Difference Frequency Generation of Ultraviolet
from X-Ray Pulses in Opaque Materials

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Abstract

I describe a new method for observing difference frequency generation (DFG) of ultraviolet (UV) radiation from two short x-ray pulses by measuring the depletion of the pumping pulses. The x-ray damage threshold is much higher than the optical damage threshold. Therefore, the maximal efficiency of difference-frequency generation from two x-ray pulses can theoretically be orders of magnitude higher than the efficiency of effects such as sum/difference - frequency mixing between high intensity x-rays and optical short-pulse sources. Furthermore, the efficiency of a DFG process from two x-ray pulses into the UV regime is estimated to be higher than the efficiency into visible wavelengths since the electronic resonance frequencies are in the UV regime.

The output generated wave is hard to measure since it is in the UV regime, where the absorption coefficient is large. In DFG of x-rays into the UV, the generated UV light is absorbed in the medium and only the x-ray pumps are detected. Therefore, I calculate the power loss of the input beams due to the DFG process. This power loss is related to the power of the generated UV wave.

Like other processes involving nonlinear interactions between x-rays and longer wavelengths, this method can lead to the development of a probe for spectroscopy of valence electrons at the atomic scale resolution.

By assuming $10^{11}$ photons per input pulse, I predict that the conversion efficiency in a diamond crystal exceeds $5 \times 10^{-5}$ and $5 \times 10^{-3}$, for a measured and a theoretical nonlinear susceptibility, respectively. The two main advantages of the method I
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.

This work serves as a foundation for experimental research, and determines the requirements (source brightness, pulse duration, etc.) to measure the phenomena. I describe a possible experimental setup with realistic specifications that are optimized with respect to the characteristics of the input pulses.
1. Introduction

Difference frequency generation (DFG) at optical frequencies was first demonstrated in 1963 [1], shortly after the observation of optical second-harmonic generation in 1961 [2], and optical sum-frequency generation in 1962 [3]. Since then, DFG in the visible regime was studied thoroughly. On the other hand, nonlinear processes in the x-ray regime remained unexplored until recently. These interactions were indeed described nearly half a century ago by Freund and colleagues [4], and by Eisenberger and colleagues [5]. However, due to the low nonlinear susceptibility, high brightness x-ray sources are required for the observation of most nonlinear x-ray effects. With earlier hard x-ray sources – x-ray tubes and synchrotrons, experimental observations of nonlinear effects have been confined to the spontaneous processes of x-ray parametric down-conversion [6–11]. I note that several pertinent effects such as third harmonic generation [12] and self-action effects [13] were analyzed theoretically.

The construction of hard x-ray free electron lasers (XFELs) producing femtosecond pulses of high brightness and peak intensity [14,15] led to the possibility of performing additional experiments exploring nonlinear effects. For example, x-ray and optical sum-frequency generation was performed by Glover et al. [16], and x-ray second harmonic generation by Shwartz et al. [17]. The efficiencies of those effects, though, are extremely small, and are 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 the efficiency
of $\sim 10^{-13}$ [18]. X-ray TPA in zirconium was observed by Ghimire and colleagues et al. [19].

DFG is a second order nonlinear optical process where two input beams interact in a nonlinear medium, and generate a field at a frequency that matches the frequency difference of the two pumps. DFG of long wavelengths from x-ray pulses can be more efficient than other nonlinear processes and can be used in opaque materials. DFG of optical radiation from two x-ray pump beams has been considered recently [20]. 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 [20]. However, it is clear that such an approach is not applicable for materials that are opaque at the photon energy of the generated signal. 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. Furthermore, the electronic resonance frequencies of valence electrons in many materials are in the ultraviolet (UV) range, thus in that regime the nonlinearities are stronger than far off-resonance nonlinearities. Consequently, the efficiencies of DFG of UV pulses from x-ray pulses are expected to be stronger than the efficiencies of DFG of visible pulses from x-ray pulses.

Here I point out that it is possible to measure the efficiency of DFG of UV pulses from x-ray pulses by measuring the depletion of the x-ray pulses. This approach can overcome the challenges described above and can be used for spectroscopy of opaque materials. I calculate the power loss of the pump beam due to the DFG process and predict that for two pump beams with a photon power of $10^{11}$ photons per pulse, which
can be achieved with available XFELs [21–23], the power depletion of the pump beam as the results of the DFG process is over $5 \times 10^6$ photons/pulse, which corresponds to an efficiency of $5 \times 10^{-5}$. I note that this efficiency is calculated using a nonlinear susceptibility, fitted from a PDC measurement in diamond [24]. A theoretical calculation results in an efficiency of $5 \times 10^{-3}$ for the same flux. I describe a proposed experimental setup, with optimized characteristics.

Like other nonlinear interactions between x-rays and longer wavelengths, DFG of UV pulses from x-ray pulses can lead to a method for probing the microscopic structure of chemical bonds and the density of valence electrons with the atomic scale resolution [4,5,9,16,25]. The nonlinear current density, which drives the DFG process, is proportional to a Fourier (that is, reciprocal-space) component of the valence electrons charge density, selected by phase matching. Therefore, the power of the DFG process is proportional to the square of the absolute value of the carrier density. A series of measurements of the Fourier components of the valence electrons together with a phase retrieval algorithm [26] can be used for the reconstruction of the valence electrons charge density.
2. Theoretical Background

2.1 Nonlinear Optics

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. [2]. Mathematically, the optical response to an electric field can be described by expressing the polarization $P(t)$, as a power series expansion of the electric field strength $E(t)$:

$$P(t) = \epsilon_0 \left[ \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \cdots \right], \quad (2.1.1)$$

where $\epsilon_0$ is the permittivity of free space, $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order nonlinear optical susceptibilities, respectively. The electric susceptibility is a macroscopic quantity that averages the response of many atoms. The response of the material to radiation is an indirect measurement of the electric susceptibility. The atomic electric fields, however, are microscopic quantities, which are hard to measure.

Second-order nonlinear optical interactions typically occur in noncentrosymmetric crystals, that is, in crystals that do not display inversion symmetry. In crystals which display inversion symmetry, $\chi^{(2)}$ vanishes identically and consequently such materials cannot produce second-order nonlinear optical interactions. Third-order nonlinear optical interactions, on the other hand (i.e., those described by $\chi^{(3)}$) can occur for both centrosymmetric and noncentrosymmetric media.
X-ray nonlinearities can be viewed as if they originate from three specific physical phenomena: Lorentz force, electron displacement, and Doppler shift [5,10]. X-ray nonlinearities are nonlocal, and second order processes may be observed even in centrosymmetric materials, but require a non-uniform electron density. Unlike visible light, which interacts only with valence electrons, x-ray radiation interacts with both the valence and core electrons.

2.2 Light-Matter Interaction

Light-matter interactions can be seen as an oscillating electromagnetic field (described by the equations of Maxwell) interacting with charged particles (Newton’s equation of motion with the electric and the Lorentz forces).

The interaction can be divided into two sub categories: linear interactions, where the induced polarization depends linearly on the electromagnetic field, and nonlinear interactions, where the dependence is nonlinear.

The linear interaction ($\chi^{(1)}$) defines the refractive index and leads to phenomena such as absorption and Bragg reflection. The nonlinear interaction, includes second order processes ($\chi^{(2)}$) such as parametric down conversion, sum and difference frequency generation, and second harmonic generation. Higher order processes ($\chi^{(3)}, \chi^{(4)}, ...$), include phenomena such as, two photon absorption, the nonlinear Kerr effect, and high harmonic generation.
2.2.1 Linear interaction

In linear optics the basic assumption is that the relation between the polarization and the electric field is linear i.e. \( \mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E} \), where \( \chi^{(1)} \) is the dielectric susceptibility.

