Probing electronic-symmetry breaking in dissociative ionizations using time-resolved RIXS

1) Scientific background of this proposal

The coupling of electronic and nuclear dynamics is fundamental to the understanding of light-induced dynamics in matter. X-ray spectroscopy (XRS) is a particularly powerful method for studying this phenomenon owing to its element selectivity and site specificity. Moreover, XRS methods offer a number of exceptional sensitivities that provide an unprecedented view of coupled electronic and nuclear dynamics. In recent years, XRS has been realized with femtosecond time resolution, fulfilling important expectations towards the technique. Most ultrafast XRS experiments to date have made use of X-ray absorption spectroscopy (XAS) or X-ray photoelectron spectroscopy (XPS). Resonant-inelastic X-ray scattering (RIXS) has been explored much less, with the notable exception of a pioneering study of $Fe(CO)_5$ in solution that achieved a temporal resolution of ~300 fs. However, time-resolved RIXS (TR-RIXS) is arguably one of the most powerful methods because of it combines the general strengths of XRS with the capability of interrogating valence-shell electron dynamics, which are the most important in defining light-induced dynamics in matter. Therefore, we propose to apply TR-RIXS to study ultrafast coupled electronic-nuclear dynamics in the dissociative ionization of molecular systems. Specifically, our proposal aims at identifying the particular strengths of TR-RIXS by addressing the following questions. Is TR-RXIS sensitive to (i) the electronic symmetry breaking induced by excitation/ionization, (ii) the change in local bonding character during a photochemical process and (iii) the change in core-hole delocalization during a large-amplitude structural rearrangement? These questions will address the fundamental potential of TR-RIXS in elucidating non-adiabatic photochemical processes from the electronic point view. This development is particularly desirable keeping in mind the upcoming possibility of extending TR-RIXS to the attosecond time scale, owing to the imminent availably of suitable attosecond pulses at XFEL facilities.

A natural class of systems to explore the three questions formulated above are highly symmetric molecules containing several identical ligand atoms, which moreover display ultrafast light-induced chemical reactions and are amenable to high-level ab-initio calculations. Two molecules fulfilling these conditions are CF4 and SF6, which have been shown to undergo ultrafast valence-ionization-induced dissociation (in 40 fs and 70 fs, respectively). These molecules have so far been studied with TR-XAS at the carbon K-edge and the sulfur L2,3-edges, but not by any other TR-XRS methods. This study has revealed the evolution of the lowest unoccupied electronic states and shape resonances from the point of view of the central atom, but could not address any of the above questions. However, single-pulse RIXS studies of both CF4 and SF6 have been performed and have hinted at the considerable additional information that can be expected from TR-RIXS studies of these systems. We therefore propose to realize TR-RIXS with the best ever-reported temporal resolution and address the fundamental questions (i)-(iii) formulated above. These measurements will not only explore the fascinating signatures of electronic-symmetry breaking in ultrafast light-induced chemical reactions but also offer important insights into the future application possibility of TR-RIXS to more complex molecular systems and to sub-femtosecond time scales.

2) Motivation for this proposal: expected results and their impact in relevant scientific area(s) (references relevant to the scientific case, not necessarily involving proposers, can be listed in this section)

We propose to exploit the novel capabilities offered by the new 1D imaging spectrometer at the SQS end station to realize TR-RIXS on the dissociative ionizations of CF4 and SF6 at the F K-edge. The dynamics will be initiated through strong-field ionization with 30-fs pulses centered at 800 nm, which have been shown to induce ultrafast (40/70 fs), barrierless, dissociation reactions of CF4+/SF6+. The use of strong-field ionization ensures that a large fraction of the sample will undergo the intended dynamics. The experiments will use SASE pulses at the F K-edge (~690 eV) with their typical ~1% bandwidth and will monitor the emission perpendicular to the direction of the incident X-ray pulses. A non-collinear geometry with a crossing angle of 15° between the laser and X-ray pulses will be used. This will remove the need of scanning the pump-probe delay. Assuming propagation of both pulses with vacuum speed of light results in a maximal temporal resolution of 1.7 fs, defined by the spatial resolution of the 1D imaging spectrometer. The total range of delays covered will amount to 230 fs, defined by the 2-mm length of the overlapping beam paths. This is more than enough to cover the known dissociation times of CF4+ and SF6+. The temporal and spectral jitter of the SASE pulses will be addressed by single-shot measurements using timing tools and time-of-flight photoelectron spectrometry, combined with ghost-imaging techniques. More details are given in Section 3.

