CHAPTER 7

PROSPECTS FOR X-RAY NONLINEAR OPTICS

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1. Introduction

After the invention of optical lasers, nonlinear optics of visible domain has developed into one of the most important fields of optics with numerous applications to both science and technology. Now its shorter-wavelength counterpart, X-ray nonlinear optics, with similarly great potentials and opportunities, is making its first steps. To the best of our knowledge, the very first publications on X-ray nonlinear optics, primarily about the parametric conversion of X-rays in solids, appeared in late 60s–early 70s. Although some experimental results were published, the entire field of X-ray nonlinear optics had to wait for X-ray lasers (XRL's) to appear. The first X-ray amplification was observed in 1984. By now, about 50 X-ray laser lines have been reported, with wavelengths ranging from 326.5 Å to 35.6 Å, output power up to 5 MW and the focused intensity up to 10^{14} W/cm². Such rapid progress in XRL research revived interest in X-ray nonlinear optics. During the last two years, a few related theoretical papers have been published, mainly on X-ray four-wave mixing in plasma and gain saturation inside an XRL. Preliminary experimental results have been reported on nonlinear interaction of noncoherent X-ray radiation with coherent visible light.

Although this list may not seem very long, we can say now that, with XRL's, X-ray nonlinear optics is coming.

Apart from pure scientific interest (in particular, for X-ray laser spectroscopy), X-ray nonlinear optics also appears to have a great potential for applications such as (i) frequency upconversion through harmonic generation and four-wave mixing; (ii) control of X-ray laser beam propagation through nonlinear refraction; (iii) generation of X-ray coherent radiation by means of stimulated Raman scattering, and so on. Basically, any nonlinear effect in visible domain may have its X-ray counterpart.

Having in mind potentials and opportunities of X-ray nonlinear optics, about two years ago, we began systematic theoretical research in this field. At that point, we realized that the main issue for X-ray nonlinear optics is not the theory of nonlinear propagation (which seemed pretty much similar to that of visible domain) per se, but the search for media in which XRN effects may be observed. Our very first estimations of X-ray nonlinearities showed that the only hope to achieve feasible effects at such short wavelengths, is to use resonances. We believe now that the entire business of X-ray nonlinear optics is about resonant couples, i.e. couples of XRL line + resonant transitions in a nonlinear media. From this point of view, plasmas are the first obvious candidates to be considered as X-ray nonlinear media. That is because there is a much larger selection of ionic spectra than that of neutral atoms. Moreover, the majority of ionic spectra consists predominantly of X-ray lines. Thus, until now, our research interests have been concentrated on identification and estimation of couples "X-ray laser + plasma" resonant enough for the feasibility of various X-ray nonlinear effects. We have gradually moved from very hot XRL plasmas to comparatively cool discharge plasmas. Lately, we have obtained first results on X-ray resonant nonlinear effects in nonionized matter (gases and vapors). Our future plans include a search for resonant liquid and solid media for X-ray nonlinear optics.

2. Saturation-Related X-ray Nonlinear Effects in Plasma

Saturation-related X-ray resonant nonlinear effects (XRNE) are chosen by us to be considered first because we want to make use of the perfect resonance between an XRL radiation and the respective transition in the lasing ions. To avoid the interference with the lasing process, we first consider nonlinearities in the case where plasma electron density \( N_e \) is too
low to excite laser action, and then draw some conclusions on XRNE’s in XRL active media. Neon-like XRL’s are most suitable for such a consideration due to well-known stability of the fraction of the neon-like ions $f_{Ne}$ in plasma over a wide range of the electron density. Assumed low $N_e$ significantly simplifies the problem by allowing us to neglect collision rates for the transitions near the neon-like ground state, and therefore to take into account only the levels coupled by X-ray radiation of interest. Such low electron density alone cannot provide any significant 3s or 3p level population, and therefore no interaction with the XRL radiation (resonant to 3s–3p transitions) can be observed. However, XRNE’s can be made feasible if the 3s level is populated, e.g. by the powerful external radiation resonant to the transition between 3s and the ground levels. This radiation is conveniently originated from the radiative decay of the 3s level in the XRL.

As a result, our model was restricted to only three levels: the upper ($u$) and the lower ($l$) levels of the lasing transitions, and the neon-like ground level ($g$) (see Fig. 1a). Levels $u$ and $l$ in low density plasma will be coupled only by the XRL radiation with the resonant frequency; we will be interested in the absorption saturation and nonlinear refraction at that transition. Level $l$ will be populated by sufficiently strong (incoherent) pumping radiated by the respective XRL as a result of the decay of its level $l$ into its ground level $g$. As an example, Se XXV plasma, as the medium of the most successful XRL so far, is considered. The energy-level diagram simplified for our purpose for the neon-like Se is given in Fig. 1a.