In the classical case, far from resonances, the dielectric susceptibility is derived from the Lorenz model, which treats the atom as a harmonic oscillator. Assuming no absorption in the medium, the dielectric susceptibility is given by \([27]\):

\[
\chi^{(1)}(\mathbf{r}) = \frac{\rho(\mathbf{r}) e^2}{\varepsilon_0 m (\omega^2 - \omega_0^2)},
\]

where \( \rho(\mathbf{r}) \) is the charge distribution, \( e \) and \( m \) are the electron charge and mass, respectively, \( \varepsilon_0 \) is the vacuum permittivity, and \( \omega_0 \) is the resonance frequency of the valence electrons. For x-ray wavelengths, far from resonances, the classical model that describes the interaction is described by the Thompson scattering. The susceptibility is given by \([28]\): \( \chi^{(1)}(\mathbf{r}) = -\frac{\rho(\mathbf{r}) R \lambda^2}{\pi} \), where \( R = \frac{e^2}{4\pi\varepsilon_0 mc^2} \) is the classical radius of the electron and \( c \) is the speed of light in vacuum. In a crystal medium where \( \rho(\mathbf{r}) \) and \( \chi(\mathbf{r}) \) are periodic functions in space, \( \rho(\mathbf{r}) \) can be expanded in a Fourier series: \( \rho_G = \int \rho(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} d^3r \) where \( \mathbf{G} \) is the reciprocal lattice vector and the integration is extended to all reciprocal lattice vectors. \( \chi^{(1)}(\mathbf{r}) \) is expanded in the same way: \( \chi_G = -\frac{RA^2 \rho_G}{\pi V} \), where \( V \) is the volume of the unit cell.

2.2.2 Nonlinear interaction

The nonlinear interaction can be expressed by the nonlinear current density. The current density is defined as the flow of electric charge, namely: \( \mathbf{J} = \rho \mathbf{v} \), where \( \rho \) is the charge density and \( \mathbf{v} \) is the electron velocity. By using a perturbative approach, the
velocity, the displacement and the charge density can be expanded in the form of a power series, namely:

\[ \mathbf{v} = \lambda \mathbf{v}^{(1)} + \lambda^2 \mathbf{v}^{(2)} + \cdots \] (2.2.2)

\[ \mathbf{r} = \lambda \mathbf{r}^{(1)} + \lambda^2 \mathbf{r}^{(2)} + \cdots \] (2.2.3)

\[ \rho = \rho^{(0)} + \lambda \rho^{(1)} + \lambda^2 \rho^{(2)} + \cdots \] (2.2.4)

where \( \lambda \) is a small perturbation parameter. Setting \( \lambda = 1 \), the second order nonlinear current density can be written as:

\[ \mathbf{J}^{(2)} = \rho^{(0)} \mathbf{v}^{(2)} + \rho^{(1)} \mathbf{v}^{(1)} \] (2.2.5)

where \( \rho^{(0)} = \sum G \rho_G e^{i \mathbf{G} \cdot \mathbf{r}} \) is the unperturbed charge density, \( \rho_G \) is the Fourier component corresponding to the reciprocal lattice vector \( \mathbf{G} \). \( \rho^{(1)} \) and \( \mathbf{v}^{(1)} \) are the first order charge density and velocity, respectively.

I consider a DFG process, where two pump beams with angular frequencies of \( \omega_1 \) and \( \omega_2 \), generate a wave with an angular frequency of \( \omega_3 = \omega_1 - \omega_2 \). All pertinent photon energies are far from any electronic resonance. The nonlinear current density for each wave in the three wave mixing can then be written as:

\[ \mathbf{J}^{(2)}_{\omega_1}(\mathbf{r}, t) = \rho^{(0)}(\mathbf{r}) \mathbf{v}_{\omega_1}^{(2)}(\mathbf{r}, t) + \rho^{(1)}_{\omega_2}(\mathbf{r}, t) \mathbf{v}_{\omega_2}^{(1)}(\mathbf{r}, t) + \rho^{(1)}_{\omega_3}(\mathbf{r}, t) \mathbf{v}_{\omega_3}^{(1)}(\mathbf{r}, t) \] (2.2.6)

\[ \mathbf{J}^{(2)}_{\omega_2}(\mathbf{r}, t) = \rho^{(0)}(\mathbf{r}) \mathbf{v}_{\omega_2}^{(2)}(\mathbf{r}, t) + \rho^{(1)}_{\omega_1}(\mathbf{r}, t) \mathbf{v}_{\omega_1}^{(1)}(\mathbf{r}, t)^* + \rho^{(1)}_{\omega_3}(\mathbf{r}, t) \mathbf{v}_{\omega_3}^{(1)}(\mathbf{r}, t)^* \] (2.2.7)

\[ \mathbf{J}^{(2)}_{\omega_3}(\mathbf{r}, t) = \rho^{(0)}(\mathbf{r}) \mathbf{v}_{\omega_3}^{(2)}(\mathbf{r}, t) + \rho^{(1)}_{\omega_1}(\mathbf{r}, t) \mathbf{v}_{\omega_1}^{(1)}(\mathbf{r}, t)^* + \rho^{(1)}_{\omega_2}(\mathbf{r}, t) \mathbf{v}_{\omega_2}^{(1)}(\mathbf{r}, t)^* \] (2.2.8)

I use a classical equation of motion for a free electron gas with a Lorentz force, to calculate the electron velocities. To calculate the perturbed electron density I use the continuity equation. The two equations necessary to describe the electron plasma are therefore [29]:

7
\[
\frac{\partial^2 \vec{r}}{\partial t^2} + (\vec{v} \cdot \nabla) \vec{v} + \omega^2_0 \vec{r} + \frac{\nabla P}{m \rho} = \frac{e}{m} (\vec{E} + \vec{v} \times \vec{B})
\]  
(2.2.9)

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0.
\]  
(2.2.10)

Here, \(\vec{r}\) is the electron displacement from equilibrium and \(P\) is the pressure. The pressure is considered to be constant throughout the nonlinear process (i.e., \(\nabla P = 0\)). \(\vec{E}\) and \(\vec{B}\) are the electric and magnetic fields of the beams, respectively. The electric field can be expressed as a product of a slowly varying envelope and a carrier field, therefore the electric field generated by each of the propagating waves is written as:

\[
\vec{E} = \frac{1}{2} E(\vec{r}, t) e^{i(\vec{k} \cdot \vec{r} - \omega t)} \hat{\epsilon} + c. c.,
\]  
(2.2.11)

where \(E(\vec{r}, t)\) is the envelope function and \(\hat{\epsilon}\) is the polarization direction of the field.

Equations (2.2.9) and (2.2.10), are solved for each perturbation order.

