

# Dissociative Electron Attachment of Water and the Relevance to Environmental and Biological Issues

Thom M. Orlando

*School of Chemistry and Biochemistry and School of Physics*

*Georgia Institute of Technology*

*Atlanta, GA 30332*

## Abstract

It is well recognized that high-energy particles, such as  $\gamma$ -rays, lose energy primarily via ionization and excitation of the target media. This produces a large number of low-energy (1-100 eV) secondary electrons which undergo both elastic and inelastic scattering events. A particularly important inelastic loss process involves the resonant capture of an electron to form a transient negative ion (TNI). A TNI can decay either via electron auto-detachment or dissociative electron attachment (DEA). DEA typically involves multi-electron resonances consisting of an excess electron bound temporarily to an electronically excited molecule. These core excited Feshbach resonances have lifetimes of  $\sim 10^{(-12)} - 10^{(-14)}$  sec and can dissociate into stable negative ion and neutral fragments.

Water is ubiquitous and is present at many environmental surfaces and interfaces. Understanding the inelastic scattering of electrons with adsorbed water is important since DEA can contribute to safety issues associated with the storage of radionuclides and radioactive waste materials [1]. This is related to i) the presence of a large number of low-energy (1-10 eV) secondary electrons at nuclear material-oxide interfaces, ii.) the fact that DEA of water on oxide surfaces can have cross sections larger than the gas-phase value and iii.) DEA resonances in condensed water can result in the production of molecular hydrogen either directly or via the reactive scattering of the H $\cdot$  fragment. Water is also a major component of all biological systems. In fact, radiation damage of DNA has received a large amount of attention, and it is now well established that single- and double-strand breaks result from both direct and indirect processes. The direct processes involve ionization of the DNA itself (primarily the base pairs), whereas the

indirect effect involves reactions with the ionization and excitation products of the surrounding “environment”. This environment can be a protein or tightly bound “inner” and weakly bound “outer” waters of hydration. It is currently believed that the reactions of OH radicals (produced from these waters of hydration) lead to DNA damage. However, recent evidence strongly suggests that DNA damage also results from the interaction of low-energy electrons and involves DEA resonances of water and the intrinsic base pairs [2].

This talk will highlight some recent work on the DEA of interfacial thin films of water. In particular, I will discuss the low-energy electron stimulated desorption (ESD) of H<sup>+</sup> (D<sup>+</sup>) and H<sub>2</sub> (D<sub>2</sub>) from nanoscale water films adsorbed on oxide surfaces and at biological interfaces. Three low-energy peaks are observed in the ESD yields of H<sup>+</sup> which are identified as arising from excitation of the <sup>2</sup>B<sub>1</sub>, <sup>2</sup>A<sub>1</sub>, and <sup>2</sup>B<sub>2</sub> DEA resonances [3,4] of water. Additional structure is observed between 18 and 32 eV, which may be due to ion-pair formation or DEA resonances involving the <sup>2</sup>A<sub>1</sub> level [3,4]. The peak positions of the <sup>2</sup>B<sub>1</sub>, <sup>2</sup>A<sub>1</sub>, and <sup>2</sup>B<sub>2</sub> resonances shift slightly to lower energy, and the ion yields increase with the thickness, temperature and morphology (local order) of the water films. These results have been discussed in terms of the local positions and configurations of the interfacial water molecules, narrowing of bandwidths and increased excited state lifetime effects. We have also used laser resonance-enhanced multiphoton ionization to monitor the translational, vibrational and rotational state distributions of the departing hydrogen molecules. We observed structure between 8-16 eV and 18-32 eV in the yield of H<sub>2</sub> (D<sub>2</sub>) (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, v=0-2, J=0-3) which we attribute to the formation of core excited negative ion resonances [5,6]. These resonances, or the excited states produced by autodetachment, decay via a molecular elimination step to yield H<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) directly. The relevance of these detailed DEA studies of interfacial water to the environmental and biological issues mentioned above will be emphasized.

### References:

- 1.) T. M. Orlando and D. Meisel, Chapter 17, “Radiation-Induced Processes in Aqueous Suspensions of Nanoparticles and Nanoscale Water Films: Relevance to H<sub>2</sub> Production in Mixed Waste and Spent Fuel”, ACS Symposium Series, Nuclear Site Remediation, P. G. Eller and W. Heineman, eds. ACS. Press, 2001
- 2.) B. Boudiffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, *Science* **287**, 1658 (2000)

3.) W. C. Simpson, M. T. Sieger, T. M. Orlando, L. Parenteau, K. Nagesha and L. Sanche, *J. Chem. Phys.* **107**, 8668 (1997).

4.) W. C. Simpson, T. M. Orlando, L. Parenteau, K. Nagesha and L. Sanche, *J. Chem. Phys.* **108**, 5027 (1998).

5.) G. A. Kimmel and T. M. Orlando, *Phys. Rev. Lett.* **77**, 3983 (1996).

6.) T. M. Orlando, G. A. Kimmel, and W. C. Simpson, *Nucl. Instru. and Methods in Phys. Res. B*, **157**, 183 (1999)