We choose plasma electron temperature to be equal to half of the neon-like ion ionization potential, i.e. equal to the temperature of the lasing plasmas. For lower temperature, the fraction of neon-like ions in Se plasma would be very small. We also assume the ion temperature $T_i = 0.4 T_e$, as in Ref. 14. (It means that $T_i \approx 400$ eV for Se.) For assumed electron temperatures, $f_{Ne}$ is almost constant for a wide range of $N_e$ below the lasing optimums and may be assumed to be 0.3 for Se plasma. Dividing $f_{Ne}$ by the average ion charge, one obtains the ratio of the neon-like ion density $N_{Ne}$ to $N_e$ equal to 0.02. Collision rates can be neglected if $N_e \ll N_{Ne}/C_{ik}$, where $A_{ik}$ and $C_{ik}$ are the radiative and downward collisional rate coefficients for transitions of interest, respectively. The atomic data from Refs. 3 and 13–15, as well as the principle of detailed balance (required to obtain downward collisional rate coefficients from upward ones), yield $N_{Ne} \approx 10^{18}$ cm$^{-3}$ for Se plasma.

Since the levels $u$ and $g$ are not coupled by radiative processes (in the dipole approximation), we can break our three-level system into two two-level subsystems consisting of the levels $l$–$g$ and $u$–$l$, respectively. As the first step, we determine the “pumping” intensity $I_p$ for the radiation with the central wavelength $\lambda_p$ of the $l$–$g$ transition, necessary to produce steady-state population density in the level $l$, sufficient for observation of nonlinear effects at the $u$–$l$ transition. Then we consider the nonlinear behavior of the absorption coefficient and refractive index for the XRL radiation resonant or near-resonant to the $u$–$l$ transition, assuming that the total sum of populations at the $l$ and $u$ levels depends only on the pumping and not on the XRL radiation intensity. The XRNE estimates based on this approximation may differ by a factor of less than two from those for a full three-level model. Two-level models modified to take into account level degeneracy and inhomogeneous broadening result in the following set of equations. First, for the dimensionless $l$-level population in the absence of the XRL radiation $\beta = N_l/N_i$ ($N_l$ denotes the population density of the $l$-level) we have

$$\beta = \sqrt{\pi \ln 2 (1 + g_l^{-1})^{-1} \Delta I_p r_l (1 + r_l)^{-1/2}},$$ (1)
where $\Delta \nu_g$ is the ratio of the Lorentzian full width on half maximum $\Delta \nu_g$ to the Doppler width $\Delta \nu_D \equiv 2\nu_D \sqrt{2kT_i/M_i c^2} \ln 2$, for the $l-g$ transition, $\nu_g$ being the central frequency; $M_i$ is the mass of the ion; $r_{lg} \equiv I_{lg}/I_{lg}'$ is the dimensionless pumping intensity with $I_{lg}' = 4\pi^2\hbar c\Delta \nu_D \nu_g^2/(1 + g_l)^{-1}$ being the $l-g$ "saturation intensity"; $g_l$ is the statistical weight of the level $l$. This equation is valid unless $r_{lg}$ is large enough ($> 50$) to destroy the implied Doppler broadening predominance. It is worth noting that no significant absorption of the pumping photons with the energy $h\nu_g$ by the excited neon-like ions is expected, since the energy $2h\nu_g$ is significantly higher than the ionization potential of these ions.

Second, for the absorption coefficient $\gamma(\nu)$ of the incident radiation with the frequency $\nu$, one obtains

$$\gamma(\nu) = \gamma_0 \frac{\Re \omega(x + ib)}{\sqrt{1 + r}}, \quad \gamma_0 \equiv \frac{\sqrt{\pi} \ln 2}{4\pi^2} \frac{\lambda_{ul}^2 A_{ul}}{\Delta \nu_{ul}^D} g_u, \quad (2)$$

$$\Delta N_0 = g_l^{-1} \beta \alpha N_0, \quad (3)$$

where $\gamma_0$ is the small-signal absorption coefficient at the central wavelength $\lambda_{ul}$ of the $u-l$ transition; $b \equiv \sqrt{\ln 2\Delta \nu - 1} + r$ describes the degree of homogeneous broadening; $r \equiv I/I_{ul}^* \ln 2(\nu_{ul} - \nu)/\Delta \nu_{ul}^D$ are the dimensionless intensity and detuning of the XRL radiation, respectively; $I_{ul}^* = 4\pi^2\hbar c\Delta \nu_D \nu_{ul}^3$ is the "saturation intensity"; $\omega(x + ib)$ denotes the complex error function (see e.g. Ref. 21); $g_u$ is the $u$-level statistical weight. Finally, the nonlinear correction $\Delta n_{NL}(r) = n(r) - n(r = 0)$ to the refractive index $n(r)$ can be written as

$$\Delta n_{NL} = (4\pi)^{-1} \lambda_{ul} \gamma_0 [\Im \omega(x + ib) - \Im \omega(x + ib_0)],$$