In the first set of experiments, the X-ray pulses will be tuned to the 5a1/6a1 resonances of CF4/SF6, located at 690/689 eV []. Strong-field ionization of the neutral molecule will induce an ultrafast dissociation of the corresponding cation. During the dissociation, the resonance position is known to shift by less than 3 eV [], such that it will always be located within the bandwidth of the SASE pulses without the necessity to tune their central photon energy. The calculated RIXS spectra for this situation are presented in Fig. 1. They show major changes in the emission spectrum from the parent species CF4/SF6 to the product species CF3+/SF5+.

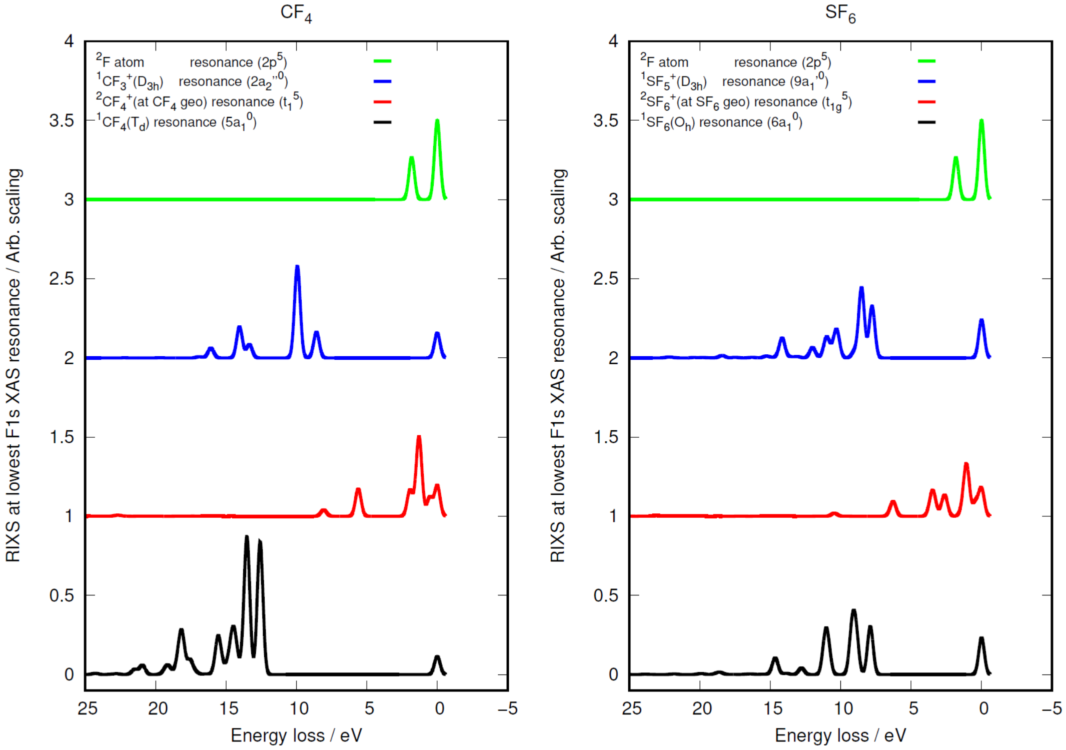

Fig. 1: Calculated RIXS spectra for CF4, SF6 and the products of their dissociative ionization