The equation of motion, taking only first order elements is:

\[
\frac{\partial^2 \vec{r}^{(1)}}{\partial t^2} + \omega^2_0 \vec{r}^{(1)} = \frac{e}{m} \vec{E}.
\]  
(2.2.12)

Inserting the electric field as written in Eq. (2.2.11) and solving the equation for each wave \((i = 1, 2, 3)\), results with:

\[
\vec{r}^{(1)}_i = \frac{e}{2m(\omega_0^2 - \omega_i^2)} E_i e^{i(\vec{k}_i \cdot \vec{r}_i - \omega_i t)} \hat{\epsilon}_i,
\]  
(2.2.13)

and therefore, the first order velocity is:

\[
\vec{v}^{(1)}_i = \frac{\partial \vec{r}^{(1)}_i}{\partial t} = -\frac{e i \omega_i}{2m(\omega_0^2 - \omega_i^2)} E_i e^{i(\vec{k}_i \cdot \vec{r}_i - \omega_i t)} \hat{\epsilon}_i.
\]  
(2.2.14)

The equation of motion, taking second order elements, has the form:

\[
\frac{\partial^2 \vec{r}^{(2)}}{\partial t^2} + (\vec{v}^{(1)} \cdot \nabla) \vec{v}^{(1)} + \omega^2_0 \vec{r}^{(2)} = \frac{e}{m} \vec{v}^{(1)} \times \vec{B}.
\]  
(2.2.15)
The Faraday equation indicates that \(- \frac{\partial \vec{B}}{\partial t} = \nabla \times \vec{E}\). By taking the Fourier transform of \(\vec{B}\), namely: 
\[
\vec{B}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \vec{B} e^{i\omega t} dt
\]
I obtain the Equation:
\[
\vec{B} = -\frac{i}{\omega} \nabla \times \vec{E}.
\tag{2.2.16}
\]

The second order velocities, which are induced by the generated wave (\(\omega_3\)) and by the pumping waves (\(\omega_1, \omega_2\)) are calculated as follows. Inserting Eq. (2.2.16) and Eq. (2.2.14) to the second order equation of motion (2.2.15), yields:
\[
\frac{\partial^2 \vec{r}^{(2)}_3}{\partial t^2} + \omega_0 \vec{r}^{(2)}_3 = -\frac{e^2}{m^2 \omega_1 \omega_2} (\vec{E}_1 \times (\nabla \times \vec{E}^*_2) + \vec{E}^*_2 \times (\nabla \times \vec{E}_1) + \vec{E}_1 \cdot \nabla \vec{E}_2^* + (\vec{E}^*_2 \cdot \nabla) \vec{E}_1).
\tag{2.2.17}
\]

Introducing a useful vector identity
\[
\nabla (\vec{A} \cdot \vec{B}) = \vec{A} \times (\nabla \times \vec{B}) + \vec{B} \times (\nabla \times \vec{A}) + (\nabla \cdot \vec{A}) \vec{B} + (\vec{B} \cdot \nabla) \vec{A},
\tag{2.2.18}
\]
greatly simplifies Eq. (2.2.17). Writing the specific form of the electric fields in the polarization directions, leads to the following equation:
\[
(\omega_0^2 - \omega_3^2) \vec{r}^{(2)}_3 = -i \frac{e^2}{m^2 \omega_1 \omega_2} \left[ \frac{E_1 E^*_2}{4} e^{i[(\vec{k}_1 - \vec{k}_2) \cdot \vec{r} - \omega_3 t]} \cos \phi_{1,2} \right],
\tag{2.2.19}
\]
where I defined \(\phi\) as the angle between the polarization vectors of the two pumps. In the specific case, where the field polarizations are in the same plane of propagation, then: \(\phi = \theta_1 + \theta_2\). When the two beams are polarized in the same direction (i.e. normal to the plane of propagation), \(\phi = 0\), and the nonlinearity is largest. If the two polarizations are perpendicular, the two pumps do not interact and the nonlinearity vanishes. Taking the first derivative over time, the second order velocity becomes:
\[
\mathbf{v}_3^{(2)} = \frac{e^2 \omega_3 (k_1 + k_2)}{4 m^2 \omega_1 \omega_2 (\omega_2^2 - \omega_0^2)} E_1 \mathbf{E}_2^* e^{i[(k_1 + k_2) \mathbf{r} - \omega_3 t]}.
\] (2.2.20)

Using the phase matching condition, namely, \( \mathbf{k}_1 - \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G} \), allows to write the second order velocity, driven by the generated wave, as:

\[
\mathbf{v}_3^{(2)} = \frac{e^2 \omega_3 (k_3 + \mathbf{G})}{4 m^2 \omega_1 \omega_2 (\omega_2^2 - \omega_0^2)} E_1 \mathbf{E}_2^* e^{i[(\mathbf{k}_1 - \mathbf{k}_2) \mathbf{r} - \omega_3 t]} ,
\] (2.2.21)

Next, I derive the second order velocity, driven by the pumping waves (\( \mathbf{E}_1 \) and \( \mathbf{E}_2 \)).

For the first pump (\( \mathbf{E}_1 \)), inserting Eq. (2.2.14) and (2.2.16) to (2.2.15) gives:

\[
\frac{\partial^2 \tilde{r}_1^{(2)}}{\partial t^2} + \omega_0 \tilde{r}_1^{(2)} = -\frac{e^2}{m^2 \omega_1 \omega_2} \left( \mathbf{E}_2 \times (\nabla \times \mathbf{E}_3) + \mathbf{E}_3 \times (\nabla \times \mathbf{E}_2) + \left( \mathbf{E}_2 \cdot \nabla \right) \mathbf{E}_3 + \left( \mathbf{E}_3 \cdot \nabla \right) \mathbf{E}_2 \right).
\] (2.2.22)

Using the vector identity in Eq. (2.2.18), leads to the second order displacement:

\[
\tilde{r}_1^{(2)} = i \frac{e^2 \omega_3}{4 m^2 \omega_2 (\omega_2^2 - \omega_0^2)} \left( \mathbf{k}_2 + \mathbf{k}_3 \right) \cos \phi_{2,3} - \frac{\omega_0^2}{\omega_2^2} \hat{e}_2 \times \left( \mathbf{k}_3 \times \hat{e}_3 \right) A_2 A_3 e^{i[(\mathbf{k}_2 + \mathbf{k}_3) \mathbf{r} - \omega_1 t]},
\] (2.2.23)

and the second order velocity is:

\[
\tilde{v}_1^{(2)} = \frac{e^2 \omega_3 \omega_1}{4 m^2 \omega_2 (\omega_2^2 - \omega_0^2)} \left( \mathbf{k}_2 + \mathbf{k}_3 \right) \cos \phi_{2,3} - \frac{\omega_0^2}{\omega_2^2} \hat{e}_2 \times \left( \mathbf{k}_3 \times \hat{e}_3 \right) E_2 E_3 e^{i[(\mathbf{k}_2 + \mathbf{k}_3) \mathbf{r} - \omega_1 t]}.
\] (2.2.24)

The derivation of the second order displacement and velocity for the second pumping wave (\( \mathbf{E}_2 \)) is in the same manner, which results with:
\[ \tilde{r}_2^{(2)} = -i \frac{e^2 \omega_3}{4m^2 \omega_1(\omega_3^2 - \omega_0^2)(\omega_0^2 - \omega_2^2)} \left( \vec{k}_1 - \vec{k}_3 \right) \cos \phi_{1,3} - \frac{\omega_0^2}{\omega_3^2} \hat{e}_1 \]

\[ \times \left( \vec{k}_3 \times \hat{e}_3 \right) \right] E_1 E_3^* e^{i([\vec{k}_1-\vec{k}_3]\vec{r}-\omega_2 t)}, \tag{2.2.25} \]

and the second order velocity is:

\[ \tilde{v}_2^{(2)} = - \frac{e^2 \omega_3 \omega_2}{4m^2 \omega_1(\omega_3^2 - \omega_0^2)(\omega_0^2 - \omega_2^2)} \left( \vec{k}_1 - \vec{k}_3 \right) \cos \phi_{1,3} - \frac{\omega_0^2}{\omega_3^2} \hat{e}_1 \]

\[ \times \left( \vec{k}_3 \times \hat{e}_3 \right) \right] E_1 E_3^* e^{i([\vec{k}_1-\vec{k}_3]\vec{r}-\omega_2 t)}. \tag{2.2.26} \]

The perturbed charge density is calculated as follows. Writing the continuity equation (Eq. (2.2.10)) for the first order perturbed charge density, while noting the vector identity: \( \nabla(a \vec{b}) = a \nabla \cdot \vec{b} + \vec{b} \cdot \nabla a \), yields:

\[ \frac{\partial \rho^{(1)}}{\partial t} + \rho^{(0)} \nabla \cdot \vec{v}^{(1)} + \vec{v}^{(1)} \cdot \nabla \rho^{(0)} = 0. \tag{2.2.27} \]

