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# Coherent Femtosecond X-ray Raman Spectroscopy of Molecules

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**Abstract.** By formulating the nonlinear response in terms of correlation functions of charge and current densities we show that coherent x-ray Raman Spectroscopy could provide an excellent local probe for valence excitation dynamics in molecules.

## 1. Introduction

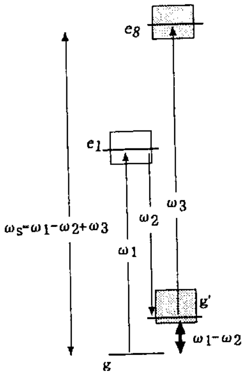
Recent progress in ultrafast x-ray pulse generation makes attosecond spectroscopy possible [1]; Electron dynamics in atoms, molecules, and solid state materials may then be directly investigated by x-ray nonlinear spectroscopies. Since x-ray $1 \sim 100\,\mathring{A}$ wavelength is comparable to a molecular size, the dipole approximation which imposes strict selection rules in optical spectroscopy does not apply, allowing the direct probing of the entire manifold of electronic transitions and inducing a strong dependence of the signal on wavevectors. Nonlinear x-ray spectroscopies thus provide detailed information on spatial coherence in excited states. By tuning the x-ray frequencies across the core excitations of various atoms it may become possible to investigate in detail the nonlocal nature of valence electronic excitations.

We have simulated time-resolved coherent x-ray Raman Scattering (TCXRS) for a model molecular system, and demonstrated its utility as a novel probe for electronic motions. TCXRS is a four wave mixing process involving three incoming x-ray beams $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$, with two coincident pulses $\mathbf{k}_1$ and $\mathbf{k}_2$, and the x-ray signal at $\mathbf{k}_s=\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3$ is detected as a function of the variable delay $\tau$ of $\mathbf{k}_3$ with respect to $\mathbf{k}_1$ and $\mathbf{k}_2$.

## 2. Model

We consider a one-dimensional 8 atom molecular wire, each having a core, an occupied valence, and an unoccupied conduction-orbital. The Hamiltonian includes the transfer of the conduction electron ($t_c$) and valence hole ($t_v$), but neglects core hole transfer. It further contains the on-site attractive Coulomb interactions between a core hole and a conduction electron (core-exciton effect) ($U_{ac}$), between the valence hole and a conduction electron (valence-exciton effect) ($U_{vc}$), and the on-site repulsive Coulomb interaction between conduction electrons ( $U_{cc}$) and between core holes ( $U_{aa}$ ).

We have calculated a three beam TCXRS where the central frequencies of the three incoming beams $\omega_1$, $\omega_2$, and $\omega_3$, and the signal $\omega_s = \omega_1 - \omega_2 + \omega_3$ are resonant with the core excited states and $\omega_1 - \omega_2$ is tuned in the optical valence excitation. The correlation function approach for the nonlinear x-ray response [2,3] was used in these calculations. In Fig.1 we depict the TCXRS process, where $e_1$ and $e_8$ are the core excited states at site 1 and 8, respectively, and $g'$ denotes the valence excited states.



## 3. Results

In Fig.2 we display the TCXRS signal calculated using rectangular 5fs pulses. $\omega_1$ is tuned at the core exciton at site 1, while $\omega_s = \omega_1 - \omega_2 + \omega_3$ is held fixed at the core exciton at site 1 (a, b, c) or site 8 (d, e, f). $\omega_1 - \omega_2$ is fixed at the resonance with the strongly bound valence exciton states (pair creation of the valence hole and the conduction electron): $\omega_1 - \omega_2 = 6.7$eV (panels a, d), $\omega_1 - \omega_2 = 7.4$eV (panels b, e), and $\omega_1 - \omega_2 = 8.9$eV (panels c, f). Shown is the Fourier transform of the signal with respect to the time delay $\tau$. The time resolved TCXRS signal is displayed in the inset.

Comparison with the calculated optical absorption spectrum (not shown) reveals that the peak positions in the frequency domain coincide with the optical absorption peaks, *i.e.* valence exciton energies. The intensity distribution, however, is completely different; the intensities of the Raman-active valence exciton modes are strong, but they are very weak in the optical absorption. This is because they are induced by the two x-ray photons ($\mathbf{k}_1$ and $\mathbf{k}_2$). The TCXRS selection rules thus complement the optical absorption. The interaction with the $\mathbf{k}_1$ and $\mathbf{k}_2$ beams induces a polarization associated with the valence exciton at site 1, and this polarization is probed by the $\mathbf{k}_3$ beam at site 1(left panel) or site 8 (right panel). Therefore these intensities depend strongly on $\omega_1 - \omega_2$, reflecting the wavepacket motion for each valence exciton. We also see a clear quantum beat in the time resolved TCXRS resulting from interference among the strong valence exciton modes (See Fig.2 (b), (e), and (f)).

