Dynamics Before Destruction: Saving the O_2 Molecule

1) Scientific background of this Proposal

One of the visions in modern science is to control chemical reactions on the atomic scale. Core hole excitations are attractive in this context as they are localized at specific atomic sites, and initiate dynamics during their short lifetime, corresponding to the natural scales for electronic-vibronic coupling. As stimulated X-ray Raman scattering (SXRS) is the essential building block [Kimberg] for any molecular method based on non-linear X-ray physics [Mukamel] it is prerequisite to understand the role played by the dynamics in the core-excited state.

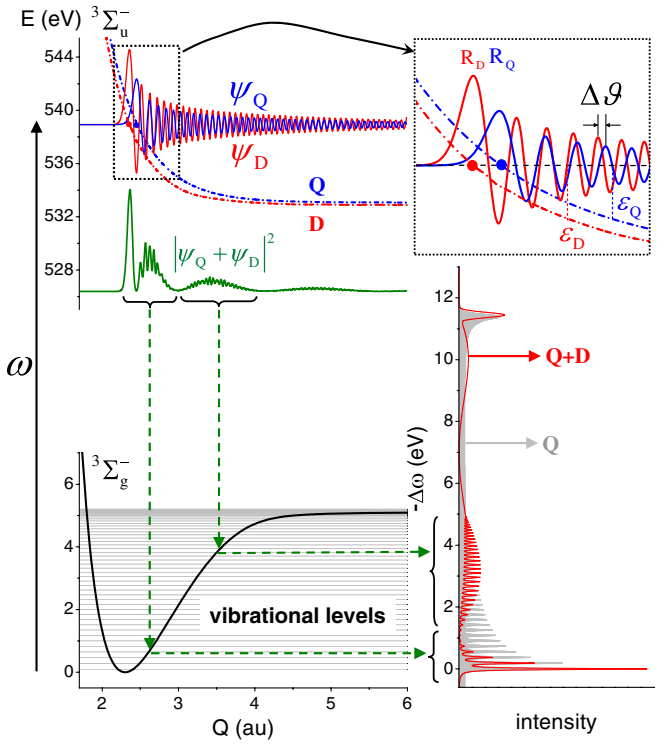

FIG. 1 (From Ref. [Pietzsch]). The scheme for RIXS spectra excited at the σ* resonance in O_2.
A long vibrational progression is observed, with a beat modulation due to the two different repulsive potential curves of the core hole state.

Core-hole induced molecular dynamics is sensitively monitored in resonant inelastic soft X-ray scattering (RIXS), and high-resolution spectra of small molecules show excessive details. The oxygen molecule is the most well-characterized showcase, where e.g., the ability to tune the vibronic wavepacket to avoided crossings has been demonstrated [Hennies], and effects due to interference with the non-resonant inelastic scattering have been observed [Sun]. Ultrafast dissociation at the σ* resonance leads to a more than 12 eV long vibrational profile that exhibits spatial quantum beats in the wavefunction of the separating atoms (Fig. 1) [Pietzsch].

To influence the dynamics in the core-excited state, intense pulses with duration comparable to the intrinsic core hole lifetimes are required. The pulse intensity available at the SQS instrument is sufficient to induce depopulation of the core excited state within its natural lifetime, thereby effectively gating the dynamics. Using the newly implemented two-color mode, one color can be used to excite a certain resonance, whereas the second color can further ionize the already core excited state, and moreover it can be tuned to selectively induce stimulated emission or resonantly excite a second core hole.

As the available pulse duration presently is larger (10-20 fs) than the core hole lifetime (4fs) time-resolved studies can only be performed in a limited fashion. With pulse durations smaller than the lifetime broadening, time-resolution will be a great asset when extending this type of experiments to time-resolved pump-probe experiments. Already now we can use the rate for competing processes to gate the dynamics by variation of pulse parameters. While the method has potential to be generalized to large molecular systems, a natural starting point is application to simple diatomic molecule with limited degrees of freedom. We anticipate that information essential for development on non-linear methods will emerge in the proposed experimental scheme.

2) Motivation for this proposal

The new 1D imaging spectrometer [1D] measures X-ray spectra perpendicularly to the incident beam with high spectral (100 meV) and spatial (15 micron) resolution. This can be used to monitor intensity variations in the RIXS spectra, and give detailed information about the pulse propagation in a medium. In connection with measurements of the transmitted spectrum in a conventional X-ray spectrometer, the interaction between intense X-rays and a molecular medium can be monitored in a new entirely photon-based way. As spectral lines are undistorted by plasma potentials and inelastic scattering of the secondary radiation can be neglected, we expect that natural lifetimes and vibrational fine structure are within reach.

Also in the linear regime, the σ^* resonance in O_2 is associated with violent nuclear dynamics, resulting in a long vibrational progression in the RIXS spectrum due to recombination of the initially excited electron and the core hole (Fig. 1). It is proposed to examine how this ultrafast core-hole induced molecular dynamics can be influenced and, to some extent, controlled in the high-field regime.

Monitoring the variations in the X-ray emission spectra along the path of the incident beam will give useful information about the pulse properties as it propagates as well as the molecular medium. The dependence of the signals on the initial pulse properties, especially concerning duration, intensity and central frequency, as well as of the medium, especially concerning density and density gradients. We anticipate that this will be an asset in the efforts to develop non-linear X-ray methods to investigate ultrafast molecular dynamics in general.