Inserting the first order velocities (Eq. (2.2.14)) to this equation and using the Gauss law which indicates that \( \nabla \cdot \vec{E} = \rho^{(1)}/\epsilon_0 \), gives:

\[ \frac{\partial \rho_i^{(1)}}{\partial t} + \frac{ie\omega_i}{m(\omega_i^2 - \omega_0^2)} \left( \frac{\rho^{(0)} \rho_i^{(1)}}{\epsilon_0} + \nabla \rho^{(0)} \cdot \vec{E}_i \right) = 0. \tag{2.2.28} \]

This equation results with the following relation for the first order perturbed charge density:

\[ \rho_i^{(1)} = \frac{e \epsilon_0 \nabla \rho^{(0)}}{m \epsilon_0 (\omega_i^2 - \omega_0^2) - e \rho^{(0)}} \vec{E}_i. \tag{2.2.29} \]

The unperturbed charge density \( \rho^{(0)} \) can be expanded in a Fourier series as discussed above. The only lattice vector that contributes is the one that satisfies the phase
matching condition. Therefore, the unperturbed charge density can be written as \( \rho^{(0)} = \rho_0 e^{i\vec{\gamma} \cdot \vec{r}} \) and Eq. (2.2.29) simplifies to:

\[
\rho_1^{(1)} = \frac{ie \varepsilon_0 \rho_0 e^{i\vec{\gamma} \cdot \vec{r}}}{me_0 (\omega_1^2 - \omega_0^2) - e \rho^{(0)}} \vec{G} \cdot \vec{E}_t.
\]

To calculate the nonlinear current density, I insert the velocity and the charge density found, into Eq. (2.2.6)-(2.2.8). The nonlinear current density, oscillating at the frequencies of the electric fields are therefore:

\[
\begin{align*}
\vec{j}_{\omega_1}^{(2)}(\vec{r}, t) &= -\frac{e^2 \rho_0}{4m} \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega_1 \omega_3 \omega_2 \omega
\end{align*}
\]

The generated frequency is close to the resonance frequency, while the x-ray frequencies are far above the resonance. Therefore, \(|(\omega_2^2 - \omega_0^2)| \ll |(\omega_1^2 - \omega_0^2)| \), and the first term is the dominant term in the nonlinear current density driven by the
The nonlinear current density oscillating at the frequency of the generated wave, can therefore be written in a simplified manner:

\[ J^{(2)}_{3} (\vec{r}, t) = \frac{\varepsilon_{G} \omega_{3} (\vec{k}_{3} + \vec{G}) \cos \phi_{1,2}}{4m^{2} \omega_{1} \omega_{2} (\omega_{3}^{2} - \omega_{0}^{2})} E_{1} E_{2}^{*} e^{i([\vec{k}_{1} - \vec{k}_{2} - \vec{G}] \cdot \vec{r} - \omega_{3} t)}. \] (2.2.34)

I 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 [16,24], but shows discrepancies when the photon energies of the long wavelengths are above the band-gap [24]. Since the energies of the photons are above the band gap in this work, a semi-empirical value for the nonlinear current density is also estimated. The semi-empirical value for the nonlinear coupling coefficient is proportional to the nonlinear current density. The nonlinear coupling coefficient is obtained by fitting the expression for the integrated count rate of PDC including losses [11] to the recently observed experimental data of PDC into the optical regime, described in Fig. 2 of ref. [24].

2.3 Phase matching

DFG is a second order nonlinear process, which involves three photons. In this process the energy and the momentum are conserved. The equations describing energy and momentum conservation are:

\[ \omega_{3} = \omega_{1} - \omega_{2} \] (2.3.1)

\[ \vec{k}_{3} + \vec{G} = \vec{k}_{1} - \vec{k}_{2}, \] (2.3.2)

where, \( \omega_{1} \) and \( \omega_{2} \) are the central frequencies of the pumping waves, \( \omega_{3} \) is the central frequency of the generated UV wave. \( \vec{k}_{1}, \vec{k}_{2} \) and \( \vec{k}_{3} \) are the wave vectors of the
pumping and generated waves respectively, and $\vec{G}$ is the reciprocal lattice vector. Phase matching is achieved by using the reciprocal lattice vectors. This is possible because wave vectors in the x-ray region are of the same order of magnitude as the reciprocal lattice vectors. From a microscopic point of view, when 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.

The phase matching diagram for DFG of UV radiation from two x-ray beams is given in Fig. 1. $\theta_1$, $\theta_2$ 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. The phase matching condition in the $x$ and $z$ directions is:

$$k_1 \sin(\theta_1) - k_2 \sin(\theta_2) - G - k_3 \sin(\theta_3) = 0 \quad (2.3.3)$$

$$k_1 \cos(\theta_1) - k_2 \cos(\theta_2) - k_3 \cos(\theta_3) = 0 \quad (2.3.4)$$

$\theta_1$ and $\theta_2$ are related by the following relation: $\theta_1 + \theta_2 = \alpha$, where $\alpha$ is the angle determined by the experimental setup as will be discussed later.

---

*Fig. 1. Phase-matching scheme. $\vec{k}_1, \vec{k}_2$ and $\theta_1, \theta_2$, are the wave vectors and angles of propagation, respectively, of the pump pulses. $\vec{k}_3$ and $\theta_3$ are the wave vector and angle of propagation, respectively, of the generated UV wave. $\vec{G}$ is the reciprocal lattice vector.*
3. Numerical Methods

3.1 Numerical approach for solving the wave equations

In order to numerically solve the coupled wave equations (Eq. (4.1.18)) in the following chapter, I convert the partial differential equations into a system of ordinary differential equations (ODEs) by using the numerical method of lines (MOL). In this method I discretize the time and the spatial coordinates parallel to the boundary surface \((x, y)\), and remain with the derivative by the spatial coordinate normal to the boundary surface. This leads to a system of ordinary differential equations. Next, I solve the system of ODEs and integrate with respect to the spatial coordinate normal to the boundary surface \((z)\) over the crystal length. The integrations are performed using high-order Runge-Kutta and finite difference methods.
4. Difference Frequency Generation of Ultraviolet from X-Ray Pulses

DFG is a second order nonlinear optical process where two input beams interact in a nonlinear medium, and generate a field at a frequency that matches the frequency difference of the two pumps. Two x-ray pulses at different wavelengths can be generated, for example, by using different tuned canted pole undulators, and the temporal delay between them is controlled by a magnetic chicane [30–32]. Another procedure to generate two x-ray pulses at different frequencies is by using the broadband self-amplified spontaneous emission from the free-electron laser together with Bragg crystals tuned to different frequencies.

I consider a nonlinear three-wave-mixing process where two intense X-ray pulses with central photon-energies far above any electronic resonance, generate a pulse at a central photon-energy above the band-gap of a nonlinear crystal. The propagation of the waves is described by the equations of Maxwell. The wave-mixing process is introduced by a classical nonlinear current density as discussed above [5,29], and by a fitted value for a recently measured nonlinear susceptibility [24].