The right panels in Fig.2 show that the temporal profile of the TCXRS is greatly changed when we tune the x-ray energies of $\mathbf{k}_3$ and $\mathbf{k}_s$ to the core resonance of site 1, even for the same detuning of $\omega_1 - \omega_2$. In this case we detect the valence exciton motion at site 1. Our calculations illustrate that TCXRS is an atomic scale selective local probe most suitable for investigating the valence exciton wavepacket motion.

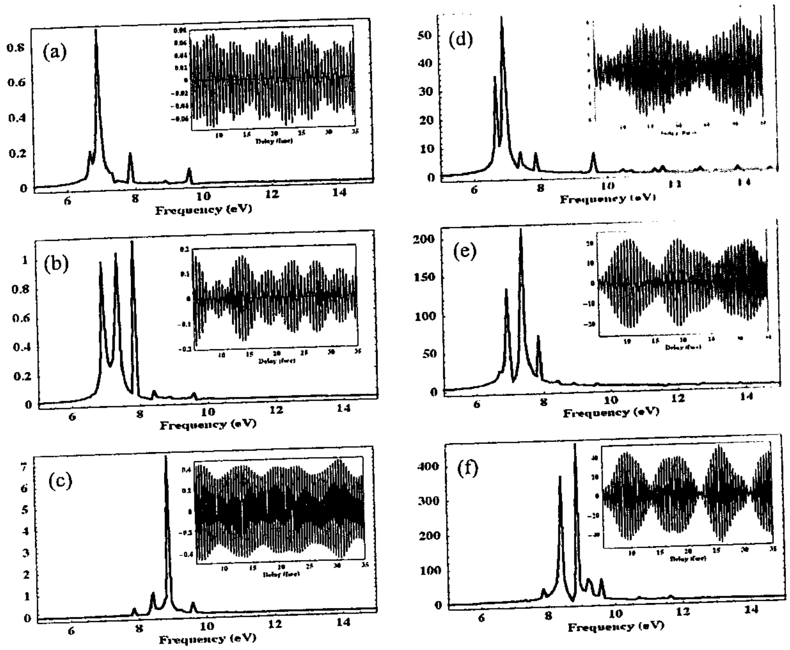


Fig. 2. The calculated TCXRS. $\omega_1$ is fixed at the core exciton at site 1, while $\omega_s$ is fixed at the core exciton at site 1 (left panels) or at site 8 (right panels). $\omega_1 - \omega_2$=6.7eV (a,d), 7.4eV (b,d), and 8.9eV (c,f). The results of the Fourier analysis of the temporal behavior of TCXRS with the time delay (inset) are shown.

When the pulses are so short that their bandwidths span the strongly bound exciton states, but are still long enough to resolve the core excited states between the sites 1 and 8, the TCXRS does not depend on $\omega_1 - \omega_2$. Tuning the x-ray energies of $\mathbf{k}_3$ and $\mathbf{k}_s$ gives rise to very different TCXRS profiles.

In addition to the temporal profile shown here, the TCXRS has a strong wavevector dependence, which provides detailed information on the *spatial coherence* of the valence excitations. TCXRS should thus be an ideal technique for investigating the real-time dynamics of valence excitons.

## Acknowledgements

The support of the National Science Foundation Grant no. CHE 0132571 and the National Institutes of Health Grant no. 1 RO1 GM59230-01A2 is gratefully acknowledged.

## References

1. M. Hentschel *et al.*, Nature Vol. 414, 519, 2001; M. Drescher *et al.*, Science Vol. 291, 1923, 2001; R. W. Schoenlein *et al.*, Science Vol. 287, 2237, 2000.
2. S. Tanaka, V. Chernyak, and S. Mukamel, Phys. Rev. A, Vol. 63, 63405, 2001.
3. S. Tanaka and S. Mukamel, J. Chem. Phys. Vol. 116, 1877, 2002.
4. "Coherent X-Ray Raman Spectroscopy", S. Tanaka and S. Mukamel, Phys. Rev. Lett. (In Press) (2002).