

NON-LINEAR ULTRAFAST X-RAY SPECTROSCOPY; THEORETICAL CHALLENGES

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The development of bright attosecond sources for soft and hard x-rays has triggered considerable interest in all-x-ray nonlinear spectroscopy. In resonant optical techniques in the visible the light is tuned to high frequency ($\sim 2\text{eV}$) electronic transitions. However, a wealth of information is provided on nuclear (vibrational and phonon), degrees of freedom with much lower frequencies ($< 0.4\text{eV}$) which are accessible through multiphoton (e.g. Raman-type) resonances with differences (and higher combinations) of visible photons. In a completely analogous manner, combinations of x-ray photons, resonant with high frequency (keV) core transitions can probe the lower frequency ($< 50\text{eV}$) electronic valence excitations. By exploiting this analogy, we can use the theoretical apparatus developed for optical transitions, to predict nonlinear x-ray signals and design new coherent experiments. For example, multidimensional techniques which provide extremely valuable information on optical excitons in molecular aggregates can be extended to probe correlations among multiple core hole states. Displaying the signals as a function of the time delays provides correlation plots of valence electron wavepackets related to charge density fluctuations.

Correlation-function expressions are derived for the coherent nonlinear response of molecules to three resonant ultrafast pulses in the x-ray regime. The ability to create two-core-hole states with controlled attosecond timing in four-wave-mixing and pump probe techniques should open up new windows into the response of valence electrons, which are not available from incoherent x-ray Raman and fluorescence techniques. The multipoint correlation functions may be calculated using several levels of theory. (i) Multiple summations over the many electron states using time dependent density functional (TDDFT) and time dependent Hartree-Fock (TDHF) theory. (ii) The transition state potential method which uses a reference system with partially filled orbitals. (iii) Many body Green function perturbative techniques. (iv) Replacing the original model by an Electron Boson Model (EBM) for charge density fluctuations. Closed expressions for

ABSTRACT

the necessary four-point correlation functions are derived for the electron-boson model by using the second order cumulant expansion to describe the fluctuating potentials. The information obtained from multidimensional nonlinear techniques could be used to test and refine this model, and establish an anharmonic oscillator picture for electronic excitations.

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