_3O^+ and $OH^\bullet$ species. Such a formation of double the amount of reactive $OH^\bullet$ radicals could have severe biological consequences.

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References

[1] Svoboda O., Hollas D., Ončák M., Slavíček P., in preparation.