$$b_0 \equiv b(r = 0) = \sqrt{\ln 2\Delta \nu_{ul}}, \quad (4)$$

In our calculations, we assume that the homogeneous linewidths are determined mainly by the lifetime of the $l-g$ transitions (similar to Ref. 22), so that $\Delta \nu_{ul} = \Delta \nu_g \simeq A_{lg}/2\pi$. Given the transitions data and plasma conditions, one can obtain the following estimations for Se plasma. Pumping intensity $I_p \simeq 10^{13} W/cm^2$ is required to attain $\beta = 0.1$. Such population yields the absorption coefficient at the central $u-l$ frequency $\gamma(\nu_{ul}) \simeq 1.5 \times 10^{-3}$, with the "saturation intensity" $I_{ul}^* \simeq 6 \times 10^7 W/cm^2$. The nonlinear part of refractive index is $\Delta n_{NL} \simeq 3 \times 10^{-8}$ for $l = 3 \times I_{ul}$, and dimensionless detuning $x = 0.8$ (such detuning corresponds to the frequency $\nu$ being within the kernel of the Doppler lineshape).

Our calculations of nonlinearities in the laser active medium show that for Se XRL they should be very large, and this conclusion does not depend on any specific model. Indeed, the power of the order of $1$ MW per line and the source size $\simeq 200 \mu m$ mean that the intensity $I \simeq 2 \times 10^9 W/cm^2$, $\simeq 35 \times I_{ul}$ has been reached in the Se active plasma. According to Eq. (2), this decreases the small-signal gain by a factor of up to 20. (This result remains almost unchanged even if, in addition to the lifetime of the $l-g$ transition, the collision dephasing time $\simeq 4 \times 10^{-13}$ s taken into account). Therefore, the discrepancy between the calculated (38 cm$^{-1}$) and measured (5 cm$^{-1}$) small-signal gain coefficients could be attributed at least in part to the gain saturation. Furthermore, even assuming the measured small-signal gain coefficient for $\gamma_0$, one obtains from Eq. (4) that for the intensities existing inside the Se XRL, the nonlinear correction to the refractive index can become fairly large in the X-ray domain, $\Delta n_{NL} \simeq 8 \times 10^{-8} - 2 \times 10^{-7}$. This nonlinear refractive index may result in the significant change ($\simeq 2\pi$ across the beam) in the phase front of the wave at the length $L_{NL} = \lambda/\Delta n_{NL} \simeq 5-15$ cm.

The nonlinear X-ray interaction which has been discussed so far is most significant for the processes inside of an XRL. Outside of an XRL, this type of interaction is not very convenient for experimental realization, because in such a case we have to deal with very hot plasma, and to use additional powerful X-ray irradiance (pumping), since the nonlinear transition occurs between excited levels. Therefore, to study X-ray nonlinear optics, it would be desirable to identify much cooler plasmas (which could be created in a much easier way, e.g., by discharge devices), and with transitions from the ion ground which are resonant to XRL radiation (see Fig. 1b).

A plasma is a good candidate for XRNE if the resonant detuning $|\nu - \nu_0|$ between XRL frequency $\nu$ and frequency $\nu_0$ of some transition from the ground to an excited level of the plasma ions, is smaller than the Doppler full width on half maximum of the respective plasma transition $\Delta \nu_D$. Search for such resonances is complicated by the lack of atomic information (wavelengths, oscillator and collisional strengths), especially on highly ionized atoms. We have identified such resonant couples "XRL line + ion transition from the ground level" for about half of all the reported XRL lines (Table 1). Since at this point our main goal is to identify as
many couples as possible (which is essentially fulfilled by the content of Table 1), we will make an estimate of nonlinearity only for couples 1 and 4 which include XRL lines with measured output power. The treatment similar to that for the above-mentioned couples can be applied to the rest of Table 1. Note that couples 10 and 11 have been included because of very good resonance, although we have not found the respective transition probabilities $g$ in the literature.

Table 1. Resonant couples “XRL radiation–plasma–ion transition”; $g$ denotes the corresponding transition probability, $\lambda$ — the plasma ionization potential, $\lambda_0$ and $\lambda_0^*$ — the wavelengths. The asterisk (*) marks XRL’s for which spectroscopic wavelengths of the lasing transitions are assumed instead of less accurately measured wavelengths of the XRL’s radiation.

