Charge Transfer in Dissociating I_2^{n+} Molecular Ions Accessed by XUV Pump-Probe Experiments

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The absorption of XUV or X-ray photons is often strongly localized at molecular constituents with high atomic number Z. The thereby locally induced charge triggers atomic movement and electron rearrangement across the entire molecular ion which mostly fragments. This situation raises the question of how fast and over which internuclear distances charge can be transferred within the molecule before it fragments into individual atoms and ions. Here, we present experiments on electron transfer between two iodine ions that emerge from fragmented I_2^{n+} molecular ions. With an XUV pump-pulse the neutral I_2 molecule is first multiply ionized and consequently dissociates. After an adjustable time delay an identical XUV probe-pulse is applied which further ionizes the molecular ion. Depending on the delay and the separation of the dissociating fragments the probe pulse may induce charge transfer along the internuclear axis. In order to decide whether charge transfer occurred we monitor the charge state yield and the kinetic energy release (KER) of coincidently detected ions as a function of the time delay.

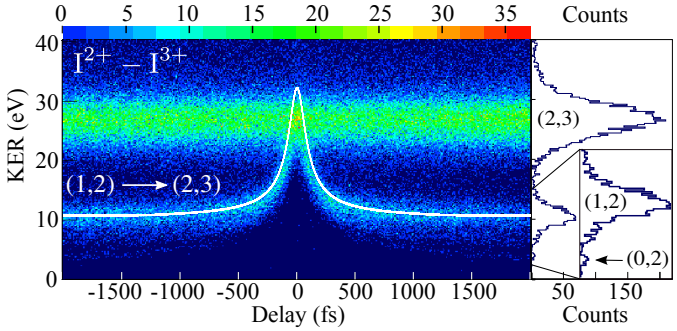

Figure 1: Delay-dependent KER spectrum of coincident $I^{2+} - I^{3+}$ ion pairs and projection onto KER axis for large delays. A classical pump-probe simulation via the precursor charge state $I^{2+} - I^{3+}$, accessed by the pump, is shown as white line.

The experiment was conducted at FLASH at BL2, which is equipped with an autocorrelator that splits, delays and reunites the incoming FEL beam to introduce an adjustable time delay [1]. We chose a photon energy of $87\,\mathrm{eV}$, a pulse duration of $\approx 60\,\mathrm{fs}$, an intensity of roughly $10^{14}\,\mathrm{W/cm^2}$ and focused the beam into a supersonic gas target containing gaseous I_2. The KER of created ions was measured by means of a reaction microscope [2] by accelerating the ions onto a time- and position-sensitive detector in a homogenous electric field. From the time-of-flight and impact position of the ions the three-dimensional momenta are reconstructed and coincident ions are matched by momentum conservation.

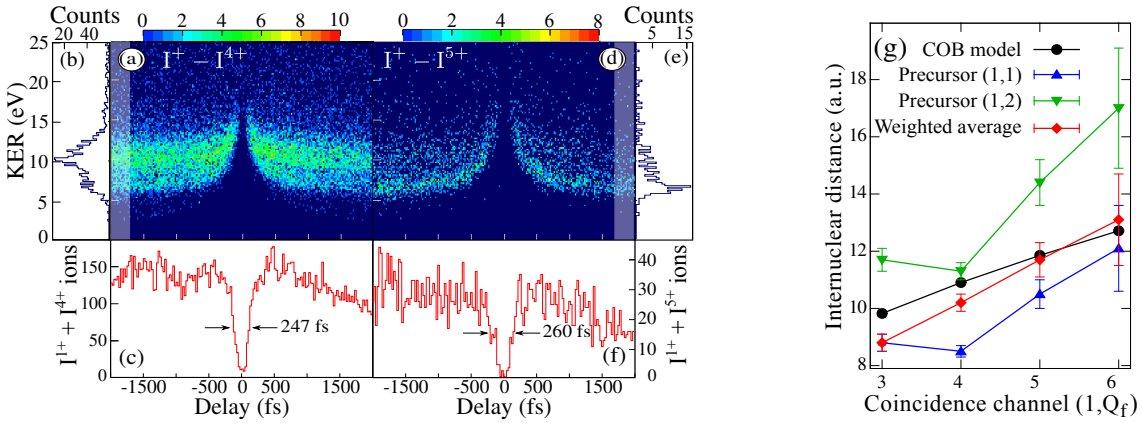

Figure 2: Delay-dependent KER spectra of (a) coincident $(1,4)$ and (b) $(1,5)$ ion pairs. Projections onto the KER axis for large delays are shown in (b) and (e), while (c) and (f) show the projection of all KERs onto the delay axis. (g) R_{crit} for the coincidence channels $(1,Q_f)$ with $Q_f \in \{3,4,5,6\}$. The ionization pathways via $(1,1)$ and $(1,2)$ are shown in blue and green respectively, the weighted average of both in red and predictions from the COB model in black.

The delay-dependent KER spectrum of the exemplary coincidence channel $I^{2+} - I^{3+}$ (in the following $(2,3)$) is shown in Fig. 1. While the constant feature around 27 eV emerges from multi-photon ionization within one pulse, the time-dependent trace is caused by the interplay of pump- and probe-pulse. Analyzing the asymptotic KER for large delays yields the ionization pathway under the assumption of instantaneous Coulomb explosion. The latter hypothesis is confirmed by the good agreement of the time-dependent experimental trace and the according classical pump-probe simulation (cf. Fig. 1).

The delay-dependent KER spectrum for an asymmetric break-up into $(1,4)$ ion pairs is shown in Fig. 2(a). Although both introduced coincidence channels feature the same total charge state, their delay-dependence is fundamentally different: $(1,4)$ exhibits a depleted ion yield for small delays and lacks a time-independent component. As a commonly observed feature, all asymmetrically charged coincidence channels are only produced from a certain delay on (cf. also Fig. 2(d)). For small delays a charge asymmetry induced by the probe pulse is balanced by charge transfer. In contrast, for large delays the dissociating fragments behave like individual ions and charge transfer is blocked. Thus, by analyzing the width of the depleted ion yield the critical time delay up to which charge transfer is possible, can be extracted. The corresponding critical internuclear distances R_{crit} are derived applying the classical pump-probe simulation, introduced in Fig. 1. The resulting distances via the present precursor states and their weighted average are shown in Fig. 2(g). We observe charge transfer over large internuclear distances of $9\,\text{a.u.} < R_{\text{crit}} < 13\,\text{a.u.}$ with increasing R_{crit} for growing charge states. In addition we find excellent agreement of our data with the predictions of the classical-over-the barrier (COB) model (cf. Fig. 2(g)), commonly used in slow ion-atom collisions [3]. The current study mimics the situation of localized X-ray absorption in a molecule leading to high charge on a single heavy-atom site, which is crucial to understand the role of damage in single molecule imaging at FELs.

References

[1] M. Wöstmann *et al.*, J. Phys. B **46**, (164005), 2013

[2] J. Ullrich *et al.*, Reports on Progress in Physics **66**, (1463), 2003

[3] H. Ryufuku *et al.*, Phys. Rev. A **21**, (745-750), 1980
A. Niehaus, J. Phys. B **19**, (2925), 1986