Stimulated X-Ray Raman Scattering with Free-Electron Laser Sources

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Abstract. Stimulated electronic x-ray Raman scattering is the building block for several proposed x-ray pump probe techniques, that would allow the study of electron dynamics at unprecedented timescales. Here, we present the first experimental demonstration of stimulated electronic x-ray Raman scattering in a gas sample of neon using a self-amplified spontaneous emission x-ray free-electron laser. Despite the limited spectral coherence of these sources, high-resolution spectra can be obtained by statistical methods, opening the path to coherent stimulated x-ray Raman spectroscopy. An extension of these ideas to molecules and the results of a recent experiment in CO are discussed.

1 Introduction

X-ray free-electron lasers (XFELs) open the pathway to transfer nonlinear spectroscopic techniques to the x-ray domain. A promising all x-ray pump probe technique is based on coherent stimulated electronic x-ray Raman scattering. Similarly to optical impulsive stimulated Raman scattering, where coherent vibrational and rotational wave packets can be created and subsequently probed [1], stimulated x-ray Raman scattering with sources of a broad bandwidth covering the range of valence excitation energies would

result in electronic wave packets, thus opening the pathway to coherently probe electronic and nuclear dynamics. The relatively small Raman-cross section at x-ray frequencies can be enhanced by near resonant excitation, which in addition gives the advantage of targeting specific elements in a molecular complex. The electronic wave packets that are created in such a stimulated Raman process are typically localized around the targeted atoms, and the evolution of the wave packet, resulting in phenomena like charge transport, charge migration or dissipation of the energy to vibrational modes, can be subsequently studied by a second, delayed x-ray pulse. A wealth of different x-ray pump-probe schemes has been suggested over the last decades [2-4], but the underlying building block of these sophisticated methods stimulated electronic x-ray Raman scattering - was only recently demonstrated [5]. Here, we give a summary of our experimental results in atomic neon and, discuss a recent experiment in carbon monoxide (CO), where stimulated Raman scattering was attempted with two XFEL pulses of distinct wavelength.

2 Stimulated X-Ray Raman Scattering in Neon

The first demonstration of resonant stimulated electronic x-ray Raman scattering was achieved in neon [5] at the LCLS XFEL in 2011. A second independent demonstration followed in 2013 with an improved spectral resolution of 0.3 eV. The XFEL parameter regime and the setup were similar in both experiments. Pulses of 40-60 fs duration were focused to spot sizes in the range of 2-3 μ m into a 1 cm long gas cell filled with neon at 500 Torr pressure. A grating spectrometer was fielded in 4 m distance downstream and the spectrum of the transmitted XFEL and emitted line radiation was collected shot-to-shot. The photon energy was tuned from 865-875 eV across the pre-K edge, core-excited resonances and the K-edge of neon (see level structure in



Fig. 1. Level scheme of the resonant scattering process with SASE pulses in neon.

Fig. 1). Stimulated resonant inelastic x-ray scattering (sRIXS) from the ground state, with the intermediate 1s⁻¹3p¹ core-excited to the final 2p⁻ ¹3p¹states results in emission lines at 849.3 and 849.7 eV. These lines are partly overlapping with the stimulated K- α emission [6,7] at 849.8 eV, resulting from inner-shell ionization. The core excited and core-ionized states predominantly decay via Auger decay and have an extremely short lifetime of 2.4 fs. Similarly to photoionization K- α x-ray laser [7,8], an avalanche of stimulated emission events sets in as the x-ray pulse propagates through the medium and prepares atoms in core-excited states, so that at saturation of the amplification process, stimulated Raman scattering dominates over the Auger decay.

Three measured single-shot spectra from our 2013 experiment are shown in Fig. 2a. The line emissions at around 850 eV show different energy position and line profiles, highlighted in the inset. A summary of the recorded spectra is depicted in Fig. 2b. The spectra are ordered with respect to the incoming central photon energy, which was determined by the electron-bunch energy of the accelerator on a shot-to-shot basis. With the improved resolution compared to 2011, the 1s⁻¹3p¹ resonant excitation can be discerned as a clear absorption dip of the XFEL pulse, 3 eV from the K-edge. Stimulated line emission is seen over the whole covered spectral range. Due to the relatively large XFEL bandwidth (5-7 eV) tuning the SASE pulses to the 1s⁻¹3p¹ core-excited resonance in neon at 867.5 eV results in partial overlap with the continuum. Therefore sRIXS competes with stimulated emission following K-shell ionization for a typical SASE pulse and the processes can not be



Fig. 2 a) Three measured spectra in neon. The central photon energy of the SASE pulse was 868 eV and the pulse energy 1 mJ. The inset shows a magnification of the normalized line emission.
b) Series of measured single-shot spectra as a function of the incoming central SASE photon energy. The color code shows the number of integrated counts in the emission line.
c) Normalized emission spectrum as a function of the central SASE photon energy.

discerned by simply analyzing at the emission strength as a function of incoming photon energ. Analyzing the emission-line profile as a function of the incoming photon energy (see Fig. 2c), a clear evidence for sRIXS can be put forward [5,6]. Whereas for energies well above the K-edge the emission profile and line position are stable, for photon energies overlapping with the resonance a shot-to-shot fluctuation of the emission energy and the line shape are observed. The emission energy of resonance scattering with a narrowband source that is tuned through the resonance follows a linear dispersion, a consequence of the Kramers-Heisenberg expression for resonance scattering, that requires energy conservation only between initial and final state, i.e. the intermediate core-resonant state does not have to be on the energy shell. The self-amplified spontaneous emission (SASE) XFEL spectra have a spiky spectral intensity profile. The average width of spectral spike (spectral coherence) scales as the inverse of the pulse duration and was estimated to 0.1 eV in our case, i.e. narrow compared to the Auger-width of the intermediate state. Individual spectral spikes of the SASE FEL therefore have random detuning from the resonance (see Fig. 1), which results in a stochastic lineshift from shot-to-shot.