<table>
<thead>
<tr>
<th>XRL $\lambda$ (Å)</th>
<th>Plasma $\lambda_0$ (Å)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$E_{\text{ion}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ge$^{22+}$ 236.26</td>
<td>Ar XIII 236.27</td>
<td>3 $\times$ 10$^8$</td>
<td>686</td>
</tr>
<tr>
<td>2. Sc$^{2+}$ 220.28</td>
<td>Sc IV 220.289</td>
<td>6 $\times$ 10$^8$</td>
<td>73</td>
</tr>
<tr>
<td>3. Sc$^{2+}$ 209.78</td>
<td>Fe X 209.776</td>
<td>1.3$\times$10$^8$</td>
<td>262</td>
</tr>
<tr>
<td>4. Sc$^{2+}$ 209.78</td>
<td>Cl XIII 209.81</td>
<td>10$^9$</td>
<td>656</td>
</tr>
<tr>
<td>5. Ge$^{22+}$ 196.06</td>
<td>Fe VII 196.046</td>
<td>4 $\times$ 10$^9$</td>
<td>125</td>
</tr>
<tr>
<td>6. Ge$^{22+}$ 196.06</td>
<td>Na III 196.054</td>
<td>1.8$\times$10$^9$</td>
<td>72</td>
</tr>
<tr>
<td>7. C$^+$ 182.097*</td>
<td>Na IV 182.123</td>
<td>1.4$\times$10$^9$</td>
<td>99</td>
</tr>
<tr>
<td>8. Al$^{10+}$ 105.69*</td>
<td>Na IV 105.6867</td>
<td>2.4$\times$10$^9$</td>
<td>99</td>
</tr>
<tr>
<td>9. Al$^{10+}$ 105.69*</td>
<td>Cr VIII 105.69</td>
<td>4.3$\times$10$^9$</td>
<td>185</td>
</tr>
<tr>
<td>10. O$^+$ 102.355*</td>
<td>Ni IX 102.340</td>
<td>1.9$\times$10$^9$</td>
<td>193</td>
</tr>
<tr>
<td>11. Eu$^{25+}$ 71.00</td>
<td>Mg VIII 71.007</td>
<td>266</td>
<td></td>
</tr>
<tr>
<td>12. Ti$^{2+}$ 44.83</td>
<td>Si X 44.83</td>
<td>401</td>
<td></td>
</tr>
<tr>
<td>13. W$^{46+}$ 43.18</td>
<td>Cl IX 43.168</td>
<td>5 $\times$ 10$^{11}$</td>
<td>400</td>
</tr>
</tbody>
</table>

In our evaluation of each couple, we follow the same procedure. At first, we solve the system of rate equations for the population at the levels of interest in the steady-state approximation. This approximation is quite adequate because the lifetime of the upper levels is shorter than XRL pulse duration $\sim 10^{-10}$ s. The XRL linewidth is neglected. Each plasma temperature is chosen at half of the ionization potential; such a choice usually assures a large enough fraction of the ions of interest in the plasma. For the assumed moderate plasma density $N_e = 3 \times 10^{17}$ cm$^{-3}$, collision rates are essentially negligible compared to radiative rates, except for transitions among levels of fine structure. As a result, many levels can be excluded from the calculations. At the same time, such a density appears to be high enough to produce significant XRNE’s. Following a standard approach,$^{19}$ only homogeneous broadening is taken into account at this step.

For all the couples in consideration, the solutions of the respective systems of rate equations can be written in the same form as for a two-level system:

$$\Delta N = \Delta N_0 \left[ 1 - \frac{(\Delta \nu)^2}{I^*} \frac{I}{(\nu - \nu_0)^2 + (\delta \nu)^2} \right]. \tag{5}$$

Here $\Delta N \equiv N_g / g_g - N_u / g_u$ is the population density difference; $N_g (g_u)$ and $N_u (g_u)$ are the population densities (statistical weights) of the ground level and the upper level of the transition of interest, respectively; $\Delta \nu$ is the homogeneous full width at half maximum of the transition; $I$ is the intensity of the incident XRL radiation; $\delta \nu = (\Delta \nu / 2) \sqrt{1 + I / I^*}$; $\Delta N_0 = \Delta N (I = 0)$, and that the “saturation intensity” $I^*$ is as

$$I^* = I_0^*, \quad I_0^* \approx 785 \lambda^{-3} \Delta \nu, \quad (R < 1) \tag{6}$$

(with $\lambda$ in Å, $I$ and $I^*$ in W/cm$^2$). Here $I_0^*$ corresponds to the saturation intensity of the two-level system with the statistical weights of all the levels not taken into account. The constant $R$ in Eq. (2) can be regarded as the effective (dimensionless) relaxation parameter of the process. If the intermediate levels delay the relaxation only slightly, $R \approx 1$; it decreases when more ions accumulate at the intermediate levels. Therefore, the specific expressions for $R$ include the oscillator and collision strengths as well as the statistical weights of all the participating levels and vary from one couple to another. For example, only one intermediate level can be taken into account for couple 4, in which case $R = X \tau (g_1 g_2^{-1} + g_2 g_1^{-1})$. Here, $X$ is the rate of collision excitation from the ground level to the intermediate level; $\tau$ is the lifetime of the upper (resonant) level; and $g_1$, $g_2$ and $g_3$ are the statistical weights of the ground, intermediate and upper levels, respectively.

