PhD project: Ultrafast charge transfer processes in condensed phase probed by resonant X-ray emission and Auger spectroscopy

Host institution : Laboratoire de Chimie Physique - Matière et Rayonnement (LCPMR), CNRS - Sorbonne Université, 4 place Jussieu, Paris, FRANCE

Contract: Fixed term, 36 months, starting October 2024

Contact: Tatiana Marchenko, email: tatiana.marchenko@sorbonne-universite.fr

Summary:

The focus of the PhD project is on the mechanisms of charge transfer in organic molecules in condensed phase (solid or liquid), susceptible to be responsible for charge transport in extended media with possible implications in the areas of photovoltaics and radiation-induced damage in biological tissue. The preliminary results on charge transfer in organic polymers and in aqueous solution of amino acids have been recently achieved using hard X-ray resonant Auger spectroscopy at SOLEIL synchrotron. We plan to reinforce this research direction with a complementary use of resonant inelastic X-ray scattering in condensed phase, provided by our recently developed state-of-the-art X-ray emission spectrometer. The PhD project will benefit from a privileged access of our group to the GALAXIES beamline at SOLEIL and from the ongoing international collaborations, providing strong experimental and theoretical support. The young researcher will also have an opportunity to join the international research network beyond the topics directly relevant to the PhD project, e.g. involvement in XFEL activity of the group, which will enhance the employability of the researcher beyond the PhD.

Scientific context:

The process of charge transfer (CT) involving electron and nuclear dynamics is a long-standing research topic, which nevertheless remains bustling, essentially due to its significance for multiple applications in chemistry, biology and materials sciences. Rapid development of time-resolved spectroscopy allows nowadays probing the dynamics of CT in various systems on femtosecond and even attosecond time scale. Meanwhile, high-resolution X-ray spectroscopy in the energy domain can also provide a useful insight into ultrafast dynamical processes in molecular systems. Relaxation of a resonantly core-excited molecule via emission of an X-ray photon or an Auger electron, occurring within the lifetime of a core-excited state, can serve as a probe of any dynamical process taking place in the molecule on the same time scale. This is the basic concept of “core-hole clock” spectroscopy, the technique that our group has successfully applied in studies of ultrafast dynamics in gas-phase and condensed-phase systems [1-6].

Methods:

The outstanding instrumental performance of the multi-crystal x-ray spectrometer (MOSARIX), developed by our group, [7] and of the Hard X-ray Photoelectron Spectrometer (HAXPES) [8] in combination with the extremely narrow bandwidth of the GALAXIES beamline at SOLEIL, so far has no analogy in the world and provides an unprecedented opportunity to perform high-resolution high-energy X-ray emission and electron spectroscopy in resonant Raman conditions enabling us to break the limit set by the natural lifetime broadening of the intermediate core-excited state. This state-of-the-art spectroscopy in the hard X-ray regime is available for dilute systems, solid samples and liquid micro-jets. Applying synchrotron X-ray radiation for excitation of molecules at deep core levels, one can monitor the dynamics in molecules using two complementary “core-hole clock” techniques: high-resolution resonant inelastic X-ray scattering (RIXS) using MOSARIX and high-resolution resonant Auger spectroscopy (RAS) using HAXPES. A combination of both techniques can provide interesting complementary information on the relaxation dynamics of core-excited systems, which occurs in competition via X-ray emission and Auger electron emission [3].

Expected results:

The CT will be locally induced in the system by resonant excitation of a marker atom at a deep core shell and monitored by RAS or RIXS. The information on the electron delocalisation can be obtained from the spectral analysis. Experimental RAS and RIXS spectra will be recorded as a function of incident photon energy thus providing detailed 2D maps [6]. The information on the electron

delocalisation will be reflected in the excitation-energy dependence of the recorded spectra. The ultrafast electron dynamics induced by the creation of a core hole upon absorption of X-ray radiation, can be simulated by real-time time-dependent density functional theory (RT-TDDFT).

Required Skills and Qualifications:

- ✓ Master's degree in physics or chemistry
- ✓ Excellent oral and written communication skills in English
- ✓ Experience in X-ray emission and photoemission spectroscopy
- ✓ Scientific creativity and strong motivation to research
- ✓ Capability to work both in a team and independently

Responsibilities:

- ➢ Design and perform experiments
- ➢ Perform data analysis and numerical modelling
- ➢ Prepare publications for peer-review journals
- ➢ Present at international conferences

References

[1] T. Marchenko et al. J. Chem. Phys. 134, 144308 (2011)
[2] T. Marchenko et al., Phys. Rev. X 5, 031021 (2015)
[3] T. Marchenko et al., Phys. Rev. Lett. 119, 133001 (2017)
[4] O. Travnikova et al., Phys. Rev. Lett. 116, 213001 (2016)
[5] O. Travnikova et al., Phys. Rev. Lett. 118, 213001 (2017)
[6] N. Velasquez et al., Phys. Chem. Chem. Phys. 26, 1234 – 1244 (2024)
[7] I. Ismail et al., Review of Scientific Instruments 92, 073104 (2021)
[8] D. Céolin et al., J. Electron Spectrosc. Relat. Phenom. 190, 188–192 (2013)

Please send your motivation letter, CV and the names and contact information (including email addresses) of two or three referees to Tatiana Marchenko

email: tatiana.marchenko@sorbonne-universite.fr