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Localized Core Four-Wave Mixing Buildup in the X-ray Spectrum of Chemical Species

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ABSTRACT: Using the Kohn–Sham density functional theory, we numerically study the four-wave mixing response of a carbon atom model system exposed to a train of femtosecond two color ω – 3ω random phase coherent X-ray pulses near the K-edge. The phase-sensitivity cancellation of the 5ω anti-Stokes component previously described in two- and three-level systems in the infrared and optical regions is extended into the X-ray. Resonances with the absorption lines in the XANES and EXAFS regions produce 5ω peak intensities that increase near the phase-sensitivity cancellation frequencies. Based on this effect, we predict that highly selective intense X-ray 5ω photon energies can be achieved in real systems. The high localization of the ω – 3ω four-wave mixing nonlinear technique that we address entails a new valuable tool in X-ray spectroscopies of chemical species as it can readily be extended to different photon energies in other atomic absorption edges, with broad applications.

Nonlinear processes that have long been studied in the infrared and optical regions are being extended to the X-ray region of the electromagnetic spectrum as a result of recent advances in the generation of coherent X-ray pulses in synchrotron and free-electron lasers (FEL), and in high-harmonic generation (HHG).^{1–12} Bright trains of femtosecond pulses are routinely produced and used in a wide range of areas such as materials science and biochemistry. The pulses in the trains produced in these sources ordinarily have a random phase and this aspect is exploited in the present work.

The evidence of four-wave mixing (FWM) processes stimulated by transient gratings produced by femtosecond coherent pulses in the extreme-ultraviolet spectral range was recently reported.⁷ Herein, we present an extension into the X-ray region of the phase-sensitivity cancellation of the FWM anti-Stokes 5ω signal produced by two-color ω – 3ω ultrashort pulses which was previously theoretically treated in two and three-level V-type systems.^{13–15} In ref 13, it was shown that in a two-level system the anti-Stokes 5ω signal is insensitive to the relative phase between the ω and 3ω pulses when the frequency of the laser follows the condition $\omega^2 = \omega_{12}^2/5$, where ω_{12} is the frequency of the two-level transition. It was shown that, for equal ω and 3ω peak intensities, the effect produced the cancellation of the ac-Stark shift in the system, and more generally,¹⁴ it was resolved that the disappearance of one of the two primary quantum paths contributing in the FWM process, namely, the $\{3\omega, \omega, \omega\}$ path, explains the 5ω phase-sensitivity cancellation also for different relative amplitudes of the input fields. Later, it was detailed how the same anti-Stokes phase-sensitivity cancellation effect is also feasible for different peak intensities

between the ω and 3ω pulses and in a three-level V-type system,¹⁵ provided the laser frequency satisfies the generalized condition

$$\omega_{ij}^2 = \frac{\Omega_i^2 + \Omega_j^2}{10} \quad (1)$$

where ω_{ij} is the phase-sensitivity laser cancellation frequency involving the frequencies of the atomic transitions Ω_i and Ω_j , and where the same electric-dipole moment is assumed for the two transitions with $|\Omega_i - \Omega_j| \ll \omega_{ij}$. The perturbation theory also shows that peak intensities of the anti-Stokes 5ω signal occur in case the involved atomic transitions resonate with the ω , 3ω , or 5ω field components.

In the present study, we investigate the interaction of ultrashort ω – 3ω laser pulses near the atom K-edge by a first-principles time-dependent density functional theory (TDDFT) in the frame of the local-density approximation.^{16,17} As a model system, we use the archetypal case of a single carbon atom with relaxed absorbing boundaries; the ionized electron wave-packets are partially backscattered in the simulation grid boundaries, so that the effect of photoelectrons scattered back from neighboring atoms altering the atom absorption coefficient is

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reproduced in a general sense.¹⁸ The FWM produced by the two-color ω – 3ω laser pulses in the absorption lines of the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)¹⁹ is analyzed. We find that the phase-sensitivity cancellation of the FWM anti-Stokes 5ω component can be achieved with precision in real systems in the XANES/EXAFS regions of the absorption spectrum with laser pulse peak intensities ranging from 10^{12} to 10^{14} W/cm². Importantly, we demonstrate that resonances associated with the two-color ω – 3ω FWM processes can be enhanced in the phase-sensitivity cancellation regions.