At this point, we introduce inhomogeneous broadening by integrating Eq. (5) over the Doppler distribution.$^{19}$ This yields the absorption coefficient $\gamma (\nu)$ and nonlinear correction $\Delta n^{\text{NL}} (r) = n (r) - n (r = 0)$ to the refractive index $n (r)$ in the presence of homogeneous or and inhomogeneous Doppler broadening in the form of Eqs. (2) and (4), respectively, where the
index $u$ is omitted and $\Delta N_0 = N_1 g_u^{-1}$. The density of the ions of interest $N_1$ can be obtained, as before, from the electron density $N_e$ by dividing the latter by the fractional abundance of the ionization stage of interest and by the average ion charge. We assume $N_g \approx N_1 \approx 0.03 N_e$ for the couples 1, and 4.

In our calculations, we assume that the homogeneous linewidth is determined mainly by the lifetime of the upper level, $\Delta \nu \approx A/2\pi$. As a result, even for rather moderate values of $T_e$, the homogeneous linewidth is significantly smaller than the Doppler linewidth. However, this "Doppler predomination" can easily be inhibited by high intensity corresponding to even very modest XRL intensities, so that use of full formulas may be required.

For the data of Table 1, Eqs. (2) and (4) yield results summarized in Table 2 for both the couples. For these intensities ($I \gg I_s$), the plasmas are essentially transparent because of the absorption saturation [$\gamma(\nu) \approx 0$]. The last column in Table 2 contains the estimates of the "nonlinear length" $L_{NL} = \lambda/\Delta n_{NL}$ at which the significant change ($\geq 2\pi$ across the beam) could result from the nonlinear refractive index for given intensity $I = 5 \times I^s$.

Table 2. Saturation-related XRLNE's in plasmas.

<table>
<thead>
<tr>
<th>Couple</th>
<th>Sources of data</th>
<th>$I$ (W/cm²)</th>
<th>$I_s$ (W/cm²)</th>
<th>$\Delta n_{NL}$</th>
<th>$L$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Refs. 24-26</td>
<td>$10^8$</td>
<td>600</td>
<td>$3 \times 10^{-7}$</td>
<td>6</td>
</tr>
<tr>
<td>4.</td>
<td>Refs. 24 and 27</td>
<td>$2 \times 10^8$</td>
<td>$5 \times 10^3$</td>
<td>$10^{-7}$</td>
<td>18</td>
</tr>
</tbody>
</table>

One can readily see from Table 2 that XRLNE's resulting from nonlinear refractive index can be observed even at much lower Ge and Se XRL intensities than the intensities available now. The expected effects based on nonlinear refractive index are: self-focusing and "running foci"\(^{29}\) (although, because of the significant probability of multiphoton processes, we do not expect a pronounced wave collapse, in contrast with the situation in liquids and solids); self-trapping of XRL radiation similar to that observed in Na vapor\(^{30}\) self-bending\(^{31}\) (also observed in Na vapor\(^{32}\)), and four-wave mixing.\(^{33}\) These effects may also be instrumental in direct measurement of nonlinear refractive index, plasma diagnostics, and for phase-conjugation amplification. Since the intensities significantly exceeding the saturation intensity have apparently been achieved in experiment, it may also be possible that self-transparency and related $2\pi$-solitons can be attained, similar to that in the optical domain.\(^{34}\) The experimental observation of XRLNE's in the resonant domain of Table 1 is greatly facilitated by the fact that the required parameters $T_e$, $N_e$, and $L$ of plasmas can be attained by using standard discharge devices (e.g. modified $z$-pinch,\(^{35}\) gas-liner pinch\(^{36}\) and $\theta$-pinch\(^{37}\)).

3. X-ray Third Harmonic Generation in Plasmas of Alkali-Like Ions

Absorption saturation and nonlinear refraction were our first research objects in X-ray nonlinear optics. Another, probably even more important, effect is higher-harmonic generation, since it is a method of choice to generate the shorter-wavelength coherent radiation. Therefore, our next problem was to identify resonant media for X-ray third-harmonic generation.\(^{11}\) (Since plasma is isotropic, the third harmonic is the lowest possible higher-harmonic, in the first-order approximation in velocities of free electrons).

![Fig. 2. A typical energy-level diagram for the near-resonant third-harmonic generation in alkali-like ions: C\(^{+2}\) XRL radiation in Na VIII ion. Only one of possible level combinations is depicted.]

We face here the same problem of resonant coupling. But in this case, the complication is, in a sense, tripled. Indeed, it is well-known that
the best resonant conditions for THG are the closest possible two-photon resonance (to the level b, Fig. 2), and near (to a few linewidths, to avoid strong absorption) one- and three-photon resonances (to the levels a and c). Strong optical coupling between levels g and a, a and c, c and c, and c and g, is also desirable. Because there is no tunable XRL available, one has to seek for plasmas that may allow for resonances to some of about 50 existing XRL lines. This search is complicated by insufficient information on energy levels and transition probabilities of ions. In this respect, plasmas of alkali-like ions present perhaps the best opportunity because of readily available atomic data. We have identified seven resonant couples for X-ray third-harmonic generation with plasmas on alkali-like ions (see Table 3).

