Resonantly-Enhanced Difference-Frequency Generation in the Core X-ray Absorption of Molecules

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Abstract

We use real-time time-dependent density functional theory simulations to numerically demonstrate that resonantly-enhanced difference-frequency generation (re-DFG) involving intense ultrashort coherent X-ray pulses can selectively excite core states of atoms in molecules. As a model case, we evaluate the spectral selectivity of re-DFG excitation of the oxygen K-edge by illumination of a single gas-phase water molecule with two-color X-ray pulses of different photon energies and durations. The re-DFG excitation is further probed by a small delayed pulse with central photon energy resonant with the oxygen K-edge peak absorption line. Based on these results, we anticipate that highly selective excitation by re-DFG X-ray nonlinear processes might be achieved in more complex molecular systems and bulk materials by using highly penetrating two-color hard X-ray pulses, with extensive applications.

Selective photodissociation of molecules by resonant excitation near a chosen core ionization edge by means of nonlinear interactions in the X-ray range is becoming conceivable due to recent advances in the development of intense ultrashort X-ray coherent pulse sources, such as synchrotron, free-electron lasers (FEL) and in high-harmonic generation.1–10 In a previous work12 we showed how the phase-sensitivity cancellation of the anti-Stokes component previously described in two- and three-level systems in the infrared and optical regions can be extended to the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)6 of chemical species by highly localized four-wave mixing (FWM) nonlinear processes. Femtosecond transient FWM grating spectroscopy with ultrafast X-rays has recently been demonstrated,13,14 showing experimentally how the large penetration depth of X-rays allows probing the bulk properties of materials, addressing core excited states, and creating excitation gratings with unprecedented nanoscale spatial resolution. Among the X-ray wave-mixing processes, difference-frequency generation (DFG) of optical and UV radiation using two-color (ω1, ω2) X-ray laser pulses, where \( h\omega_i \) is the central photon energy of the pulses, has been studied theoretically.15,16

Here we address atomic core resonantly-enhanced difference-frequency generation (re-DFG) from X-ray pulses, considering the oxygen K-edge in a single gas-phase water molecule as a model system. We numerically show how the illumination of a water molecule with two-color (3ω, 4ω) femtosecond X-ray pulses produces a difference-frequency component \( \omega \) that
is enhanced at the core resonance $\omega = \omega_0$, with $\omega_0$ being in this case the oxygen K-edge in the gas-phase water molecule, and evaluate the degree of excitation selectivity as a function of the duration of the two-color pulses.

The first step is to calculate the absorption spectrum of the molecule around the target absorption edge. Figure 1 shows the computed water linear spectrum considering different field polarizations, together with the absorption spectrum obtained by adding the different polarization contributions. The simulations have been performed using the NWChem real-time TDDFT module.\textsuperscript{17} Core absorption spectra are calculated using the spectroscopic real-time approach, by exciting the system with a delta-function electric field perturbation.\textsuperscript{18} In the present calculations we have considered the Gaussian basis set aug-cc-pVTZ for the nuclear geometry optimization in the y-z plane together with the exchange-correlation functional PBE0, and the 6-31G basis set with PBE0 for the real-time TDDFT.

The absorption spectrum around the oxygen K-edge that we obtain agrees qualitatively well with the experiments.\textsuperscript{19} The calculated oxygen K-edge main absorption peak is at 543 eV, which differs by 7 eV from the experimental value. The theory level that we consider is hence adequate for describing the fundamental physics of the re-DFG processes that we address.