4.1 Wave propagation

The propagation of all waves in a nonlinear medium is described by the time and special dependent wave equation with a nonlinear term, which is given by:
\[ \nabla^2 \vec{E} = \mu_0 \left( \frac{\partial \vec{j}^{NL}}{\partial t} + \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} + \epsilon_0 \chi^{(1)} \frac{\partial^2 \vec{E}}{\partial t^2} \right), \tag{4.1.1} \]

where \( \vec{E}(\vec{r}, t) \) is the electric field, \( \mu_0 \) is the vacuum permeability, \( \epsilon_0 \) is the vacuum permittivity, \( \chi^{(1)} = \chi + i \chi' \) is the linear (first order) suscepibility, and \( \vec{j}(\vec{r}, t) \) is the nonlinear current density. The refractive index is defined as: \( \tilde{n}^2 = 1 + \chi^{(1)} \), where the real and imaginary parts of the refractive index are defined by: \( \tilde{n} = n + in' \). The wave equation therefore becomes:

\[ \nabla^2 \vec{E} - \frac{\partial^2 \vec{E}}{\partial t^2} \left[ \frac{n^2}{c^2} - \frac{n'^2}{c^2} + \frac{2inn'}{c^2} \right] = \mu_0 \left( \frac{\partial \vec{j}^{NL}}{\partial t} \right). \tag{4.1.2} \]

I write the nonlinear current density and the electric fields as:

\[ \vec{j}_{1,2,3}(\vec{r}, t) = \frac{1}{2} j_{1,2,3}(\vec{r}, t) e^{i(k_{1,2,3} \cdot \vec{r} - \omega_{1,2,3} t)} \hat{e}_{1,2,3} + \text{c.c.} \tag{4.1.3} \]

\[ \vec{E}_{1,2,3}(\vec{r}, t) = \frac{1}{2} E_{1,2,3}(\vec{r}, t) e^{i(k_{1,2,3} \cdot \vec{r} - \omega_{1,2,3} t)} \hat{e}_{1,2,3} + \text{c.c.}, \tag{4.1.4} \]

where \( E_{1,2,3} \) and \( j_{1,2,3} \), are the envelope functions that vary slowly as compared to the wave-number, \( k_{i} \) and frequency, \( \omega_{i} \). \( \hat{e} \) is the polarization vector of the fields. With this simplification I can use the slowly varying envelope approximation (SVEA) in all spatial and time dimensions:

\[ |k_{q}^2 E| \gg \left| 2ik_{q} \frac{\partial E}{\partial q} \right| \gg \left| \frac{\partial^2 E}{\partial q^2} \right| \tag{4.1.5} \]

\[ |\omega^2 E| \gg \left| 2i \omega \frac{\partial E}{\partial t} \right| \gg \left| \frac{\partial^2 E}{\partial t^2} \right| \tag{4.1.6} \]

\[ |i \omega J| \gg \left| \frac{\partial J}{\partial t} \right|, \tag{4.1.7} \]
where \( q = x, y, z \). Since the propagation of all waves is in the \( xz \) plane, I develop the equations without the dependence on \( y \), and get for each wave:

\[
-k_i^2 E_i + 2i k_{ix} \frac{\partial E_i}{\partial x} - k_{iz}^2 E_i + 2i k_{iz} \frac{\partial E_i}{\partial z} + \frac{\omega n_i^2}{c^2} E_i + 2i \frac{\omega n_i^2}{c^2} \frac{\partial E_i}{\partial t} - 2i \frac{\omega n_i^2}{c^2} \frac{\partial E_i}{\partial t} = -i \mu_0 n_i \frac{\partial E_i}{\partial t}.
\]

(4.1.8)

I note that \( k^2 = k_x^2 + k_z^2 \), and \( k = n(\omega) \omega / c \). The imaginary part of the refractive index is small compared to the real part, namely \( n' \ll n \). Neglecting second order small terms results with the following equations:

\[
2i k_{ix} \frac{\partial E_i}{\partial x} + 2i k_{iz} \frac{\partial E_i}{\partial z} + 2i \frac{\omega n_i^2}{c^2} \frac{\partial E_i}{\partial t} + 2i \frac{\omega n_i^2}{c^2} \frac{\partial E_i}{\partial t} = -i \mu_0 \omega j_i.
\]

(4.1.9)

I note that \( k_{ix} = k_i \sin \theta_i \), and \( k_{iz} = k_i \cos \theta_i \) in my scheme (see Fig. 1). I define \( \alpha = \frac{\omega n_i}{c} \) as the absorption coefficient, and insert it into Eq. (4.1.9) to receive:

\[
\sin(\theta_i) \frac{\partial E_i}{\partial x} + \cos(\theta_i) \frac{\partial E_i}{\partial z} + n_i \frac{\partial E_i}{\partial t} + \frac{n_i}{c} \frac{\partial E_i}{\partial t} + \alpha_i E_i = -\frac{\eta_0}{2n_i} j_i,
\]

(4.1.10)

denoting \( \eta_0 = \sqrt{\mu_0 / \varepsilon_0} \) as the impedance of free space. The nonlinear current density is defined in the direction of the electric field polarization, namely \( J_i \cdot \hat{e}_i = J_i e^{i(k_i \cdot \hat{r} - \omega_i t)} \). Calculating Eq. (2.2.34) in the polarization direction results with:

\[
\tilde{J}_{i}(\hat{r}, t) \cdot \hat{e}_3 = \frac{e^2 \rho G \omega_3 \cos(\theta_3) \cos \phi_{1,2}}{4m^2 \omega_1 \omega_2 (\omega_3^2 - \omega_0^2)} E_1 E_2^* e^{i[(\vec{k}_1 - \vec{k}_2 - \vec{G}) \cdot \hat{r} - \omega_3 t]}.
\]

(4.1.11)

It is convenient to normalize the complex envelopes by defining the variables \( A_i = E_i / \sqrt{2 \eta_i \hbar \omega_i} \), where \( \eta_i = \eta_0 / n_i \) is the impedance of the medium. This normalization corresponds with photon flux densities (photons/s \cdot m^2) for the coupled waves, defined as: \( \phi_i = |A_i|^2 \). Normalizing Eq. (4.1.10) in this manner, results in a convenient
way to describe the propagation of the light in the medium. Inserting this normalization and Eq. (4.1.11) to Eq. (4.1.10) gives:

$$\sin(\theta_i) \frac{\partial A_i}{\partial x} + \cos(\theta_i) \frac{\partial A_i}{\partial z} + \frac{n_i}{c} \frac{\partial A_i}{\partial t} + \alpha_i A_i = -\frac{\sqrt{2\hbar \eta_1 \eta_2 \eta_3 \omega_1 \omega_2 \omega_3}}{2\omega_i} J_i \quad (4.1.12)$$

Where I introduced the normalized nonlinear coefficient $J_i$, which is defined by the ratio between the nonlinear current density $J_i$ and the normalized envelopes of the electric field. For example, $J_3 = J_3/\sqrt{4\eta_1 \eta_2 \hbar^2 \omega_1 \omega_2}$. Next, I introduce the nonlinear coefficient $\tilde{\kappa}$. The nonlinear coefficient is the coefficient that determines the strength of the nonlinearity and couples the different waves, and is related to the nonlinear current density by the following relation:

$$\tilde{\kappa}_i = \frac{\sqrt{2\hbar \eta_1 \eta_2 \eta_3 \omega_1 \omega_2 \omega_3} J_i}{2\omega_i} \quad (4.1.13)$$

I write the nonlinear coefficient specifically for all fields:

$$\tilde{\kappa}_1 = \kappa_1 A_2 A_3 e^{-i(\tilde{k}_1 - \tilde{k}_2 - \tilde{k}_3 - \tilde{G})\cdot \hat{r}} \quad (4.1.14)$$

$$\tilde{\kappa}_2 = \kappa_2 A_1 A_3^* e^{i(\tilde{k}_1 - \tilde{k}_2 - \tilde{k}_3 - \tilde{G})\cdot \hat{r}} \quad (4.1.15)$$

$$\tilde{\kappa}_3 = \kappa_3 A_1 A_2^* e^{i(\tilde{k}_1 - \tilde{k}_2 - \tilde{k}_3 - \tilde{G})\cdot \hat{r}} \quad (4.1.16)$$

In order to conserve energy, the nonlinear coefficient has the same value for all waves, namely, $\kappa_i = \kappa$ for $i = 1, 2, 3$. Since $J_3$ has the simplest form, I use the nonlinear current density of the generated wave to achieve the nonlinear coefficient. Therefore, the nonlinear coefficient can be written as: $\kappa = \frac{\sqrt{2\hbar \eta_1 \eta_2 \eta_3 \omega_1 \omega_2 \omega_3}}{8m^2 \omega_1 \omega_2 (\omega_3^2 - \omega_0^2)} e^{2\rho \rho G \cos(\theta_3) \cos \phi_{1,2}}$.

