We suggest a new approach for observing x-ray nonlinear wave mixing in opaque materials. We focus on difference frequency generation of ultraviolet radiation from two short x-ray pulses by measuring the depletion of the pumping pulses. Like other processes involving nonlinear interactions between x-rays and longer wavelengths, our method can lead to the development of a probe for spectroscopy of valence electrons at the atomic scale resolution. The two main advantages of the method we propose over the direct observation of the generated signal are the ability to probe the properties of materials at wavelengths where they are opaque and the higher predicted efficiency in the ultraviolet regime. We describe a possible experimental setup with realistic specifications optimized with respect to the characteristics of the input pulses. We expect that experimental observations of the effect will be feasible with the new emerging high-repetition-rate x-ray free-electron lasers.

1. INTRODUCTION

Although nonlinear processes at optical frequencies were first demonstrated more than 50 years ago [1–3], nonlinear light–matter interactions at x-ray wavelengths were hardly explored until recently. These interactions were indeed described nearly half a century ago by Freund and colleagues [4], and by Eisenberger and colleagues [5]. However, with earlier hard x-ray sources such as x-ray tubes and synchrotrons, experimental observations of nonlinear effects have been confined to the spontaneous processes of x-ray parametric down-conversion (PDC) [6–11]. We note that several pertinent effects such as third harmonic generation [12] and self-action effects [13] were analyzed theoretically.

In addition to being almost unexplored, nonlinear interactions between x-rays and longer wavelengths can lead to a method for probing the microscopic structure of chemical bonds and the density of valence electrons with the atomic scale resolution [5,9,14,15].

The new x-ray free-electron lasers (XFELs) producing femtosecond pulses of high brightness and peak intensity [16,17] make possible further novel experiments exploring nonlinear effects with x-rays. For example, x-ray and optical sum-frequency generation (SFG) in a diamond crystal was performed by Glover et al. [14]. X-ray second harmonic generation (SHG) in a diamond was observed by Shwartz et al. [18]. The efficiencies of those effects, though, are extremely small, no more than $10^{-7}$. Higher-order nonlinear processes are orders of magnitude less efficient. For example, Tamasaku and colleagues reported the observation of x-ray two-photon absorption (TPA) in germanium with an efficiency of $\sim 10^{-13}$ [19], and in metallic copper [20]. X-ray TPA in zirconium was observed by Ghimire and colleagues et al. [21].

In difference frequency generation (DFG) of ultraviolet (UV) or visible pulses from two x-ray pulses, the frequency of the generated wave is equal to the difference of the two input frequencies. The DFG of optical radiation from two x-ray pump beams has been recently analyzed theoretically [22]. The approach considered in that work, which predicted an efficiency of $10^{-4}$, is to directly measure the generated beam, while assuming that the pump is undepleted [22]. However, it is clear that such an approach is not applicable for materials that are opaque at the photon energy of the generated signal. This restriction limits the applicability of model to a very narrow range of wavelengths and materials. In addition, the measurement of the generated signal requires a careful design that can overcome the strong fluorescence noise in the optical regime, which is originated from the absorption of the x-ray pulses.

Here we extend the previous work on DFG to optically opaque materials. We show that it is possible to evaluate the efficiency of DFG by measuring the depletion of the x-ray pulses rather than the direct measurement of the intensity of the generated signal. This approach can overcome the challenges described above and opens the possibility to use DFG for spectroscopy of opaque materials. We estimate the pulse...
2. MODEL