In order to examine the re-DFG nonlinear effect, the water molecule is illuminated with two-color ($3\omega , 4\omega$) laser pulses and the resulting DFG component is evaluated by varying $\omega$. The two-color pulses are linearly polarized in the x, y and z directions, with all polarizations in phase with each other, so that the resulting polarization is not aligned with any of the molecular axis. The two-color field components in each direction have the form

$$E(t) = E_0 \cos^2 (\pi / 2\tau) \ast (t - t_0) \{ \cos(3\omega(t - t_0)) + \cos(4\omega(t - t_0)) \},$$

where $E_0$ is the peak amplitude of the two-color pulse components, $\tau$ gives the duration of the pulses, which in the present simulations are

![Figure 1: Oxygen K-edge linear absorption lines obtained from the imaginary part of the Fourier transform of the time-dependent dipole moments, after the system has been excited with a small electric field kick of $10^{-4}$ a.u. $\approx 51$ mV/nm. The peaks have been broadened to account for core relaxation effects by damping the dipole time signal by $e^{-t/t_0}$, with $t_0=20$ a.u. $\approx 480$ as. The absorption obtained with different linear field polarizations together with the sum in the three directions is shown.](image)

taken of 1.67 fs, 2.56 fs, and 3.43 fs (FWHM), $3\omega$ and $4\omega$ are the respective central angular frequencies and $t_0$ centers the pulses in the temporal grid. The peak intensity of each two-color field component is $10^{12}$ W/cm$^2$.

Figure 2 shows the spectral signal obtained for three different central photon energy values of the incident two-color pulses that produce a DFG component very close to the calculated oxygen K-edge. The inset shows how the signal peaks exactly at the oxygen K-edge, which is the demonstration that the DFG signal is enhanced by the core oxygen K-edge resonance ($\hbar \omega = \hbar \omega_0 = 543$ eV). Other frequency mixing effects can also be seen at larger spectral values, which is limited by the calculated spectral range, corresponding to the second harmonic of the $3\omega$ field ($6\omega$) and the sum-frequency generation $3\omega + 4\omega$ signal ($7\omega$). The central photon energy of the input two-color pulses ($3\omega, 4\omega$) has been scanned by varying $\omega$ to give DFG signals from about 535 eV to 550 eV, and the resulting spectrally integrated DFG signal is plotted.
Figure 2: Spectral signal obtained by Fourier transform of the time-dependent dipole resulting from the interaction of the two-color \((3\omega, 4\omega)\) pulses with the water molecule, for three different values of \(\omega\). The inset is a zoom of the spectra near the oxygen K-edge showing the enhancement of the DFG signal at resonance \((\omega = \omega_0 = 543 \text{ eV})\).

in Figure 3 for three different durations of the two-color input pulses, as indicated. Here we can clearly see the peak of the integrated DFG signal at the oxygen K-edge (543 eV), which as it can be expected, is narrower as the duration of the incident pulses is increased. The integrated DFG values in Figure 3 have been normalized for clarity. It is worth noting that the durations of the pulses that we have considered in our simulations are remarkably short (1.67 fs, 2.55 fs, and 3.43 fs), and therefore much narrower peaks in Figure 3 can be expected by considering longer incident pulses, which would consequently result in a more selective re-DFG effect.

After the two-color \((3\omega, 4\omega)\) laser pulse interacts with the water molecule, the system remains core excited due to re-DFG when \(\omega = \omega_0 = 543 \text{ eV}\), since no relaxation processes are considered in the simulations. The difference between the excited and ground state charge densities (density-difference)\textsuperscript{18} follow complicated dynamics around the oxygen atom, with a periodicity that corresponds to the oxygen K-edge absorption photon energy. This is illustrated in Figure 4, where snapshots of the density-difference are evaluated after the exciting two-color pulse is over and for a duration corresponding to the oxygen K-edge period (7.6 as). The density-difference dynamics clearly shows how the core states of the oxygen atom have been excited by the nonlinear re-DFG effect.

![Figure 3: Integrated DFG spectral signal around the oxygen K-edge (500 – 600 eV) as a function of the incident photon energy (\(\hbar \omega\)) of the two-color \((3\omega, 4\omega)\) pulses.](image)