A simulation of the emission spectrum based on a generalized Maxwell-Liouville-von-Neumann approach qualitatively reproduces this stochastic shift in the line emission [5,6]. Studying the covariance of the recorded spectra would yield a highly resolved sRIXS spectrum, for which all the fine-structural levels and different emission lines can be uncovered [6]. The spectral resolution of sRIXS with SASE sources is hence determined by the spectral coherence of the source, rather than the overall broad SASE bandwidth. A covariance analysis requires the recording of a large number of single shot spectra and a high dynamic range for measuring the SASE absorption profile, which was unfortunately beyond the scope of our experiment.

3 Stimulated X-Ray Raman Scattering in CO

In our recent experiment, an attempt was made to demonstrate stimulated Raman scattering in CO at 500 Torr pressure, by resonantly pumping the $O1s^{-1}\pi^{*1}\Pi^{e}$ state at ≈ 534 eV (see Fig. 3 b). In RIXS experiments, three partially overlapping spectator states are observed $({}^{1}\Pi, {}^{1}\Delta$ and ${}^{1}\Sigma^{-}$) [9], with oscillator strengths that are small compared to the $O1s^{-1}\pi^{*1}\Pi^{e}$ transition. With a strong pump pulse, stimulated scattering back to the ground state is therefore the strongest channel. Seeding with a red shifted second pulse ("dump" pulse) is therefore a possibility to enhance the electronically inelastic channel. To that end the XFEL was operated in a two-color mode, producing a strong pump pulse and a weak dump pulse shifted by 10 eV, to overlap with

the transition to the states $1\pi^{-1}\pi^*I^{1}\Sigma^{+/-}$ at 525 eV, that is expected to be the strongest emission line for parallel polarization directions of the pump and dump pulse. Fig. 3a shows the recorded spectra as a function of the central photon energy of the SASE-pump pulse. The broad absorption band to the $O1s^{-1}\pi^{*1}\Pi^{e}$ state is clearly visible at a 534.2 eV (orange line). The pair of SASE pulses shows side bands to the low-energy side (the side bands are highlighted by white dashed lines). Strong stimulated electronic x-ray scattering would be visible as enhanced intensities in the black box at around 525 eV. A statistical evidence for enhanced intensities can no be seen in the data. Numerical calculations for the actual experimental conditions (pumppulse energies of 0.5-0.9 mJ) with a theory similar to that presented in reference [10] predict a stimulated Raman amplification of only $\approx 5\%$ (in contrast to 10^6 in neon) [11], unfortunately too small to be seen on top of the SASE shot-to-shot fluctuations of the spectral intensities. The experimental conditions were therefore in the best case 'at the onset' of stimulated Raman scattering and we have no evidence of the effect in molecules. Another important observation is clear absorption lines in the region from 526-533 eV (highlighted by red dashed lines). Competing processes to stimulated Raman scattering, i.e. core-ionization of C1s and core-excitation of O1s followed by Auger decay, valence ionization, etc. produce a substantial amount of excited molecular ions of different charge states, that can absorb part of the pump, but also seeding dump radiation. This means that spectral regions of stimulated Raman emission can overlap with absorption bands of the molecular ions that are produced in the sample. At small Raman gain cross-sections this can pose substantial problems to the spectral analysis and the distinction between absorption dips and emission peaks.



Fig. 3 a) Measured single-shot spectra as a function of the central photon energy of the incoming pump pulse. **b)** Level Scheme of sRIXS in CO.

4 Conclusion

We presented the results of a recent experiment on stimulated electronic x-ray Raman scattering in a dense gas of neon and CO. In neon, stimulated resonant Raman scattering was identified by a stochastic line shift of the emission, that is due to pumping with incoherent, structured SASE pulses. The attempt of demonstrating stimulated resonant Raman scattering by pumping the broad $O1s^{-1}\pi^{*1}\Pi^{e}$ resonance and seeding the transition to the $1\pi^{-1}\pi^{*1}\Gamma^{2}\Sigma^{+/-}$ states by a second SASE color was unsuccessful, since at the relatively low pulse-energies available in the experiments, the Raman gain was far below the SASE intensity fluctuations of the seed pulse. Moreover, several absorption bands of molecular ions that are produced by photoionization and Augerdecay of the targets have been identified in a broad energy range. In order to unveil the typically small stimulated Raman signal in molecular spectra, advanced statistical methods, beyond simple covariance methods, will have to be developed, to separate emission and absorption spectra.

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