In our TDDFT simulations, the carbon atom is described by a full atomic potential represented by an elemental delta charge distribution, which is a relatively simple model that gives an atomic carbon K-edge red-shifted significantly with respect to experimental data and also to other calculations using different Gaussian basis sets and applied functionals.^{20–22} This theory level is computationally efficient and describes with high accuracy the fundamental physics of the FWM processes that we outline. The grid shape is taken as spherical with a radius of 5 Å, considering a typical distance for EXAFS oscillations to be observed.¹⁷ Complex absorbing boundaries are implemented with 0.5 Å weight and 0.5 Å width. In order to obtain the linear absorption spectrum, we obtain the Kohn–Sham wave functions of the ground state, perturb the system with an infinitesimal linearly polarized electric-field pulse, and propagate the time-dependent Kohn–Sham equations. The spectrum is then evaluated from the time-dependent dipole moment. In Figure 1, the absorption spectrum in the XANES/EXAFS

Figure 1. Linear absorption in XANES/EXAFS regions.

Figure 1 are numbered in Table 1. We see that in this case the absorption lines Ω_7 and Ω_8 above the K-edge (Ω_4) have the higher strengths, which is relevant for the effects observed in our study as it will be further shown below.

As long as typical relaxation rates of the atomic systems, such as core relaxation processes which occur at approximately 10 fs after core excitation, are much faster than state-of-the-art FEL repetition rates, that are of a few MHz (with the outlook of the GHz),¹¹ we can describe the effect of the consecutive phase random pulses separately. The carbon atom is illuminated with two-color ω – 3ω laser pulses that have an electric field as

$$E(t) = E_0 \cos^2((\pi/2\tau) \times (t - t_0)) \{ \cos(\omega(t - t_0)) + \cos(3\omega(t - t_0) + \phi_n) \} \quad (2)$$

where E_0 is the peak amplitude of the two pulse components, τ gives the duration of the pulses that are taken of 60 fs ($E(t)$ fwhm), ω and 3ω are the respective angular frequencies, and t_0 centers the pulses in the temporal grid. The relative phase between ω and 3ω pulses is given by ϕ_n , with calculations performed for ϕ_n increasing from 0 to 2π rad by $\pi/5$ rad steps. The pulse pair given in eq 2 can describe the output of a seeded FEL pulse and also the output from parametrically amplified HHG pulses.¹² In these cases, the phase between different harmonics can in principle be controlled,²³ and therefore, there is also the option of scanning the phase. In the case of self-amplified spontaneous emission (SASE) FELs, the pulses are made by a sum of multiple longitudinal modes, with random phase relations among them, so that the phase cancellation that we discuss in the present work may be profitably exploited.¹¹

Figure 2 illustrates the effect of the phase-sensitivity cancellation of the FWM anti-Stokes 5ω signal. In Figure 2a,

Figure 2. Anti-Stokes 5ω component obtained for different relative phases between the ω and 3ω pulses, as indicated. In (a), $\omega = 99.9$ eV, which corresponds to the intensity peak #2 in Figure 3b, well in a phase-sensitivity cancellation region. In (b), $\omega = 103.4$ eV, which corresponds to the intensity peak #3 in Figure 3b.

the value of the laser central photon energy is $\omega = 99.9$ eV, which corresponds to the peak intensity #2 in Figure 3b. Clearly, the strength of the FWM 5ω signal calculated for different relative phases between the ω and 3ω pulses is basically not affected. Contrarily, Figure 2b shows the case for a laser central photon energy as $\omega = 103.4$ eV, which corresponds to the peak intensity

Table 1. Absorption Lines in Figure 1 (eV)

Ω_1	Ω_2	Ω_3	Ω_4	Ω_5	Ω_6	Ω_7	Ω_8	Ω_9
188.4	200.2	209.8	225.1	232.9	239.4	249.4	262.7	279.0
Ω_{10}	Ω_{11}	Ω_{12}	Ω_{13}	Ω_{14}	Ω_{15}	Ω_{16}	Ω_{17}	Ω_{18}
298.4	320.8	346.4	374.9	406.3	440.7	478.3	517.6	560.6

Figure 3. (a) Relative standard deviation of the spectrally integrated intensities of the 5ω signals. (b) Mean of the spectrally integrated intensities (black lines) and maximum of them with respect to the relative phase ϕ_n (red dotted lines). The laser peak intensity of the ω and 3ω pulses is 10^{12} W/cm 2 .

for the ten different relative phases ϕ_n as a function of ω (Figures 3a and 4a); the mean of these integrated intensities (black full lines); and the maximum of the integrated intensities that is obtained at each ω for a particular value of ϕ_n (red dotted lines) (Figures 3b and 4b). For the calculations in Figure 3, we have used a laser peak intensity of 10^{12} W/cm 2 and for the ones shown in Figure 4 of 10^{14} W/cm 2 . The relative minima of the standard deviation denote the phase-sensitivity cancellation regions of the FWM anti-Stokes 5ω signals and are specified in the figures by the letters “a”, “b”, “c”, and so forth. The precise values of the minima as well as the absorption lines involved in the FWM process that have been resolved are given in Tables 2a and 3a.