We begin by describing the theoretical model, which is similar to the model that has been used to describe the DFG of x-rays into the optical regime where the material is transparent [22]. The main differences are the addition of the absorption to the generated wave and, since we propose to measure the depletion of the pump beam, we also include the depletion in the calculations, which is in contrast to our previous work [22]. The propagation of the waves in a nonlinear medium is described by the wave equation with a nonlinear term, which is given by

\[ \nabla^2 \tilde{E} = \mu_0 \left( \frac{\partial \tilde{E}^{\text{NL}}}{\partial t} + \varepsilon_0 \frac{\partial^2 \tilde{E}}{\partial t^2} + \varepsilon_0 \chi^{(1)} \frac{\partial^2 \tilde{E}}{\partial t^2} \right), \]  

where \( \tilde{E}(\vec{r}, t) \) is the electric field, \( \mu_0 \) is the vacuum permeability, \( \varepsilon_0 \) is the vacuum permittivity, \( \chi^{(1)} \) is the linear (first order) susceptibility, and \( \tilde{E}^{\text{NL}}(\vec{r}, t) \) is the nonlinear field. We write the fields as \( \tilde{E}_{1,2,3}(\vec{r}, t) = \frac{1}{c} E_{1,2,3} \varepsilon^{(i)}(\vec{k}_{1,2,3}, \omega_{1,2,3}, t) e^{i (\vec{k}_{1,2,3} \cdot \vec{r} - \omega_{1,2,3} t)}, \) where \( E_{1,2,3} \) is the envelope function that varies slowly compared to the wave-number, \( \vec{k}_{1,2,3} \), and frequency, \( \omega_{1,2,3} \). This polarizes the vector of the field. With this simplification we can use the slowly varying envelope approximation (SVEA). This leads to coupled wave equations, which relate the pumping fields and the generated field envelopes, so

\[ \frac{n_1}{c} \frac{\partial E_1}{\partial t} + \sin(\theta_1) \frac{\partial E_1}{\partial x} + \cos(\theta_1) \frac{\partial E_1}{\partial y} + \alpha_1 E_1 = \kappa E_2 E_3, \]
\[ \frac{n_2}{c} \frac{\partial E_2}{\partial t} + \sin(\theta_2) \frac{\partial E_2}{\partial x} + \cos(\theta_2) \frac{\partial E_2}{\partial y} + \alpha_2 E_2 = \kappa E_1 E_3 \]
\[ \frac{n_3}{c} \frac{\partial E_3}{\partial t} + \sin(\theta_3) \frac{\partial E_3}{\partial x} + \cos(\theta_3) \frac{\partial E_3}{\partial y} + \alpha_3 E_3 = \kappa E_1 E_2. \]

We denote \( E_1 \) and \( E_2 \) as the envelopes of the pumping beams and \( E_3 \) as the envelope of the generated beam. \( n_1 \) is the refractive index, \( c \) is the speed of light in vacuum, \( \alpha_1 \) is the absorption coefficient, and \( \kappa \) is the nonlinear coefficient. \( \theta_1, \theta_2 \) are the propagation angles of the pump beams, and \( \theta_3 \) is the propagation angle of the generated beam with respect to the normal to the crystal surface (see Fig. 1). The angles are determined by the phase-matching condition \( \vec{k}_3 + \vec{G} = \vec{k}_1 - \vec{k}_2 \). The phase matching is achieved using the reciprocal lattice vector. This is possible because wave vectors in the x-ray region are of the same order of magnitude as the reciprocal lattice vector. When a perfect phase matching is fulfilled, the individual atomic dipoles that constitute the material are properly phased. The field emitted by each dipole adds coherently in the propagating direction and the generated wave extracts energy most efficiently from the pumping waves. We note that the coupled equations shown in Eq. (2) include the conditions for phase matching and are correct as long as the wave envelopes vary slowly with respect to the UV period and wavelength, and the condition that the absorption length of each of the waves is much smaller than the wavelength is satisfied for all waves.