Among the processes we expect to influence the signal are stimulated emission and SXRS [Mukamel] and further ionization and excitation within the core-hole lifetime, including resonant excitation of additional core holes. The signal measured in the perpendicular direction will also show how the background in the transmitted spectrum [Kimberg2016] due to multiply ionized species is formed.

3) Experimental plan

RIXS spectra will be measured perpendicularly to the incident radiation with spatial resolution using the new 1D imaging spectrometer [1D]. To measure resonant spectra with high energy resolution, the scheme where each SASE pulse is characterized using time-of-flight electron spectroscopy and ghost imaging [Li] will be applied.

The SASE pulse will be tuned to the σ^* resonance in O_2 at 540 eV. This resonance has a width of around 5 eV, matching the 1% bandwidth of the SASE pulses.

Initially, the SASE pulse will be tuned to the σ^* resonance in O_2 at 540 eV. This resonance has a width of around 5 eV, matching the 1% bandwidth of the incident radiation. At the lower intensities we expect that the conventional RIXS spectrum is observed in the perpendicular direction, and that the pulse will be modified by Beer-Lambert absorption in the forward direction. Increasing the pulse intensity will result in a background due to an increasing abundance of molecular and atomic ions. Kimberg et al, showed for the CO molecule, that the C K ionization gives rise to a major multiple ionization channel for 0.1-0.2 mJ pulses [Kimberg2016], while direct valence ionization and resonant Auger will be the main sources for O_2. The contribution from ions to the background is further attenuated with selective excitation. The σ^* resonance in O_2^+ peaks at 546 eV [Kjellsson], predominantly outside the pulse range, and we expect resonances in O_2^{2+} to be shifted even further. Transitions in atomic ions within the energy range are easily identified as sharp peaks in the spectra and can be used for calibration purposes [Leutenegger].

At higher intensity we expect the role of stimulated emission to increase. The primary beam will seed stimulated emission, thereby influencing the perpendicular signal and the background due to ionized species. The spatially resolved signal monitors how the processes evolve in the medium.

After characterizing this behavior we turn to two-color experiments. While the first color remains at the σ^* resonance, the second is tuned to 535 eV, with the aim to depopulate the core-excited state during the nuclear wavepacket evolution. Using “low” intensity for the excitation, and high-intensity for the second color, we expect to see a modification of the perpendicular RIXS spectrum. Attenuation of the intensity ratio between the atomic and molecular peaks is direct evidence that the molecule can be saved from dissociation.

Tuning the second color to 530 eV the pulse will cover molecular transition corresponding to $1\pi_u^{-1}3\sigma_u$ (525 eV) and Rydberg excited final states (523-525 eV) [Kimberg2012, Sun], atomic 2p→1s transitions (527 eV), as well as the π^* resonance of the neutral molecule (531 eV). A rich phenomenology is expected, which will be highly dependent on the intensity of the two incident pulses. We expect that seeding the molecular transitions induces stimulated emission that halts the ultrafast dissociation, and the intensity may also be sufficient to seed lasing in the atomic fragment. The ratio between the “conventional” RIXS signal from π^* and σ^* resonances will be highly dependent on the incident pulse properties.

If time allows the we will explore the possibility to excite a second core hole color by tuning to the resonances, expected to be around 630 eV (check!) for single-site, and 550 eV (check!) for two-site core holes. This, again, will

gate the evolution of the vibrational wave packet, directly observable in the perpendicular RIXS spectrum. Intensity may even be sufficient to directly observe the emission from the double core holes.

High target density (0.1-1 bar) and steep pressure gradients are mandatory to accomplish that the crucial processes occur in sight of the spectrometer, and that self-absorption of the secondary radiation is minimized. Simultaneously, a high target density must be maintained. For this purpose we will use a gas-cell with a thin convex surface facing the spectrometer. Using a high-precision manipulator this surface will be moved into the XFEL beam, which will cut a slit with a length adapted to the spectrometer acceptance (2 mm), and a width tailored to the cross section of the interaction region (a few micron). With this cell the conductance is kept small and sufficient target density can be maintained in the interaction region.

If technically feasible, the transmitted radiation will be simultaneously measured in the conventional "Viking" spectrometer mounted downstream. It has earlier been used for this purpose in several successful measurement campaigns [Kimberg2016, Barillot, SCS].

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

Exploring non-linear X-ray physics for investigation of ultrafast molecular dynamics requires X-ray pulses that are only available at FEL facilities. The 1D imaging spectrometer, installed at the SQS instrument opens a new window of information about such processes. These experiments cannot be done elsewhere.

b) Justification for the number of shifts requested

From simple linear considerations we estimate that the count rate will be limited by the detector capacity to detect 100 counts/pulse. Although this would allow for fast data collection, this investigation of the spectral dependence on the parameters can only start during one week of beamtime.

Day One: Shift 1-2: The gas-cell concepts will be tested. The conventional cell will be used for the measurements if the membrane window is resilient against rupture and contamination due to the plasma. If not, the new gas-cell concept will be implemented. The 1D spectrometer will fine adjusted to the relevant energy range

Day Two: Shift 3-4: The correlation with the time-of-flight spectrometers will be carried out, and the limits for recording conventional RIXS spectra with SASE pulses at low intensities will be explored.

Day Three: Shift 5-6: The dependence of the spectra on pulse energy, pulse duration and target density will be mapped.

Day Four: Shift 7-8: Opportunities with two-color mode will be explored

Day Five: Shift 9-10: Continued data collection.

References:

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