Table 2. (a) Positions of the Relative Standard Deviation Minima in Figure 3a in Terms of the Laser Frequency ω and Its Fifth Harmonic 5ω , To Be Compared with the Phase-Sensitivity Laser Cancellation Frequencies ω_{ij} Obtained from eq 1 (eV). (b) Positions of the Maxima of $I_{5\omega}$ in Figure 3b in Terms of the Laser Frequencies ω and 3ω ^a

Figure 3a	ω	5ω	ω_{14}	ω_{44}	ω_{47}
a	93.2	466.0	92.8	-	-
b	99.4	496.9	-	100.7	-
c	105.6	528.0	-	-	106.2

Figure 3b	ω	3ω	5ω	absorption line	FWM resonance
1	95.7	287.1	478.7	478.3 (Ω_{13})	5ω
2	99.9	299.7	499.5	298.4 (Ω_{10})	3ω
3	103.4	310.2	517.6	517.6 (Ω_{14})	5ω
4	112.2	336.6	561.0	559.1 (Ω_{15})	5ω

^aThe observed FWM resonances with the different absorption lines are indicated (eV).

Table 3. (a) Positions of the Relative Standard Deviation Minima in Figure 4a in Terms of the Laser Frequency ω and Its Fifth Harmonic 5ω , To Be Compared with the Phase-Sensitivity Laser Cancellation Frequencies ω_{ij} Obtained from eq 1 (eV). (b) Positions of the Maxima of $I_{5\omega}$ in Figure 4b in Terms of the Laser Frequencies ω and 3ω ^a

Figure 4a	ω	5ω	ω_{23}	ω_{24}	ω_{44}	ω_{48}	ω_{67}
a	91.6	458.2	91.7	-	-	-	-
b	100.9	504.4	-	-	100.7	-	-
c	108.9	544.4	-	-	-	109.4	109.3
d	94.4	472.1	-	95.3	-	-	-

Figure 4b	ω	3ω	5ω	absorption line	FWM resonance
1	95.7	287.1	478.5	478.6 (Ω_{13})	5ω
2	100.4	301.2	502.1	298.4 (Ω_{10})	3ω
3	104.1	312.3	520.4	517.6 (Ω_{14})	5ω
4	112.2	336.6	561.2	559.1 (Ω_{15})	5ω

^aThe observed FWM resonances with the different absorption lines are indicated (eV).

Figure 4. Same data sets as Figure 3 for a laser peak intensity of 10^{14} W/cm 2 .

The principal and broadest minima in Figure 3a (“b” label, which has been shaded in the figure) corresponds to the expected phase-cancellation frequency $\omega_{44} = 100.7$ eV involving only the K-edge absorption line Ω_4 (line #4 in Figure 1). Indeed, the accurate value of the laser photon energy ω corresponding to this relative minimum (99.4 eV) demonstrates that the phase-sensitivity cancellation of the FWM anti-Stokes 5ω described previously for two- and three-level V-type systems^{13–15} is achievable with high precision using the K-edge of a real atom. Other secondary phase-sensitivity cancellation regions can be observed in Figure 3a. The weak relative minimum labeled with

"a" at 466 eV is due to the three-level V-type system defined by the absorption lines Ω_1 and Ω_4 , as shown in Table 2a, and therefore, it involves weak absorption lines in the XANES region before the K-edge. This minimum is, however, almost on the noise level in the data set and probably could not be exploited in practice. The relatively strong minimum labeled with "c" at 528 eV is produced by the absorption lines Ω_4 and Ω_7 (see Table 2a), and appears as a narrow phase-sensitivity cancellation region. Importantly, the phase-sensitivity cancellation effect in this case is significant, because Ω_7 is the strongest absorption line in the XANES/EXAFS region.