Equation (2) can be simplified by assuming that the depletion of the input waves is much smaller than their initial values, thus allowing us to write each wave as \( \hat{E}(x, y, z, t) = E_0(x, y, z = 0, t) + \delta E(x, y, z, t) \), where \( \delta E \ll E_0 \) and solve the equations by keeping only the first order terms,

\[ \frac{n_1}{c} \frac{\partial \delta E_1}{\partial t} + \sin(\theta_1) \frac{\partial \delta E_1}{\partial x} + \frac{\partial \delta E_1}{\partial y} + \alpha_1 \delta E_1 = \kappa \delta E_2 \delta E_3, \]
\[ \frac{n_2}{c} \frac{\partial \delta E_2}{\partial t} + \sin(\theta_2) \frac{\partial \delta E_2}{\partial x} + \frac{\partial \delta E_2}{\partial y} + \alpha_2 \delta E_2 = \kappa \delta E_1 \delta E_3 \]
\[ \frac{n_3}{c} \frac{\partial \delta E_3}{\partial t} + \sin(\theta_3) \frac{\partial \delta E_3}{\partial x} + \frac{\partial \delta E_3}{\partial y} + \alpha_3 \delta E_3 = \kappa \delta E_1 \delta E_2. \]

We denote \( \eta_1 \) as the impedance of the medium, and \( \omega_1 \) as the angular frequency. FNL is the nonlinear current density that we estimate using the classical theoretical model for nonlinearity, and using the recently observed data of PDC into the optical regime, where we consider the nonlinearity coefficient as a fitting parameter.

In previous works the undepleted pump approximation was assumed. This assumption leads to a simplified model with no coupled equations that can be solved analytically [22]. Here, on the other hand, this simplification cannot be made inherently, since the depletion of the pump is the quantity we want to measure. Therefore, we need to solve the coupled equations shown in Eq. (3). These equations possess no analytical solution and are solved numerically. The theoretical value for the nonlinear current density is calculated in the same manner as in previous works, by using the classical model for x-ray and optical wave mixing [5,26]. The origin of the nonlinearity is the combination of three phenomena that include the Lorentz force, the perturbed charge density, and the Doppler shift.
where $\rho_0$ is the electron density in the absence of the pumping beam (electron density in uniform plasma), and $\hat{G}$ is the reciprocal lattice vector. $E_i$ and $\hat{k}_i$ are the envelope and wave vector of the beam, oscillating at frequency $\omega_i$. We note that this model agrees with the reported experimental results of interactions between x-rays and optical wavelengths when the optical wavelengths are below the band gap [28]. The semi-empirical value for the nonlinear coupling coefficient is obtained by fitting the expression for the integrated count rate of PDC, including losses [11], to the experimental data described in Fig. 2 of [28].

We write the envelope of each of the fields as a transform-limited (TL) Gaussian,

$$E(x,y,z,t) = \sqrt{\frac{N}{\omega_{x,1,2} \omega_{y,1,2} \tau_{1,2} \sec(\theta_{1,2})}} \exp\left(-\frac{1}{4}\left(z^2 \omega_{x,1,2}^2 + z^2 \omega_{y,1,2}^2 + \frac{1}{\tau_{1,2}^2}\right)\right),$$

where $N$ is the number of photons per pulse, and $\omega_{x,1,2}$ and $\omega_{y,1,2}$ are the width of the waist of the beams in the $x$ and $y$ directions. $\tau_{1,2}$ is the pulse duration at the full width half maximum (FWHM), for each of the pulses, $\Delta \tau$ is the time delay between the two pulses, and $v_x$ is the group velocity of the pump pulses. We define $x_{1,2} = x \cos \theta_{1,2} - z \sin \theta_{1,2}$ and $z_{1,2} = x \sin \theta_{1,2} + z \cos \theta_{1,2}$. We solve Eq. (3) together with the estimation of the nonlinear coupling coefficient as we described above, to find the electric fields of all waves. We obtain the figures below by integrating the solution of Eq. (3) for $E_1$ (the field of the first input beam) over the pulse duration and spatial coordinates perpendicular to the normal to the surface of the crystal ($x, y$).