To estimate conversion efficiency, we use standard results of the theory of THG in gases and vapors, modifying them mainly to account for the specifics of the plasma dispersion. The X-ray refractive index due to free plasma electrons is $n_p(\omega) \approx 1 - \omega_p^2/\omega^2$, where $\omega$ is the (angular) frequency of the incident XRL radiation, $\omega_p = (N_e e^2/\epsilon_0 m)^{1/2}$ is the plasma frequency, and $N_e$ is the plasma electron density. For all but one (the couple “XRL line-plasma” in Table 3), this free-electron component of the refractive index is much larger than the resonant (bound-electron) one, which can therefore be neglected. We also assume that the plasma is homogeneous enough for us to neglect the refraction due to inhomogeneous electron distribution across the laser beam. As a result, the phase mismatch $\Delta k_p = 6\pi \lambda^{-1}[n_p(2\omega) - n_p(\omega)]$, where $\lambda$ denotes the XRL radiation wavelength, is positive (which prevents one from using too tight focusing of XRL beam that in such a case may inhibit THG). Thus, we assume loose focusing of the XRL beam, $L_d \gg L$, where $L_d = 2\pi\omega_0^2/\lambda$ is the diffraction length of the beam, $\omega_0$ is the beam radius at the waist, $L$ is the length of the plasma column. Conversion efficiency $C_{eff} \equiv P(3)/P$ ($P$ and $P(3)$ are the power of the fundamental and the third harmonic, respectively) can be written then as

$$C_{eff} = \frac{(3\pi^2/4\lambda^2c_0^2)|x_{THG}|^2N_1I_2^2L^2\sin^2(\Delta k L/2)}{7 \times 10^{10}}$$

(in SI units). Here $I = P/A$ describes the intensity of the XRL radiation, $A = L_d\lambda/4$ is the effective area of the Gaussian beam, and $\sin c(x) \equiv x^{-1}\sin(x)$. The third-harmonic susceptibility $x_{THG}$ in Eq. (7) in the case of linear polarization of the fundamental harmonic is

$$x_{THG} = \frac{1}{\hbar^2\epsilon_0} \sum_{abc} \left( \frac{\mu_{g0}\mu_{ah}\mu_{hc}}{(\omega_g - 3\omega)(\omega_g - 2\omega)(\omega_g - \omega)} \right)$$

where $\omega_{kb}$ and $\mu_{kb}$ are the frequencies and the dipole-moment matrix elements of the transitions between the levels of interest, respectively. Note that there is no summation over the "g" index, since we have excluded weighting over initial states, assuming that almost all the ions of interest in the unperturbed plasma are only at the non-degenerated ion ground level.
Hence, \( E_i = 0 \) and \( \omega_{ig} = E_i/\hbar \) etc., where \( i = a, b, c, \) and \( E_i \) are the energies of the levels. Theoretically, the summation in Eq. (2) includes all the ion excited levels. Usually, however, only a few resonant level combinations dominate, and the rest can be neglected. General expressions for \( C_{\text{eff}} \) and \( x_{\text{THG}} \) include the laser linewidth and the the widths of the transitions. The coherence of the existing XRL's is far from perfect (the relative linewidth of Se XRL 20.6 and 20.9 nm lines is \( 42 \approx 2 \times 10^{-4} \)). However, detunings are larger than \( 10^{-3} \) for all the couples in Table 3 (except for the third one, for which some of the detunings are only slightly larger than \( 2 \times 10^{-4} \)). Therefore, our estimates are not significantly affected by insufficiently high coherence of existing XRL. Requiring Ref. 40, the finite linewidths at all the resonant transitions in Eq. (2) are also neglected, since they are significantly smaller than detunings for all the couples in Table 3.

Direct calculations of \( \mu_{ik} \) require knowledge of the wavefunctions of the ions and are not available in most of the cases. Following Ref. 39, we express the \( \mu_{ik} \)'s through the transition probabilities \( A_{ik} \) which are better known; \( \mu_{ik} = s_{ik}(\pi e^2 A_{ik}/2m_0^2)^1/2 \), where the signs \( s_{ik} = \pm 1 \) for a Li (Na) like ion are assumed the same as for the Li (Na) atom in Ref. 39. (To receive universal estimates, we do not take into account the dependence of \( \mu_{ik} \) on the angular momentum.) This assumption may reduce estimate conversion efficiency by a factor of up to 5.) The maximum value of \( C_{\text{eff}} \) for a given mismatch \( \Delta k \) is achieved at \( L = L_{\text{max}} = \pi/\Delta k \), or \( L_{\text{max}}(\text{cm}) \approx 4.2 \times 10^{10}\lambda^{-1}(\text{nm})N_e^{-1}(\text{cm}^{-3}) \). With all these assumptions, we can rewrite Eq. (7) as:

