

Femtosecond interatomic charge and energy transfer in molecules and atomic dimers

**T. Marchenko^{1,2}, M.Simon^{1,2}, K.Schnorr³, R.Moshhammer³, B. Erk⁴, D.Rolles^{4,5},
A.Rudenko⁵**

¹*Sorbonne Universités, UPMC Univ Paris 06, UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, 11 rue Pierre et Marie Curie, 75005 Paris, France*

²*CNRS, UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, 11 rue Pierre et Marie Curie, 75005 Paris, France*

³*Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany*

⁴*Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany*

⁵*J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506, USA*

tatiana.marchenko@upmc.fr

A remarkable effort of the international scientific community in the development and application of a new generation of light sources – x-ray free electron lasers (XFEL) – is currently focused on the challenge of pinning down the mechanisms and time scales of the x-ray induced radiation damage in molecules. Understanding the interaction of intense ultrafast x-ray radiation with small molecules is essential for further studies of dynamic processes in complex systems.

Here we present two recent experimental studies performed at FLASH (Free electron LASer in Hamburg) and LCLS (Linac Coherent Light Source, Stanford) XFEL facilities. The time-resolved pump-probe measurements allow addressing the dynamics of x-ray induced processes on the femtosecond time scale.

The first example addresses the dynamics of the Interatomic Coulombic decay (ICD) in Neon dimers. The ICD mechanism of energy transfer between loosely bound atoms through Coulomb interaction of active electrons was theoretically predicted by L. Cederbaum [1] and remains a hot topic of experimental and theoretical investigations. A pump-probe experiment performed at FLASH in the extreme ultraviolet wavelength regime allowed a direct measurement of the ICD lifetime in Neon dimers. In the experimental scheme, the pump pulse creates a 2s inner-shell vacancy in one of the two Ne atoms. Consequently, the ionized dimer undergoes ICD: the 2s hole in the Ne⁺ ion is filled with a 2p electron from the same ion, whereas the neighboring neutral Ne atom is ionized at the 2p shell through the Coulomb interaction. A repulsive Ne⁺(2p⁻¹)–Ne⁺(2p⁻¹) state resulting from ICD, is further ionized with a probe pulse arriving after a certain time delay. The yield of coincident Ne⁺ - Ne²⁺ pairs recorded as a function of the pump-probe delay, allows deducing the ICD lifetime of the Ne₂^{+(2s⁻¹)} state. The lifetime value of (150±50) fs, obtained in our measurements, is in agreement with quantum calculations [2].

The second experimental study concerns time-resolved investigations of ultrafast charge rearrangement and local radiation damage in dissociating CH₃I molecules. Exploiting an infrared pump laser pulse for triggering the dissociation process, a localized multiple XFEL ionization of a heavy iodine atom embedded in a molecular environment was probed as a function of the internuclear distance increasing with the IR-pump/XFEL-probe delay. We focused our study on the influence of molecular environment on multiple ionization of the iodine atom in a dissociating CH₃I molecule. We observe considerable enhancement of the

production of the highest charge states of iodine at very large internuclear distances, essentially originating from the ionization of the atomic iodine. For shorter distances the iodine charge state distribution shifts towards lower charge states reflecting electron transfer from the methyl group to the iodine atom. This result clearly shows that an interatomic charge redistribution plays an important role in the inner-shell molecular ionization for the CH_3I molecule [3].

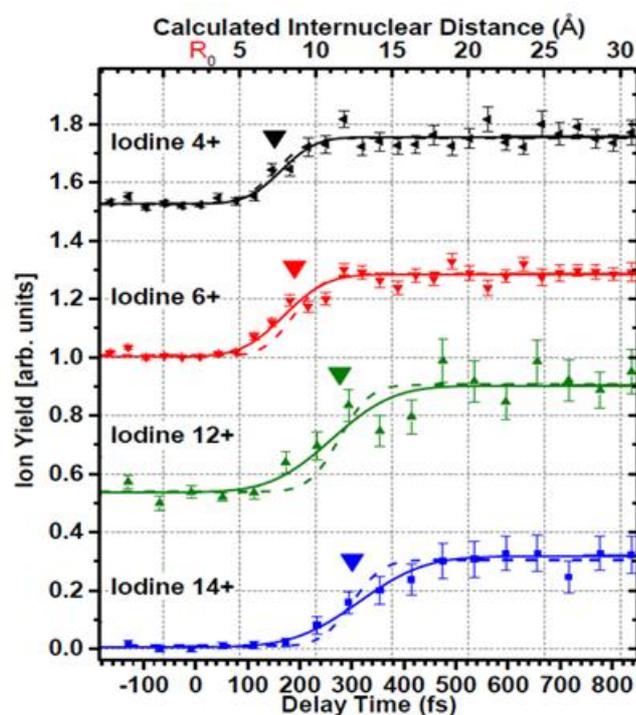


Figure : (taken from [3]) Yields of different iodine charge states resulting from the iodomethane CH_3I dissociation into I^{n+} and neutral CH_3 . Here the delay time can be mapped into an internuclear distance R , as indicated on the top axis. The solid lines show fits to the data. The triangles indicate critical distances beyond which the charge transfer is forbidden within the classical over-the-barrier model. The dashed lines depict the predictions of this model convolved with the experimental temporal resolution. The high charge states can be efficiently reached only from the atomic iodine fragment, hence, beyond a certain internuclear distance between the fragments (or time delay), where the electron transfer becomes impossible.

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