I note the phase mismatch as: $\Delta \tilde{k} = \tilde{k}_1 - \tilde{k}_2 - \tilde{k}_3 - \tilde{G}$. When the phase matching condition is fulfilled, $\Delta \tilde{k} = 0$ and the nonlinear effect is maximized.
Using the notations written above, the second order vector wave equation can be written as a system of three scalar first order coupled wave equations, which relate the pumping fields and the generated field envelopes:

\[
\begin{align*}
\frac{n_1}{c} \frac{\partial A_1}{\partial t} + \sin(\theta_1) \frac{\partial A_1}{\partial x} + \cos(\theta_1) \frac{\partial A_1}{\partial z} + \alpha_1 A_1 &= \kappa A_2 A_3 e^{-i\Delta \vec{k} \cdot \vec{r}} \\
\frac{n_2}{c} \frac{\partial A_2}{\partial t} + \sin(\theta_2) \frac{\partial A_2}{\partial x} + \cos(\theta_2) \frac{\partial A_2}{\partial z} + \alpha_2 A_2 &= \kappa A_1 A_3^* e^{i\Delta \vec{k} \cdot \vec{r}} \\
\frac{n_3}{c} \frac{\partial A_3}{\partial t} + \sin(\theta_3) \frac{\partial A_3}{\partial x} + \cos(\theta_3) \frac{\partial A_3}{\partial z} + \alpha_3 A_3 &= \kappa A_1 A_2^* e^{i\Delta \vec{k} \cdot \vec{r}}.
\end{align*}
\]

(4.1.17)

Since the propagation of all fields is in the \(x-z\) plane, an expansion to a three dimensional coupled equations can be made, by simply adding to the equations a derivative over \(y\).

I note that the coupled equations shown in Eq. (4.1.17) are accurate as long as the wave envelopes vary slowly with respect to the period and wavelength of the generated wave. Therefore, the method I present can be used for a variety of scenarios.

Eq. (4.1.17) can be simplified by assuming that the variations of the input waves are much smaller than their initial values, thus allowing me to write each wave as:

\[ A_i(x, y, z, t) = A_{i0}(x, y, z = 0, t) + \delta A_i(x, y, z, t), \] where \(\delta A_i \ll A_{i0}\), and solving the equations by keeping only the first order terms:

\[
\begin{align*}
\frac{n_1}{c} \frac{\partial \delta A_1}{\partial t} + \sin(\theta_1) \frac{\partial \delta A_1}{\partial x} + \cos(\theta_1) \frac{\partial \delta A_1}{\partial z} + \alpha_1 \delta A_1 &= \kappa A_2 \delta A_3 \\
\end{align*}
\]

(4.1.18)
\[
\frac{n_3 \partial \delta A_3}{c \partial t} + \sin(\theta_3) \frac{\partial \delta A_3}{\partial x} + \frac{\partial \delta A_3}{\partial y} + \cos(\theta_3) \frac{\partial \delta A_3}{\partial z} + \alpha_3 \delta A_3 = \kappa (A_{10} A_{20}^* + A_{10} \delta A_2^* + \delta A_1 A_{20}^*) \, .
\]

I write the envelope of each of the fields as a transform-limited Gaussian:

\[
E(x, y, z, t) = \sqrt{\frac{(\pi)^{1.5} N}{w_{x1,2} w_{y1,2} \tau_{1,2} \sec(\theta_{1,2})}} e^{-\left(\frac{x_{1,2}}{w_{x1,2}}\right)^2 - \left(\frac{y}{w_{y1,2}}\right)^2 - \left(\frac{t+\Delta \tau-z_{1,2}}{\tau_{1,2}} / v_g\right)^2}, \tag{4.1.19}
\]

where \(N\) is the number of photons per pulse, \(w_{x1,2}\) and \(w_{y1,2}\) are the width of the waist of the beams in the \(\hat{x}\) and \(\hat{y}\) direction. \(\tau_{1,2}\) 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 \(v_g\) is the group velocity of the pump pulses. I define \(x_{1,2} = x \cos \theta_{1,2} - z \sin \theta_{1,2}\) and \(z_{1,2} = x \sin \theta_{1,2} + z \cos \theta_{1,2}\). I solve Eq. (4.1.18) together with the estimation of the nonlinear coupling coefficient as described above, to find the electric fields of all waves. I obtain the pulse energy depletion by integrating the solution of Eq. (4.1.18) 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 \((x, y)\) as will be discussed below.

### 4.2 Efficiency Calculation

The generated beam is not directly measured, therefore I estimate the number of generated photons as: \(N_{DFG} = N_l - N_{nl}\), where \(N_l\) is the number of pump photons detected in the absence of the second beam (only linear absorption) and \(N_{nl}\) is the number of the pump photons detected, when the second beam is present (linear absorption and the nonlinear process) and represents the number of photons depleted
from the pump due to the linear and nonlinear processes. \( N_{nl} \) is given by solving Eq. (4.1.18) and integrating \( A_1(x, y, z, t)^2 \) (the photon flux, \( \phi \)), over the time and the transverse directions of the propagation direction, specifically:

\[
N_{nl} = \int_{-\infty}^{\infty} (A_1(x, y, t) + \delta A_1(x, y, z, t))^2 dx dy dt. \tag{3.2.1}
\]

\( N_l \) is calculated as follows. I solve the linear wave equation \( J^{NL} = 0 \) for the input pump beam:

\[
\nabla^2 \tilde{E}_1 - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}_1}{\partial t^2} - \frac{n'^2}{c^2} \frac{\partial^2 \tilde{E}_1}{\partial t^2} = 0, \tag{3.2.2}
\]

I Fourier transform the field with respect to time and the coordinates parallel to the surface of the slab and use the SVEA to receive:

\[
\cos(\theta_1) \frac{\partial \mathcal{A}_1(k_x, k_y, z, \omega)}{\partial z} + \alpha_1 \mathcal{A}_1(k_x, k_y, z, \omega) = 0, \tag{3.2.3}
\]

When the Fourier transform is defined as:

\[
\mathcal{A}_1(k_x, k_y, z, \omega) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} A(x, y, z, t) e^{i(k_x x + k_y y - \omega t)} dx dy dt. \tag{3.2.4}
\]

\( N_l \) is given by solving Eq. (3.2.3) and integrating \( \mathcal{A}_1(k_x, k_y, z, \omega)^2 \), over \( k_x, k_y, \omega \):

\[
N_l = \int_{-\infty}^{\infty} \mathcal{A}_1(k_x, k_y, z, \omega)^2 dk_x dk_y d\omega. \tag{3.2.5}
\]

The efficiency of the process is defined as the ratio between the number of the DFG photons and the number of incident pump photons. The efficiency is therefore given by:
\[ \xi_{\text{eff}} = \frac{(N_t - N_{nl})}{N_{in}}, \tag{3.2.6} \]

where \( N_{in} \) is the number of incident pump photons entering the nonlinear medium.

