

Ultrafast Dynamics in Donor-Acceptor Prototype Molecules by XUV-IR Attosecond Spectroscopy

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Photoinduced charge transfer processes are at the basis of core technologies aiming, for example, at effective conversion of solar energy into electrical energy. A deeper understanding of these processes requires real-time imaging of the electronic-nuclear motion on the few-femtosecond time scales [1]. Here we investigate the dynamics following photoionization in the simplest donor-acceptor systems, through XUV-NIR pump-probe attosecond spectroscopy, in combination with photo-electron photo-ion coincidence energy-resolved (PEPICO) measurements and semi-classical trajectories simulations. We explore three systems with different functionalization of the donor-acceptor groups (4-nitroaniline, 4-NA; 3-nitroaniline, 3-NA; N,N-Dimethyl-4-nitroaniline, nd-NA; chemical structures shown in Fig. 1). After ionization by an isolated attosecond-XUV pulse, the ultrafast dynamics of the cation is probed by 4-fs NIR infrared pulse by measuring the production yield of the different fragments and their kinetic energy distributions, shown in Fig. 1a and Fig. 1b, respectively as a function of the delay.

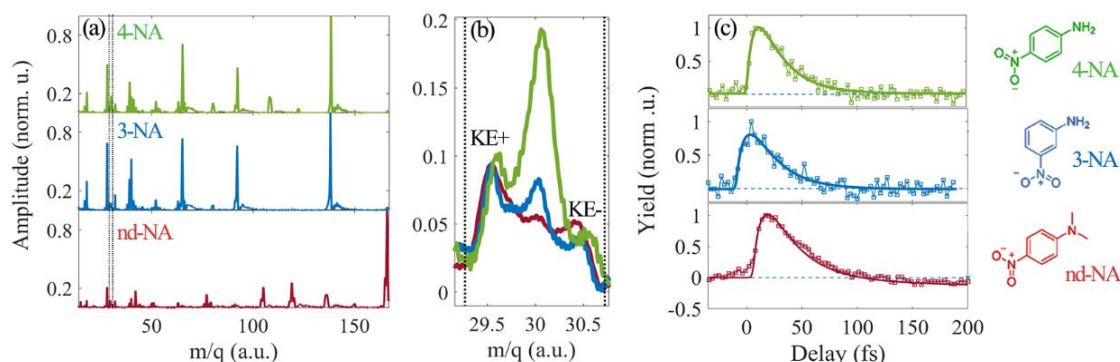


Fig. 1 a) Mass spectra of the molecules after ionization by the XUV radiation. b) Zoom of the dotted region showing the details of the NO^+ fragment ($m/q=30$). c) Relative yield of the high kinetic energy NO^+ fragment as function of the pump-probe delay.

In particular, the NO^+ fragments with high kinetic energy (KE+ and KE- in Fig 1. (b)) display an ultrafast transient signal, with a formation time of ~ 10 fs and a relaxation decay with a time constant of 22 fs (4-NA), 23 fs (3-NA) and 28 fs (nd-NA) (Fig. 1(c)). Comparison with PEPICO measurements allows us to unambiguously assign these fragmentation pathways mediated by Coulomb explosion [2]. Numerical simulations, using semi-classical trajectories with the surface-hopping method at the CASSCF level of theory, reveal that the observed transient features are related to a non-adiabatic ultrafast charge transfer followed by an efficient spreading of the cation nuclear wave packet. Thanks to a combination of diverse experimental approaches with theoretical calculations we thoroughly address the role of electron-nuclear dynamics in highly excited states of the cation for prototypical donor-acceptor systems.

[1] M. Nisoli, et al, Chem. Reviews **117**, 10760-10825 (2017).

[2] L. Cooper, L. G. Shpinkova, E. et al., Int. J. Mass Spectrometry **207**, 223-239 (2001).