Specifically, the black traces show the calculated RIXS spectra of the neutral parent molecules, revealing a number of energy-loss features associated with each of the valence shells of the molecule. The blue traces show the spectra of the CF_3^+/SF_5^+ products of the dissociation reaction. These calculations impressively convey the ability of TR-RIXS to map out the entire valence electronic structure of these molecules in a single shot – and therefore along each time step of the dissociative pathway. Instead of only capturing the evolution of the unoccupied electronic states as in TR-XAS, TR-RIXS additionally accesses all of the occupied valence states. The most striking predicted feature is the large decrease of the minimal energy loss from CF4 to CF3+, which is caused by the symmetry breaking from T_d to C_{3v} and the corresponding rearrangement of the electronic structure. Beyond the time-resolved electronic-structure information, this first-of-a-kind experiment will also reveal the sensitivity of TR-RIXS to the electronic symmetries and their dynamical evolutions. Previous RIXS measurements of the static SF6 molecule have shown that the electronic-parity allowed dipole transitions dominated in the RIXS spectra, but the parity-forbidden transitions were nevertheless observed with lower intensity []. This was explained by dynamics in the core-excited state, which induced nuclear-wave-packet motion along non-totally-symmetric vibrational modes, thereby breaking the inversion symmetry of the molecule and inducing mixing between g and u electronic states. This measurement on static SF6 molecules therefore revealed an interesting sensitivity of RIXS to the electronic symmetry. In the proposed experiments, we plan to explore how this sensitivity to electronic symmetry can be transposed to probe coupled electronic and nuclear dynamics in the dissociation of CF4+/SF6+. Starting with the case of SF6+, we propose to study the manifestation of electronic symmetry breaking from the initial strong-field ionization through the evolving dissociation reaction SF6+→SF5++F to the final products. This will be done in two ways, first, through excitation of the 6a1 resonances of SF6+ and monitoring the TR-RIXS signal, as mentioned above, and second through excitation of the F1s→HOMO resonance of SF6+, again monitoring the TR-RIXS signal. This latter approach has the benefit of being sensitive to, both, the time evolution of the valence-shell of SF6+ as it dissociates to SF5+ and the appearance of the atomic fragment. The corresponding RIXS spectra are shown in Fig. 1 as red and green traces, respectively.

Whereas this first set of measurements will be performed with parallel polarizations of the 800-nm and X-ray pulses, we will then turn to perpendicular polarizations. This will provide direct experimental insight into the local σ/π character of the valence electronic states and how it evolves along the dissociative pathway. The sensitivity of static RIXS to the local σ/π character of the molecule was nicely demonstrated in [] by studying the polarization dependence of the RIXS signal. Specifically, it was shown that when exciting the 6a1 resonance of local σ character, horizontal polarization emphasizes the emission from p orbitals, whereas vertical polarization leads to the observation of both σ and π orbitals. This sensitivity can be very nicely applied to study the evolution of the local bonding/antibonding character of the molecular orbitals in the time-resolved experiments, by exploiting the anisotropic dissociation of CF4+/SF6+ induced by strong-field ionization. Specifically, it has been shown that both molecules preferentially dissociate with the C-F/S-F bond pointing along the IR-polarization direction. This creates a strong anisotropy of the dissociating molecules, which can be used to induce dissociation primarily parallel to the X-ray polarization direction or perpendicular to it. The comparison of the TR-RIXS signals obtained in both polarization geometries will then reveal the evolution of the local symmetries of the molecular orbitals along the dissociation pathway. This is particularly interesting in the case of the frontier orbitals, which gradually evolve from bonding/anti-bonding to degenerate non-bonding orbitals as the bond is broken.