We now analyze the resonances of the FWM which, as mentioned above, are expected to develop as relative maximum intensities of the anti-Stokes 5ω signal as a function of ω , in the cases that the involved absorption lines coincide with ω , 3ω , or 5ω . The resonances that are in the region of our interest, which appear as relative maxima in Figure 3b and Figure 4b (red dotted lines), precisely correspond to coincidences of the photon energies 3ω and 5ω with different absorption lines of the absorption spectrum Ω_i , as given in Tables 2b and 3b. In Figure 3b (shaded region), the second important result of our analysis is displayed. Remarkably, in the present calculations we obtain two significant intensity relative maxima, namely, peaks #2 and #3 in Figure 3b, that are in regions of low and high values of the standard deviation, respectively. Peak #2 is due to the FWM resonance between 3ω and the absorption line Ω_{10} , and peak #3 is due to the FWM resonance between 5ω and the absorption line Ω_{14} (see Table 2b). Since the #2 5ω intensity peak is in the phase-sensitivity cancellation region "b", the signal accumulates for the different relative phases ϕ_n and the mean of these realizations (black full line) consequently basically coincides with the maximum of them (red dotted lines). Differently, since peak #3 is not in a phase-sensitivity cancellation region, the mean of the realizations considering the different relative phases ϕ_n is substantially weakened than the maximum. The spectra corresponding to these two particular intensity peaks have been illustrated in Figure 2 for a clear comparison. We therefore conclude that anti-Stokes FWM 5ω signals in the XANES and EXAFS regions can be discerned with high precision in real systems by taking advantage of the phase-sensitivity cancellation effect that we report.

As mentioned earlier, Figure 4 shows the results that have been obtained by using a peak intensity of the laser pulses as 10^{14} W/cm². Comparable effects to the ones described in Figure 3 are observed, and the corresponding data is detailed in Table 3. We observe in Figure 4 a slight blue shift of the peaks with respect to the linear absorption spectrum. We attribute this small spectral blue shift to the stronger ac-Stark effect produced by the more intense fields on the absorption lines of the atom. The 5ω intensity peaks in Figure 4b are increased by a factor of $\sim 2 \times 10^4$ with respect to the peaks in Figure 3b. This value differs by a factor of ~ 50 with respect to the results expected from the perturbation theory¹⁴ when assuming the linear absorption spectrum, but it agrees with precision with the perturbation theory when considering the frequency shifts obtained in the simulations. We also note that the phase-sensitivity cancellation region labeled with "c" at 544.4 eV in Figure 4a involves contributions from two close phase-sensitivity laser cancellation frequencies, namely, ω_{48} (109.4 eV), which involves the K-edge (Ω_4) and the relatively high peak in the absorption spectrum (Ω_8), and ω_{67} (109.3 eV), as shown in Table 3(a). We also made calculations with higher laser peak intensities such as 10^{15} – 10^{16} W/cm² and observed that the phase-sensitivity cancellation

effect is blurred for these stronger fields due to non-negligible nonlinear contributions from HHG.

With the aim of discussing applications in experiments from the geometry and parameters used in the present simulations, it is worth mentioning that the peak intensities that we have considered, 10^{12} W/cm² and 10^{14} W/cm², using 60 fs laser pulses, correspond in terms of flux densities to 60 mJ/cm² and 6 J/cm², respectively, which for a typical absorption length of 100 nm at 100 eV photon energy in solids gives an energy density of 6 kJ/cm³ and 600 kJ/cm³, the last being far above the damage threshold of most solids. However, on one hand, the effect that we report might be observed for intensities lower than 10^{12} W/cm², and on the other hand, this fact does not preclude carrying out experiments such as raster scans, or using liquid jets or molecular injectors, for instance. Besides, the duration of 60 fs that we have implemented gives a bandwidth of ~ 30 meV, which is very spectrally selective, so that shorter pulses may also be employed. Also in this context, we note that the FWM 5ω intensity peak signal that we calculate is estimated from the time-dependent dipole moment to be a factor of $\sim 10^9$ weaker than the ω and 3ω signals in the case of the 10^{12} W/cm² peak intensity, and a factor of $\sim 5 \times 10^6$ in the case of 10^{14} W/cm², which give intensity peaks for the 5ω signals as $\sim 10^3$ W/cm² and $\sim 2 \times 10^7$ W/cm², respectively, the former being clearly in the linear regime.

In the frame of a first-principles TDDFT and using a relatively simple model, we have demonstrated that the phase-sensitivity cancellation of the FWM anti-Stokes 5ω component previously described in two- and three-level V-type systems can be achieved with accuracy in the XANES/EXAFS regions of an absorbing atom. Resonances produced in the XANES/EXAFS absorption regions by two-color ω – 3ω FWM processes bring the possibility to gain new insight into the complex properties emerging from correlated phenomena in atoms, molecules, and solids, which provides a new general high sensitivity tool in X-ray absorption spectroscopy. The fundamental anti-Stokes FWM 5ω buildup that we report in carbon as a model example can directly be extended to other photon energies and atomic absorption edges. The strong localization in space and spectral selectivity of core-level transitions therefore make ultrafast core FWM techniques especially powerful, as in our study the generated anti-Stokes 5ω component might be sufficiently intense to manipulate chemical species in neighboring regions,^{24–27} with potential for applications in medicine, biology, chemistry, and materials sciences.

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