\[
(C_{\text{eff}})_{\text{max}} \approx 0.003M^2(N_e/N_i)^{1/2},
\]

with

\[
M = \lambda^{-2} \sum_{abc} s_{abc} \frac{(E_aE_bE_c - E_aE_bE_c)^{3/2}(A_{ab}A_{bc}A_{ac})}{(E_a - 3\lambda^{-1})(E_b - 2\lambda^{-1})(E_c - \lambda^{-1})},
\]

where the XRL radiation intensity is in W/cm\(^2\), the energy of the levels is in eV/cm\(^2\) (as it is usual in spectroscopic tables), \( \lambda \) is in cm, and \( s_{abc} = s_{gab}s_{abc}e_{abc} \). As a result of plasma dispersion, \( C_{\text{eff}} \) does not depend on the plasma density, although \( L_{\text{max}} \) depends on \( N_i \); e.g., for a very low \( N_i \), the length \( L_{\text{max}} \) would become unrealistically large.

The results of calculations based on Eqs. (9) and (10) can be found in Table 1 in terms of the XRL intensities required to attain \( C_{\text{eff}} \approx 10^{-8} \).

They show that the observable THG intensities can be attained by available XRL's. (For example, the power of Ce\(^{3+} \) XRL required for \( C_{\text{eff}} \approx 10^{-8} \) in the loose focusing limit can be estimated as several MW which is close to the peak power of the existing XRL. It corresponds to the input energy of several hundreds of microjoules in a 100 ps pulse.) One of the ways to improve the X-ray THG is to facilitate ideal phase matching condition \( \Delta k = 0 \). Similarly to the optical THG, \( C_{\text{eff}} \approx 10^{-8} \) can be done by adding a "buffer" medium or, in our case, buffer ions. Let some transition from the ground level of the buffer ions be resonant to the third harmonic, \( \lambda/3 < \lambda_0 \), where \( \lambda_0 \) is the central wavelength of the transition, and let no transition be in close resonance to the fundamental harmonic. Then the resonant retraction by buffer ions may compensate for free-electron phase mismatch if

\[
n_p(3\omega) - n_p(\omega) = n_{\text{buf}}(\omega) - n_{\text{buf}}(3\omega) \approx 1 - n_{\text{buf}}(3\omega),
\]

where \( n_{\text{buf}} \) is the index of refraction due to buffer ions. Following Ref. 9, and assuming that (i) the Doppler broadening of the "buffer transition" is much larger than the homogeneous broadening, (ii) the upper level of this transition is almost empty, and (iii) the generated third harmonic is weak enough for one to neglect saturation effects, one can write:

\[
1 - n_{\text{buf}}(3\omega) \approx 2 \times 10^{-3}(\lambda/3)(f/\Delta\nu_D)N_i^{1/2}(\omega),
\]

with the buffer ion density \( N_i \) in cm\(^{-3}\) and \( \lambda \) in cm. Here, \( f \) and \( \Delta\nu_D \) are the oscillator strength and the Doppler width of the "buffer transition", respectively; \( \omega(x) \equiv f\omega(x + iy) \) at \( y = 0 \), with \( \omega(x + iy) \) being the complex error function; and \( x = 2\sqrt{\ln(2\nu_D - \nu_0)}/\Delta\nu_D \). Equations (11) and (12) yield the following condition for \( \Delta k = 0 \):

\[
(N_i/N_e)\omega(x) \approx 4 \times 10^{-4}f^{-1}(T_i^0/\hbar M_0'(amu))^{1/2},
\]

where \( T_i^0 \) and \( M_0' \) are the buffer ion temperature and mass, respectively. In addition, the ionization potentials of active and buffer plasma should not differ substantially so that significant abundances of both ions could exist at the same temperature. Some of possible choices of buffer plasmas are presented in Table 3 (corresponding abundances of both ions can be found in Refs. 44-48). For \( \Delta k = 0 \), Eq. (7) yields

\[
C_{\text{eff}} \approx 4.5 \times 10^{-28}\lambda^2M^2N_e^2L^2T_i^0
\]

(14)
where } N_e \text{ is in cm}^{-3}, L \text{ is in cm. For } N_e \approx 10^{30} \text{ cm}^{-3} \text{ (or } 10^{18} \text{ cm}^{-3} \text{ for Se}^{2+} \text{ 18.243 nm line, to avoid strong, and in this case, resonant third-harmonic absorption), } L = 30 \text{ cm}, \text{ Eq. (8) gives the conversion efficiency (Table 3), enhanced by many orders of magnitude compared to the efficiency of ”unbuffered” THG. Such enhancement may be ascribed to the increase of } L \text{ from } L_{\text{max}} \text{ (which would be in the micron range for such dense plasmas) to 30 cm, made possible by buffer plasma. Required plasma conditions may conceivably be attained in some discharge devices.}^{49,50}

It is worth noting that for C$^{5+}$ XRL radiation in Ne VIII plasma, phase matching can be attained without a “buffer” plasma, due to a favorable Ne VIII ion energy level configuration. For } N_e/N_c \approx 0.1, \text{ one may expect the phase mismatch to be substantially compensated by the resonant refraction at the third harmonic.}

Our quantitative results should be viewed as preliminary estimates, in particular because at this stage some of the competing processes have been neglected. Nevertheless, we expect substantial TH intensities at the state of the art of both X-ray lasers and plasma technology. Further significant enhancement of the efficiency (up to several orders of magnitude for the same XRL intensity) require search for better resonant “XRL line-plasma” couples.