\section{Numerical Simulations}

To demonstrate the feasibility of the method we propose, we consider an example where two quasi-monochromatic pumping beams with center energies at 8.05 keV ($\lambda = 0.154$ nm) and 8.0435 keV ($\lambda = 0.15415$ nm) enter a diamond crystal at angles $\theta_1, \theta_2$ relative to the \textit{z} direction and generate a wave with a center energy at 6.5 eV ($\lambda = 190$ nm), which propagates at an angle of $\theta_3$, relative to the \textit{z} direction (see Fig. 1). The reciprocal lattice vector normal to the C(111) atomic planes is used to fulfill the phase-matching condition. The phase-matching equations imply that the incident angles of the pumps are $\theta_1 = 21.856^\circ$ and $\theta_2 = -22.103^\circ$, and that the angle between the normal to the surface and the generated UV wave is $\theta_3 = 7.6^\circ$. The pump input angles with respect to the atomic planes deviates from the Bragg angle by $\sim 0.15^\circ$. The absorption coefficients and the refractive index for the x-ray pumps and for the generated UV were taken from tabulated data [29,30]. We consider two beams with equal waists.

We first consider the dependencies on the various properties of the pumping beams and identify the parameters that result in the maximum efficiency. We show our results in Fig. 2. The efficiency of the process is defined as the ratio between the number of the DFG photons and the number of incident pump photons. Since the generated beam is not directly measured, the number of generated photons is estimated as $N_{\text{DFG}} = N_x - N_{\text{nl}}$, where $N_x$ is the number of pump photons that are detected in the absence of the second beam (only linear absorption) and $N_{\text{nl}}$ is the number of the pump photons that are detected when the second beam is present (linear absorption and the nonlinear process). The efficiency is therefore given by $\eta_{\text{eff}} = (N_x - N_{\text{nl}}) / N_x$, where $N_{\text{nl}}$ is the number of incident pump photons entering the nonlinear medium. We calculate the efficiency by calculating the number of photons per pulse of the pump with the nonlinear interaction and in its absence. This is obtained by integrating $E_i(x,y,z,t)^2$ over the time and the transverse directions of the propagation direction.

It is clear that the maximum efficiency is expected when phase matching is satisfied. However, it is also important to consider the dependence of the phase matching on the angular deviation from the perfect phase-matching angle. We plot the angular distribution of the DFG efficiency in Fig. 2(a). The width of this distribution is 0.8 mrad at full FWHM. As we discuss below, this width is expected to be adequate for a practical setup.

Due to the weakness of the nonlinearity, intense focused pulses are required to achieve measurable efficiencies. However, as the beams are focused more tightly, their spatial
The pulses at phase matching with a beam waist of 15 μm. As expected, we therefore plot the dependence of the efficiency as can be seen in Fig. 2(b). We find that the maximum DFG effect is observed for a beam width of 15 μm.

When examining the efficiency dependence on the pulse duration, the group velocity mismatch must also be considered. Since the two pumps propagate at different velocities, short pulses will suffer also from temporal walk-off. This effect contributes greatly for short pulses. However, we find that for pulse durations of 35 fs the dominant walk-off term is the spatial term, whereas for pulses shorter than 20 fs, the temporal term dominates [32,33]. We find that the maximum DFG effect is observed for a pulse duration of 35 fs, as can be seen in Fig. 2(c).

By introducing a delay between the two input pulses, we note that it is possible to get the temporal structure of the pulses. We therefore plot the dependence of the efficiency on the delay between the input pulses in Fig. 3. As expected, the most efficient wave mixing occurs when the delay approaches zero. We find that the FWHM is 70 fs. The distribution is slightly asymmetric because of the slightly different group velocities of the two pump beams.

After optimizing the pulses characteristics (duration, width, direction, and delay), we estimate the energy depletion of the pumping beams due to the nonlinear DFG process.

We note that the estimation of the efficiency is highly dependent on the estimation of the nonlinear coupling coefficient, which can only be estimated since there is no comprehensive theory for nonlinear interactions between x-rays and UV radiation in the range near the band-gap of the material. We therefore estimate the nonlinear susceptibility by fitting the experimental data of the recently observed PDC of x-rays into the optical regime [28]. This procedure leads to a nonlinear susceptibility of $\chi^{(2)}_{(2,2,0)} = 2 \times 10^{-17}$ $\text{esu}$ and the corresponding DFG estimated efficiency for an input flux of $10^{11}$ photons per pulse is $1.5 \times 10^{-4}$. The calculation based on the classical model for nonlinearity, which has been used to describe the nonlinear interaction between x-rays and optical radiation [26], results in a nonlinear susceptibility of $2 \times 10^{-16}$ $\text{esu}$, and the efficiency for an input flux of $10^{11}$ photons per pulse is $10^{-2}$. We note that this model agrees with the experimental results when the optical wave is at photon energies below the energy band gap, but shows discrepancies with the experimental results of PDC, for photon energies above the band gap [14,28].