Finally, we propose to explore the sensitivity of TR-RIXS to inversion symmetry at an even more fundamental level by inducing a spatially anisotropic dissociation of SF6+ using a phase-controlled two-color (800+400-nm) laser field. Such two-color femtosecond pulses have been used extensively to control dissociative ionization, molecular orientation and high-harmonic generation. Here, we propose to induce a spatial anisotropy in the dissociation of SF6+→SF5++F by using the two-color field for strong-field ionization. Such a spatial control of SFI has recently been demonstrated for CF4 []. Here, we will use the two-color field to break inversion symmetry macroscopically and will study its effect on the TR-RIXS signal. The case of SF6+ is particularly interesting because SFI can populate both the (t1g)-1 ground state of the cation and the (t2u)-1 first-excited state. The two electronic states of SF6+ are separated by ~1.4 eV in the Franck-Condon region. This will give rise to an electronic wave packet with a period of ~2.9 fs. Since the potential-energy curves of these two dissociative states are nearly parallel in the Franck-Condon region and then slowly merge along the dissociative pathway, the electronic coherence can be expected to survive for tens of femtoseconds, before the created electron hole localizes and defines which one of the two anti-parallel S-F bond breaks. Time-resolved RIXS following excitation from F1s to these two states will simultaneously probe the electronic dynamics, the electronic symmetry breaking induced by the electron-hole localization, and the ensuing anisotropic photodissociation reaction. This would provide the most complete picture of the interplay of electronic and structural dynamics in such ultrafast dissociation reactions and reveal the particular strengths of TR-RIXS in revealing such coupled dynamics on ultrashort time scales. Importantly, it will also reveal opportunities for TR-RIXS on the attosecond time scale, which might become possible in the near future.

References

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3) Experimental plan

This proposal will optimally benefit from the new 1D imaging spectrometer at the SQS end station. Strong-field ionization will be induced by focusing the available 800-nm, 15-fs laser pulses to an intensity of ~1013 W/cm2 to induced strong-field ionization of the gaseous samples (CF4/SF6). For the last experiment, an in-line non-linear-optics setup consisting of a BBO crystal, a zero-order waveplate and a calcite plate will be used to generate a phase-controlled 800/400-nm two-color laser field.

For the excitation energy we need photons with energies lying between 675 eV and 690 eV with the typical 1% SASE bandwidth. The relative arrival time of pump and probe is an important parameter, such that the best available timing tools will be needed.

The experimental plan is as follows:

1. Recording X-ray-only RIXS maps of CF4 and SF6
2. Time-resolved experiments of the dissociative ionization of CF4/SF6 using 800-nm SFI with X-rays tuned to the 5a1/6a1 resonance
3. Time-resolved experiments of the dissociative ionization of SF6 using 800-nm SFI with X-rays tuned to the HOMO resonance
4. Time-resolved experiments of the spatially controlled dissociative ionization of SF6 using phase-controlled 800/400-nm SFI with X-rays tuned to the HOMO resonance

a) Justification for the use of an X-ray free-electron laser facility and motivation for the selected instrument

The 1D imaging spectrometer is currently unique in its capabilities and is optimally suited to realize the proposed femtosecond-time-resolved RIXS experiments, which cannot be performed elsewhere.

b) Justification for the number of shifts requested

Based on a 07:00 to 23:00 operation plan, we apply for a total of five 16-hour shifts for this experiment. Based on the information available to us, we plan 1 shift for optimizing the experimental conditions, i.e. recording static RIXS maps, X-ray + laser spot characterizing, temporal and spatial overlap, energy resolution of the 1D imaging spectrometer. Shift 2 for realizing the time-resolved experiments using SFI with 800-nm pulses and X-rays tuned to the 5a1/6a1 resonance of CF4/SF6. Shift 3 for TR-RIXS measurements with the X-rays tunes to the HOMO resonance. Shift 4 for realizing the TR-RIXS measurements with phase-controlled 800/400-nm two-color laser pulses. One remaining shift is foreseen trouble-shooting and data contingency.