![Figure 4: Snapshots of the density-difference after the exciting two-color field is over, in the case of resonance \((3\omega_0, 4\omega_0)\). The period of the calculated oxygen K-edge is 7.6 as. The illustration shows a complete cycle of the core oxygen excitation, the temporal resolution of the numerical integration is 0.48 as.](image)
pulse, we add a cos² envelope probe pulse of 0.8 fs (FWHM) duration and 10⁴ W/cm² peak intensity, with the central photon energy of the calculated oxygen K-edge (ω = 543 eV). The probe is delayed 240 as from the end of the input two-color pulse. The absorption of the weak probe pulse following the nonlinear excitation of the system is given by the imaginary part of the Fourier transform of the resulting time-dependent dipole moment time-windowed in the region of the probe pulse.²⁰ The integrated absorption spectrum as a function of the central photon energy of the input two-color pulses (3ω, 4ω), i.e. as a function of ℏω, is shown in Figure 5. We observe clear oscillations of the absorption rate around the oxygen K-edge, which provide the evidence that the atom is excited about 543 eV, as it has already been illustrated in Figure 3. Also clear in Figure 5 is the spectral width of the excitation, which is established by the duration of the input pulses, as commented above. The period of the oscillations in the integrated absorption spectrum corresponds to the Fourier limited bandwidth of the input pulses, which is roughly 1.6 eV for the 1.67 fs pulses, 1.1 eV for the 2.55 fs, and 0.8 eV for the 3.43 fs, as the result of the periodic convolution between the probe field and the nonlinearly DFG generated time-dependent dipole moment, which modulates their time-delay and therefore also the probe absorption rate.²⁰

Figure 5: Integrated absorption spectrum of the probe pulse around the oxygen K-edge (500 – 600 eV) as a function of the incident photon energy (ℏω) of the two-color (3ω, 4ω) pulses.

In conclusion we have numerically shown that two-color (3ω, 4ω) re-DFG can be implemented using synchronized femtosecond X-ray pulses for the selective excitation of atomic core states, considering a single gas-phase water molecule as a model system. The duration of the two-color pulses determine the spectral selectivity that can be achieved by the nonlinear re-DFG effect.

The results that we have described might be extended to larger molecules. Resonant excitation near a core atomic ionization edge in a molecule can follow a rapid redistribution of charge beginning in less than a femtosecond via Auger processes, so that multiple charged molecular ions can be formed and the molecule generally will become unstable and dissociate.²¹ From this perspective, considering that a spectral fingerprint of the particular state of a molecule can generally be obtained by its XANES/EXAFS linear absorption spectra at the different atomic absorption edges, the selectivity of the re-DFG process that we outline could further be optimized using a combination of several synchronized two-color (ω₁, ω₂) pulses, which can produce re-DFG signals resonant with several XANES/EXAFS absorption lines simultaneously, resulting in additional selective local excitation of the molecule.

Beyond the fundamental and applied interest of the nonlinear re-DFG X-ray matter interaction process that we have presented in a single gas-phase water molecule, our motivation also anticipates the potential of extending it to higher photon energies following the rapid advances in FEL sources, such as considering two-color hard X-rays to core excite higher atomic number atoms by re-DFG. The essential in this hard X-ray approach is that the two-color (ω₁, ω₂) pulses can be highly penetrating in bulk, while the core resonant re-DFG signals ω₂ − ω₁ are not. Therefore, by virtue of the results from the water model that have detailed, we may consider re-DFG be achieved in the atomic edges of e.g. biomolecular zinc complexes²² (Zn K-edge ∼ 10 keV), using two-color (ω₁, ω₂) pulses of highly penetrating ℏω₁ and ℏω₂ hard X-ray central photon energies. Consistently, it was recently reported that exposure
to laser-produced hard X-rays pulses with relatively high peak intensities does not lead to increased harm to mammalian cells exposed in vitro compared with the harm induced from exposure to hard X-rays with the same dose from conventional medical sources, concluding that the use of high-power laser facilities for medical imaging is justified.\textsuperscript{23} In this regard, the optimal two-color pulse peak intensities and durations to attain a harmless dose in different tissues and materials using hard X-ray re-DFG needs to be addressed, likewise experimentally. We can hence envisage extensive potential applications of the nonlinear X-ray re-DFG effect that we describe, which include, in general, the local and selective manipulation of atoms and molecules in bulk matter, and in particular in medicine, it might be significant for local and selective cancellation of the active center of biomolecules.\textsuperscript{22,24,25}

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