We next address the ability to measure the effect with present-day technology. The ability to measure the depletion energy of the input beams depends on the ratio between the energy loss due to linear absorption and the energy depleted from the beam due to the nonlinear process. The pulses emerging from the SASE beam, however, do not have a Gaussian temporal shape but rather have the form of a sequence of spikes with stochastic phases and amplitudes. Therefore, we also estimate the depletion energy for temporally stochastic (TS) pulses in addition to the TL Gaussian pulses. These pulses resemble the temporal shape of the SASE beam [33]. As shown in [33], we describe the TS pulses as a chain of short Gaussian pulses with random phases,

$$E_{\text{TS}}(x,y,z,t) = E(x,y,z,t) \sum_{m=-\infty}^{\infty} e^{i\phi_m} \times e^{-\left(\frac{(m\Delta \tau_0 + \tau_0)/\tau_0}{2}\right)}$$

(8)

where $E(x,y,z,t)$ is the TL Gaussian envelope given in Eq. (7). $\tau_0 = 2\sqrt{2 \log(2) h/\Delta E}$ is the minimal pulse duration, where $\Delta E$, the FWHM of the power spectrum, was taken to be 1 eV. $\Delta \tau_0$ is the duration between adjacent spikes (taken to be $\Delta \tau_0 = \tau_0/5$), and $\phi_m$ is a randomly assigned phase.

In Fig. 4, we show the normalized pulse energy of one input beam as a function of the crystal length in the absence of the second beam (orange line) and when the second Gaussian beam (blue line) or TS beam (red dashed) is present. It is clear that the nonlinear effect is most pronounced when the energy transfer due to the nonlinear process is maximized at $z = 30$ μm. The length where the efficiency reaches its maximal value is determined by the overlap between the input beams. At this
distance the ratio between the pulse energy loss due to the non-linearity and the pulse energy loss without the nonlinearity (linear absorption) is the largest and is equal to $1.2 \times 10^{-2}$ when a TL Gaussian beam is assumed ($1 \times 10^{-2}$ for a TS beam). Since we propose to use a monochromator, which restricts the bandwidth of the input beams at the nonlinear crystal, the difference between the spectra of the TL Gaussian pulses and the TS pulses are smaller than without the monochromator. In addition, an average over a large number of these TS pulses results with the assumed TL Gaussian pulse shape [33,34]. Therefore, the energy depletions of the two pulses are comparable. The small deviation between them is due to the nonlinear characteristics of the interaction, which becomes more pronounced at larger propagation distances.

### 4. SUGGESTED EXPERIMENTAL SETUP

To complete our proposal for the measurement of the depletion of the pulse energy of the input beams as a means to measure the nonlinear effect of DFG of UV pulses from two x-ray pulses, we describe a possible experimental setup. The two quasi-monochromatic pump beams must satisfy the phase-matching condition. Consequently, the angle between the two beams is nearly equal to twice the Bragg angle. This requirement can be fulfilled by the arrangement of crystals described in Fig. 5. All the crystals in this example are diamond crystals, where we use the same reflection (in this example we use the C(111) reflection). The input beam is the broad-spectrum self-amplified spontaneous emitted (SASE) beam. Crystal 1 and crystal 2 are tuned to the Bragg angle of the first beam (8.05 keV) at $\theta_B = 21.96^{\circ}$. Crystal 1 reflects the beam in the direction of crystal 2, and crystal 2 reflects the first beam into the DFG crystal. Crystal 3 is tuned to the photon energy of the second beam at 8.0435 keV (the Bragg angle is $\beta = 21.98^{\circ}$), and it reflects the second beam into the DFG crystal. With this setup, the angle between the two pump beams is $\theta_1 + \theta_2 = 43.96^{\circ}$. Crystal 4 is the DFG crystal.

