Stimulated Raman Spectroscopy With Femtosecond Optical Or Attosecond X-Ray Pulses

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Coherent nonlinear optical signals are commonly calculated using a semiclassical approach that assumes quantum molecules interacting with classical fields. We present an alternative approach based on a quantum description of both matter and field. The signals are recast in terms of transition amplitudes which provide a clearer picture for the underlying molecular processes.

Using this approach we show that stimulated coherent anti-stokes Raman spectroscopy (CARS) resonances originate from double-slit interference of two-photon *Stokes* pathways. CARS uses vibrational resonances to study nuclear wavepacket motions and is widely used in imaging applications. The resonances usually lie on top of a parametric component that involves no change in the molecular state and creates an undesirable background which reduces the sensitivity of the technique. By examining the process from the perspective of the molecule, rather than the field, we are able to separate the two components and recast each resonance as a modulus square of a transition amplitude which contains an interference between two Stokes pathways, each involving a different pair of field modes. We further show that dissipative signals obtained by measuring the total absorption of all field modes in a convenient collinear pulse geometry can eliminate the parametric component. Desired vibrational resonances may then be readily detected using pulse shapers through derivatives with respect to pulse parameters.

Time-domain experiments that employ sequences of attosecond x-ray pulses are made possible by newly developed bright coherent ultrafast sources for soft and hard x-rays. By creating multiple core holes at selected atoms and controlled times it is possible to study the dynamics and correlations of valence electrons as they respond to these perturbations. Electron motions can thus be directly probed with sub femtosecond time scale and atomic spatial resolution.

Attosecond coherent stimulated resonant Raman X-ray spectra of the nitrogen and oxygen kedges in glycine in response to two soft x-ray pulses are simulated at the Hartree-Fock staticexchange (HF-STEX) level. This is an attosecond extension of resonant inelastic x-ray spectra (RIXS). The effects of orbital relaxation upon core excitations are compared with the equivalentcore approximation (ECA). The signals are interpreted in terms of the dynamics of valence electronic wave packets prepared and detected in the vicinity of the selected atom (Nitrogen or Oxygen). These wave

packets are visualized using valence particle-hole pairs recast in the natural orbital representation.

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