

Stimulated X-Ray Emission Spectroscopy for Chemical Analysis

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X-ray free-electron lasers (XFEL) deliver X-ray pulses of fs duration, at unprecedented intensities that open avenues for studying nonlinear optical effects and stimulated X-ray emission and scattering. An intriguing future perspective is the development of coherent attosecond nonlinear pump-probe techniques, to study charge and energy transport in chemical reactions and photocatalysis. Stimulated X-ray emission and stimulated X-ray scattering are the fundamental building blocks of these nonlinear spectroscopic techniques. Here we present results on amplified spontaneous K- α spectroscopy of Mn compounds in solution [1]. We show amplification of the K- α emission at 5.9 keV photon energy in MnCl₂ 5-molar solution by over 4 orders of magnitude up to a saturated signal, containing 10⁶ detected photons in a single shot. The spectrum of the emission is studied as a function of the amplification and shows stark differences from the spontaneous K- α spectrum: For low amplification we could demonstrate gain narrowing with an emission width below the natural life time width of the 1s core hole. In the exponential gain region, the stronger K- α_1 component outcompetes amplification of the weaker K- α_2 line manifold. Within the K- α_1 spectral manifold we observe, that only a few of the underlying multiplet lines contribute to the spectrum. At high amplification levels, entering the strong-field limit, the lines get broader and show a shift towards the K- α_2 line at lower photon energies. All these measured features are well produced by our numerical simulation, based on the self-consistent solution of the Liouville – von Neumann equations for the ionic density matrix and Maxwell's equations in paraxial approximation. Results of Mn(II)Cl₂ are compared to NaMn(VII)O₄ emission spectra. These compounds contain Mn in different oxidation states, and the K- $\alpha_{1,2}$ emission energies are different by few eV. This shift in emission energy between different chemical compounds is termed chemical shift and is the essence of X-ray emission spectroscopy. Importantly, this energy shift in the emission peaks is clearly present in the stimulated emission spectra. Despite the stark differences to the spontaneous X-ray spectra, stimulated X-ray emission spectroscopy thus prevails the chemical sensitivity and opens the door to more advanced nonlinear X-ray spectroscopic techniques.

References

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