### 4.3 Geometrical analysis of DFG experimental setup

The generation of two quasi-monochromatic pump beams from a broad-spectrum self-amplified spontaneous emitted (SASE) input beam, which arrive with no or fixed delay between them, is not trivial [33]. The requirements that must be met are discussed in this paragraph. I start by arranging the crystals as described in Fig. 2. In the figure, \( \theta_B \) and \( \theta_\beta \) are the Bragg angles for the two energy shifted pump beams, determined from the condition for Bragg diffraction, \( 2d \sin(\theta) = \lambda \), where \( d \) is the lattice spacing. \( \theta_\beta = \theta_B + \Delta\theta_B \), where \( \Delta\theta_B \) is the Bragg angle difference for two waves with a slight energy deviation. \( \delta \) is the deviation of the exact Bragg angle for the Bragg case diffraction. \( \delta \) is given by the following relation: \( \delta_{1,2} = \arcsin[\sin(\theta_{B,\beta})/n(\omega_{1,2})] - \theta_{B,\beta} \). The difference between \( \delta_1 \) and \( \delta_2 \) is in the order of magnitude of nano radians, therefore in further references \( \delta_1 = \delta_2 = \delta \). This setup implies that the angle between the two quasi-monochromatic pump beams is: \( \theta_1 + \theta_2 = 2(\theta_\beta + 2\delta) \), I denote this angle by \( \alpha = \theta_1 + \theta_2 \).
Fig. 2. Schematic drawing of the setup for a DFG experiment. A broadband beam enters the first crystal. A quasi-monochromatic beam tuned to the Bragg angle of the first crystal, is reflected to crystal 3, and the other wavelengths are transmitted to crystal 2. The quasi-monochromatic beam entering crystal 3 is Bragg reflected to the DFG crystal. A second quasi-monochromatic beam tuned to the Bragg angle of the second crystal is reflected from crystal 2 to the DFG crystal.

The first crystal, $C_1$, is placed in the origin and acts as a reference point in the coordinate system. The second crystal $C_2$, is placed on the axis at a distance $z$ from the first crystal. Crystal 3 ($C_3$) is placed a distance $D$ from the first crystal and its position can be expressed as: $C_3(Dcos2\theta_B, Dsin2\theta_B)$. The vector from $C_2$ ($C_3$) to the cross point is expressed as $\vec{l}_1$ ($\vec{l}_2$), and can be written as:

$$\vec{l}_1 = l_1\left(\cos[2(\theta_B + \delta)]\right), \quad \vec{l}_2 = l_2\left(\cos(2\delta)\right),$$

(3.2.1)

where $l_1$ and $l_2$ are the lengths of $\vec{l}_1$ and $\vec{l}_2$. The path of the first beam ($L_1$) can be written as: $L_1 = z + l_1$, and the path of the second beam ($L_2$) can be written as: $L_2 = D + l_2$. In order for the two beams to have a cross point the following condition must be met: $\vec{c}_2 + \vec{l}_1 = \vec{c}_3 + \vec{l}_2$, which can be written as a set of two equations:
\[ l_1 \cos[2(\theta_B + \delta)] + z = l_2 \cos(2\delta) + D \cos(2\theta_B) \] (3.2.2)

\[ l_1 \sin[2(\theta_B + \delta)] = l_2 \sin(2\delta) + D \sin(2\theta_B) \] (3.2.3)

Solving these equations results with the following expressions:

\[ l_1 = \frac{z \sin(2\delta) + D \sin[2(\theta_B - \delta)]}{\sin(2\theta_B)} \] (3.2.4)

\[ l_2 = \frac{z \sin[2(\theta_B + \delta)] - D \sin[2(\theta_B - \theta_B + \delta)]}{\sin(2\theta_B)} \] (3.2.5)

Therefore, the path length difference can be written as:

\[ L_1 - L_2 = \left( \cos\left(\frac{2\delta - 2\theta_B + \theta_B}{\cos\theta_B}\right) - 1 \right) D - \left( \cos\left(\frac{2\delta + \theta_B}{\cos\theta_B}\right) - 1 \right) z \] (3.2.6)

For producing no time delay between the pulses, the requirement is that \( L_1 - L_2 = 0 \).

The only unknown variable in Eq. (3.2.6) is the spacing between crystal 1 and crystal 2 (\( z \)) [33], which is determined by this requirement.

### 4.4 Example

To demonstrate the feasibility of the method proposed, I consider an example where two quasi-monochromatic pumping beams with center energies at 8.05 keV (\( \lambda = 1.54 \) Å) and 8.043 keV (\( \lambda = 1.5415 \) Å) enter a diamond crystal at angles \( \theta_1, \theta_2 \) relative to the \( \hat{z} \) direction, and generate a wave with a center energy at 7 eV (\( \lambda = 177 \) nm), which propagates at an angle of \( \theta_3 \), relative to the \( \hat{z} \) direction (see Fig. 1). The reciprocal lattice vector normal to the C(111) atomic planes is used in order to fulfill
the phase matching condition. The phase matching equations (Eq. (2.3.3) and (2.3.4)) and the setup requirement ($\alpha = \theta_1 + \theta_2$), imply that the incident angles of the pumps are $\theta_1 = 21.825^\circ$ and $\theta_2 = -22.136^\circ$, and that the angle between the normal to the surface and the generated UV wave is $\theta_3 = 6.77^\circ$. 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 [34,35]. I consider two beams with equal waists.

I first consider the dependencies on the various properties of the pumping beams and identify the parameters that result in the maximum efficiency, as defined in Eq. (3.2.6). The results are shown in Fig. 3.

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. The angular distribution of the DFG normalized efficiency is plotted in Fig. 3(a). The width of this distribution is 0.7 mrad at full width half maximum (FWHM). As will be 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 overlap decreases since they propagate at different directions with an angle of $\theta_1 + \theta_2$ between them. Thus there is a spatial walk-off and the interaction length is shorter [36]. Therefore, I expect to have a beam width, which leads to a maximal conversion
efficiency as can be seen in Fig. 3(b). I 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 taken into account. Since the two pumps propagate at different velocities, short pulses will suffer also from temporal walk-off. This effect contributes greatly for short pulses.

In the case of two Gaussian pulses, the characteristic overlap length of the two pumps, the spatiotemporal walk-off length, $l_{S-T}$, is defined by [37,38]:

$$l_{S-T} = \left( \frac{\tan \alpha}{w_{0x}} + \frac{1}{\tau^2} \left[ \frac{1}{v_g(\omega_1)} \cos \alpha - \frac{1}{v_g(\omega_2)} \right]^2 \right)^{-1/2},$$  \hspace{1cm} (3.3.1)

here, $\alpha$ is the angle between the propagation directions of the two pumps, $w_{0x}$ is the beam width in the $x$ direction, $\tau$ is the pulse duration, and $v_g$ is the group velocity. $l_{S-T}$ represents an effective walk-off length that considers both the spatial and temporal walk-off effects, causing the limited interaction length between the two pump beams.

For a beam width of 15 μm, the dominant walk-off term is the spatial term for pulse durations longer than 35 fs, whereas for pulses shorter than 20 fs, the temporal term dominates. I find that the maximum DFG effect is observed for a pulse duration of 35 fs as can be seen in Fig. 3(c).
Fig. 3. Normalized efficiency of the DFG process in arbitrary units as a function of: (a) Deviation from phase-matching angle, where the FWHM is 0.7 mrad. The pulses duration is 35 fs and the beam waist is 15 μm. (b) The width of the beams at phase matching and with pulses duration of 35 fs. (c) The duration of the pulses at phase matching with a beam waist of 15 μm.

By introducing a delay between the two input pulses it is possible to get the temporal structure of the pulses. I therefore plot the dependence of the efficiency on the delay between the input pulses in Fig. 4. As expected, the most efficient wave mixing occurs when the delay approaches zero. The FWHM is 70 fs. The distribution is slightly asymmetric because of the slightly different group velocities of the two pump beams.