We note that the input SASE beam suffers from large pulse energy and spectral fluctuations. Since the proposed setup relies on the use of a Bragg beam splitter and reflectors similar to those that are used in current split and delay systems [35,36], the central photon energies of the input beams at the input of the nonlinear crystal are fixed but their intensities (and spectra) fluctuate stronger than the intensity of a SASE beam before the first crystal. Therefore, the comparison between the linear and the nonlinear depletion as shown in Fig. 4 requires very careful shot-to-shot measurements of the pulse energies and spectra of the input beams before and after the nonlinear crystal. Real-time detectors can be used to measure the quantities of the input beam using a thin foil that scatters a small portion of the intensity into a photodiode. The uncertainty in the pulse intensity due to the strong SASE fluctuations is linearly dependent on the intensity. Therefore, the variation of the pulse intensity will not affect the pulse detection statistics. We conclude that counting statistics is the main source for errors that cannot be eliminated. Current detectors can measure the number of photons per pulse with an absolute uncertainty of $< 10\%$ [37–39]. Hence, about $10^6$ pulses are required to obtain a standard error of $10^{-4}$, which is sufficient to differentiate the nonlinear depletion according to our stringent estimation of the effect, from the linear depletion. Consequently, the measurement of the effect is expected to gain significantly using high-repetition-rate FELs. For example, using the European XFEL, which can deliver $2.7 \times 10^9$ pulses per second, the measurement time is expected to be $\sim 40$ seconds; using LCLS II, where the number of pulses per second will be $\sim 10^9$, the measurement time will be only a few seconds [40–44]. We also note that the nonlinear depletion depends on the intensity of the input beam; therefore, a more intense source will require less repetitions to differentiate the two effects. The dependence of the depletion originating from the DFG effect is expected to vary linearly with the pump intensities, in contrast to the efficiencies of linear depletion processes, which are independent of the intensities. Therefore, measuring this dependence indicates that the depletion is
due to DFG and can be used to distinguish the effect from other effects. In addition, it is also possible to discriminate the DFG from other effects that are not wave mixing by blocking one of the beams, since the DFG effect should vanish with only one beam. Another possible mechanism to estimate the absorption is by detecting the fluorescence. However, in diamond for example, only the visible wavelengths will be detected while the UV wavelengths will be absorbed.

5. SUMMARY AND CONCLUSIONS

In conclusion, we considered a new approach to measure the nonlinear mixing of x-rays and longer wavelengths by measuring the depletion of the pumping pulses. We then analyzed the effect of the DFG of ultraviolet radiation from two short x-ray pulses. This method opens the possibility to measure DFG in the x-ray regime with various materials, including materials that are opaque at the generated signal wavelength. Our work predicts efficiencies that are higher than x-ray and visible wave pulses. This method opens the possibility to measure DFG in the x-ray regime with various materials, including materials that are opaque at the generated signal wavelength. Our work predicts efficiencies that are higher than x-ray and visible wave mixing, which we relate to the resonant enhancement of the nonlinearity near the binding energies of the valence electrons in the sample. Despite the resonant enhancement, our calculations indicate that the measurement of the effect requires high-repletion-rate XFELs.

Finally, the method we propose advances the possibility to use x-ray nonlinear interactions as a probe for valence electron spectroscopy at the atomic scale resolution. The nonlinear current density, which drives the nonlinear process, is related to the atomic charge density, as can be seen from Eq. (6). Hence, it is possible to reconstruct the valence electron charge distribution using a series of measurements of the Fourier components of the nonlinear susceptibility [9]. Because it is possible to control the delay between the input pulses, we believe our method can lead to the development of a probe for the dynamics of events associated with the charge distribution of valence electrons with temporal resolution of sub-femtoseconds.

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