4. Soft-X-ray Nonlinear Optics in Non-Ionized Media

One can notice that in our search for X-ray resonant nonlinear media, we have come to low-ionized, almost neutral atoms (e.g., only doubly ionized Na III in Table 1). The natural question of whether it is possible to have nonionized resonant media for X-ray nonlinear optics, has a positive answer. In particular, soft X-ray radiation with the wavelength 100–200 Å may be resonant to so-called core-excited (or multiply excited) atomic levels (see, e.g., the review of Ref. 51). Core-excited levels correspond to atomic states with at least one of the inner electrons excited. The energy of core-excited levels is usually much higher than the binding energy of outer electrons (the latter corresponds to the first ionization potential). For example, some of the transitions from single-excited to double-excited levels of the Li atom are resonant to XRL lines near 200 Å. Similar to that is the energy-level structure of the He atom. It is important to note, however, that transitions between core-excited levels correspond to visible or ultraviolet radiation. This combination of optical and X-ray transitions makes it natural for one to expect stimulated electronic Raman scattering$^{52}$ (SERS) in such media (Fig. 3). SERS is important as a way to achieve lasing at new short wavelengths.

Table 4. X-ray stimulated Raman scattering in nonionized media.

<table>
<thead>
<tr>
<th>XRL wavelength (intensity)</th>
<th>Nonlinear medium (conditions)</th>
<th>Raman wavelength (gain coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>(2 × 10$^{13}$ W/cm$^2$)</td>
<td>314.20 Å</td>
</tr>
<tr>
<td>Li vapor</td>
<td>(10$^{18}$ cm$^{-3}$)</td>
<td>222.48 Å</td>
</tr>
<tr>
<td>Se 269.78 Å</td>
<td>(10$^{18}$ cm$^{-3}$)</td>
<td>(40 cm$^{-1}$)</td>
</tr>
<tr>
<td>Se 269.78 Å (3 × 10$^{12}$ W/cm$^2$)</td>
<td>Li vapor</td>
<td>222.48 Å</td>
</tr>
</tbody>
</table>

We briefly present (Table 4) our first results on X-ray nonlinear optics in nonionized media: feasibility of SERS in He and Li vapor excited by the most prominent Se XRL lines. Small-signal Raman gain has been estimated through the calculated resonant Raman susceptibility,$^{52}$ with the Doppler width assumed for the Raman width. Suggested XRL intensity corresponds to the focused beam (from the original size of 200 μm × 200 μm to 10 μm ×10 μm). For Se XRL output intensity of 10$^{12}$ W/cm$^2$, we
estimate Raman gain of 7 cm\(^{-1}\) in Li vapor of 10\(^{14}\) cm\(^{-3}\) density and of 60 cm\(^{-1}\) in Ie under the pressure of 10 mtorr. The coherent output is expected on the wavelengths of 222.48 Å for Ie and 314.20 Å for Li vapor.

5. Conclusion

In conclusion, in the framework of our theoretical research on X-ray nonlinear optics, we have identified resonant nonlinear media (mainly plasmas) for about a third of existing XRL lines. For these resonant media, we have also theoretically demonstrated the feasibility of some of the basic X-ray nonlinear optical effects, such as nonlinear refraction and absorption saturation, third-harmonic generation, and stimulated electronic Raman scattering. We believe that our results are promising enough to encourage experiments. Our future plans include investigations of solids as possible media for X-ray nonlinear transformations.

*Added in proof.* Since this chapter was submitted for publication, a new development has taken place in X-ray nonlinear optics. In collaboration with MIT X-ray laser group, we considered four-wave mixing of coherent X-ray and optical radiation for a number of available X-ray lasers.\(^{54}\) Due to high expected conversion efficiency of such a process and its good potential for phase-matching optimization, X-ray-optical mixing presents the best, as of now, opportunity for experimental realization. Then, we studied detailed dynamics of X-ray stimulated electronic Raman scattering in atomic Li and Ie.\(^{54}\) Also, following a pioneering work of C. Rhodes’s group,\(^{55}\) there has been rapid recent progress in generating very high-order harmonics of optical lasers, with the output well within the soft-X-ray domain.\(^{56}\) We developed a two-level model\(^{57}\) which, for the first time, allowed for an analytical description of this process and predicted a number of new effects.

References

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