Fig. 4. Normalized efficiency of the DFG process in arbitrary units as a function of the delay between the two x-ray pumps.
After optimizing the pulses characteristics (duration, width, direction, and delay), I estimate the energy depletion of the pumping beams due to the nonlinear DFG process. The estimation of the efficiency is highly dependent on the estimation of the nonlinear coupling coefficient ($\xi_{\text{eff}} \propto \kappa^2$), 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. I therefore estimate the nonlinear susceptibility by fitting the experimental data of the recently observed PDC of x-rays into the optical regime [24]. This procedure leads to a nonlinear susceptibility of $\chi^{(2)}_{(2,2,0)} = 5 \times 10^{-17} \text{m V}^{-1}$ and the corresponding DFG estimated efficiency for an input flux of $10^{11}$ photons per pulse is $8 \times 10^{-5}$. The calculation based on the classical model for the nonlinearity (Eq. (2.2.34)), which has been used to describe the nonlinear interaction between x-rays and optical radiation [29], results in a nonlinear susceptibility of $5 \times 10^{-16} \text{m V}^{-1}$ and the efficiency for an input flux of $10^{11}$ photons per pulse is $8 \times 10^{-3}$. I 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 [16,24].

The efficiency for the classical model for the nonlinearity as a function of crystal length is given in Fig. 5(a). The efficiency is given in Eq. (3.2.6), where in this example, $N_{\text{in}} = 10^{11}$. $N_l$ is calculated by inserting the transform-limited Gaussian envelope (Eq. (4.1.19)) into Eq. (3.2.3), this results with:

$$N_l(z = L) = N_{\text{in}} e^{-\frac{2\alpha}{\cos(\theta)} L},$$

(3.3.2)
where $\alpha$ is the absorption coefficient and $L$ is the length of the crystal. It is clear that after 30 $\mu$m the efficiency reaches its maximal value. This length is determined by overlap between the input beams.

Next, I address the ability to measure the effect with the 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 that is depleted from the beam due to the nonlinear process. In Fig. 5(b) I show the normalized pulse energy of one input beam as a function of the crystal length in the absent of the second beam (blue line) and when the second beam is present (orange line). It is clear that the two beams are most distinguishable when the energy transfer due to the nonlinear process is maximized at $z = 30 \mu$m. At this distance the ratio between the pulse energy loss due to the nonlinearity and pulse energy loss without the nonlinearity (linear absorption) is the largest and is equal to $9 \times 10^{-3}$, as can be seen in the inset of Fig. 5(b).
Fig. 5. (a) DFG efficiency versus the crystal length when the pulses duration is 35 fs and the width of the beam is 15 μm. (b) Comparison between the pulse energy depletion of the pump with the nonlinear process (orange) and in its absent where the depletion is only due to the linear absorption (blue). Inset: the ratio between the pulse energy depletion of the pump due to the linear absorption and the nonlinear process (NL), and the energy depletion of the pump due to linear absorption only (L).

To complete my proposal for the measurement of the depletion of the pulse energy of the input beams as a mean for the measurement of the nonlinear effect of DFG of UV pulses from two x-ray pulses, I describe a possible experimental setup. The two quasi-monochromatic pump beams need to 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 that is described in Fig. 6. All the crystals in this example are diamond crystals where I use the same reflection (in this example I 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 \( \theta_B = 22.105° \), where \( \delta \) is approximately zero and neglected (see chapter 4.3 for more details). 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 8.043 keV (The Bragg angle is $\beta = 22.108^\circ$) and it reflects the second beam into the DFG crystal. With this setup the angle between the two pump beams is $\theta_1 + \theta_2 = 43.96^\circ$. The phase matching condition as described in Eq. (2.3.3)-(2.3.4) can be achieved for the proposed setup.

*Fig. 6.* Schematic of a possible experimental setup. A beam with a broad spectrum hits the first Bragg crystal. Crystal 1 and crystal 2 are tuned to the same Bragg angle and crystal 3 is tuned to the Bragg angle of the second wavelength. Crystal 4 is the crystal that is used for the DFG process. The detector measures the pulse energy after crystal 4. Another detector (not shown) is used for the measurement of the pulse energy of the input beam.
5. Summary and Outlook

In this work I analyzed theoretically the effect of DFG of ultraviolet radiation from two short x-ray pulses. I suggested a new approach to measure the effect by measuring the depletion of the pumping pulses. I assumed two short transform limited Gaussian pulses, which vary slowly compared to the wavelength and frequency. The pulse specification I assume, is within the performance range of the available XFELs. I note that coherent, transform limited bandwidth pulses have been demonstrated [21]. At LCLS, a pulse with a duration of 35 fs, and with a flux of $10^{11}$ photons per pulse after a monochromator can be achieved [22,23]. My calculations predict that the conversion efficiency of two pumps with center energies at 8.05 keV ($\lambda = 0.154$ nm) and 8.043 keV ($\lambda = 0.15415$ nm), with $10^{11}$ photons per pulse, generating a wave with a center energy at 7 eV ($\lambda = 177$ nm), exceeds $5 \times 10^{-3}$ and $5 \times 10^{-5}$, for a theoretical and semi-empirical nonlinear coefficient respectively. These efficiencies correspond to a flux depletion of at least $5 \times 10^6$ pump photons, as a result of the DFG effect. the FWHM of the angular distribution was found to be 0.7 mrad, which is an order of magnitude narrower than in the visible regime [20]. This suggests that the dominant effect which determines the angular distribution, is dispersion, rather than absorption.

This method opens the possibility of measuring DFG in the x-ray regime with various materials, including materials which are opaque at the generated signal wavelength. My work predicts efficiencies that are higher than x-ray and visible wave mixing, which I relate to resonant enhancement of the nonlinearity near the binding energies of the valence electrons in the sample. In addition, I note that since the damage threshold
at x-ray wavelengths for many materials is larger by orders of magnitude than the damage threshold for visible wavelengths, the use of two x-ray input beams, allows to pump the nonlinear process with higher intensities than in the case of SFG. Since the nonlinear coefficient is on the same order, DFG with two-x-ray beams can be expected to lead to higher efficiencies than SFG when one of the input beam is at optical wavelengths.

My method 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. (2.2.34). Hence it is possible to reconstruct the valence electron charge distribution, by a series of measurements of the Fourier components of the nonlinear susceptibility [9]. Since it is possible to control the delay between the input pulses, our method can lead to a probe for the dynamics of events associated with the valence electrons charge distribution with temporal resolution of sub-femtoseconds.
6. References


Work this describes the newcomer to the method of measuring the effect of creating periodic perturbations in the ultraviolet by two short X-ray pulses. This is done by measuring the amount of energy that fell from the pulses absorbing (X-rays) without the entrance of the material into the crystals. Since the damage of the material for X-rays is much larger than the damage for visible light, the process of creating periodic perturbations in the ultraviolet could be orders of magnitude higher than the efficiency of other nonlinear processes involving X-rays and longer wavelengths. Additionally, creating periodic perturbations in the ultraviolet by X-rays is expected to be more efficient than creating perturbations in the visible range, as the resonances of electronic levels in light materials are in the ultraviolet.

The process is non-linear, and the energy of the formed wave is determined by the decay of the X-rays entering the material. This energy decay, related to the energy of the formed wave, is estimated by 1.1 x 10^{-11} photons per pulse at the entrance, assuming a high efficiency of the nonlinear process. The efficiency is estimated as x x 10^{-5} for the material and x x 10^{-3} for the material calculated theoretically. Two of the advantages of this method over direct measurement of the created wave are the ability to study atomic materials and the possibility of obtaining higher efficiencies.
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יצירת תדירויות הפרש באולטרה סגול מפולסי קרני X בחומרים אטומיים

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