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Nonlinear Soft X-Ray Spectroscopy

Permalink

<https://escholarship.org/uc/item/5pt0j23p>

ISBN

9789819967131

Authors

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Publication Date

2023

DOI

10.1007/978-981-99-6714-8_4

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Chapter 4 Nonlinear Soft X-ray Spectroscopy

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Keywords: soft X-ray spectroscopy, soft X-ray nonlinear optics, multiphoton absorption, stimulated Raman scattering, four wave mixing, second harmonic generation, sum frequency generation, X-ray free electron laser, synchrotron radiation

Abstract – The history and current state of the field of soft X-ray nonlinear optics is discussed. The development of soft X-ray nonlinear optics has been largely based upon the earlier work done with visible and infrared spectroscopy. While nonlinear optics in those frequency regimes are relatively mature today, soft X-ray nonlinear optics is a young field. This delayed development was due to the lack of intense ultrafast X-ray light sources, but with the recent rise of X-ray free electron lasers and other intense X-ray sources there has been an explosion in the field. The specific soft X-ray nonlinear optics techniques that have been employed so far are discussed in detail and the underlying physical principles are discussed. These include non-sequential multiple photon absorption, stimulated emission to drive lasing, and various forms of stimulated Raman scattering. These techniques have enabled new measurements that were previously infeasible, providing access to dipole forbidden states, driving anisotropic X-ray emission, and allowing for the understanding of excited state surfaces in an unprecedented way. Additionally, four-wave mixing has been demonstrated and a dedicated four-wave beamline built for the study of complex phenomena such as diffusional dynamics. By performing four-wave mixing in the soft X-ray region, one accesses particularly large momentum transfer and thus spatially small volumes. Second harmonic generation has also been demonstrated in the soft X-ray region, allowing for the study of symmetry breaking and surfaces in materials ranging from batteries to graphite. This technique has recently been extended to a variation of sum frequency generation, where the soft X-ray beam is mixed with a visible laser pulse and has been shown to be a sensitive probe of charge localization. Finally, the available computational methods which can be used to model and understand these phenomena are discussed.

4.1 Nonlinear spectroscopy - development in the visible light

Over the course of an average day, a person may see all sorts of wondrous things, but they will all be in the regime of linear optics. That is to say, almost all everyday visual occurrences happen in a regime where the electric field associated with light can be considered weak. This means that if one makes the light brighter, a material illuminated by that light will appear brighter, but otherwise its appearance will not fundamentally change. [1] This was the state of the observable world for most of human existence, and only the relatively recent development of bright light sources (notably lasers) has allowed for the development of nonlinear optics. [2,3]

While it may seem like magic, strong fields enable phenomena to be seen which otherwise are not possible as shown in Figure 4.1. Specifically, the advent of a strong electric field can lead to all sorts of phenomena which otherwise would not be observable. Strong laser fields lead to a strong polarization density in a material which then reacts nonlinearly with the electric field. One of the first applications of lasers was to demonstrate second harmonic generation (SHG) on a crystal, a phenomenon which combines two photons of the same energy to generate a single photon of twice the energy. [3] While the energy is linear (two photons combine to give identical energy as from the single generated photon), SHG is a nonlinear effect as the signal scales quadratically with respect to input power. Unfortunately, even with the advent of lasers, the signal was so weak compared to the much stronger input energy (fundamental) that the small signal shown in the first manuscript figure was believed by the journal editors to be a speck of dust and was removed. The electric fields required are typically quite large ($> 10^8$ V/m) but can be readily achieved with modern lasers. [4,5]

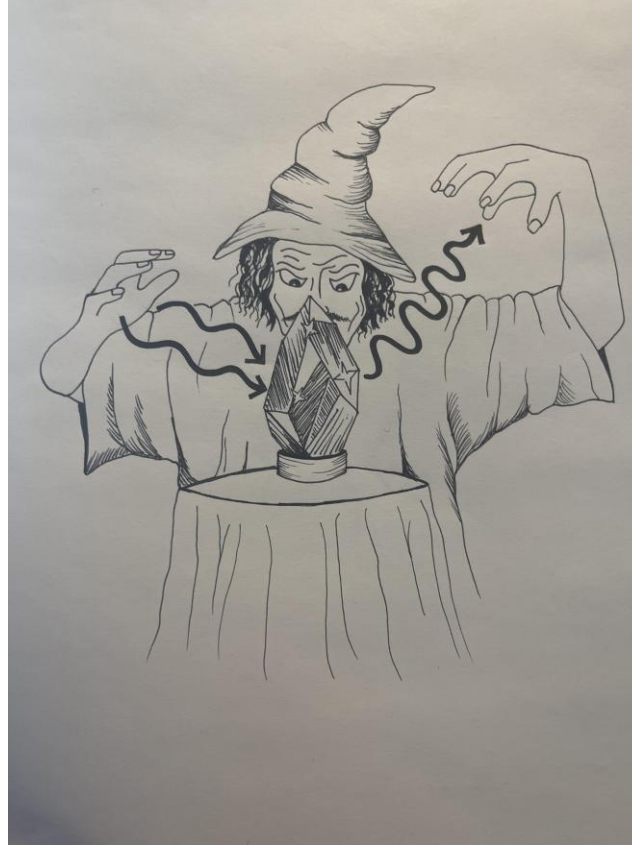


Fig. 4.1 –Second harmonic generation (SHG), can seem like magic, combining two photons to generate a single photon at twice the energy. As the signal (2ω) varies as the square of the input field (ω), a strong field is required. This particular technique is often used to probe surfaces and symmetry breaking.

Given the small signal, it is reasonable to ask why there has been so much work on nonlinear optics. This is because, in a variety of cases, the only way to determine certain properties of materials is by using nonlinear optics. Many types of information cannot be obtained by other methods, such as surface specific phenomena, access to diffusion rates for phenomena such as heat transfer, self-focusing, generation of different frequencies of light, and spectroscopy with different selection rules; these have provided insight in fields ranging from biology to electrical engineering. Most of these phenomena and the related information simply cannot be obtained in any other manner besides using nonlinear optics. The exploitation of nonlinear optics is therefore essential in many fields. For instance, to study buried interfaces, the only widely accessible measurements use nonlinear optics.

An optical event is when as an incoming light wave induces electric polarization in a material that generates the outgoing light wave. Nonlinear optics are defined by being sensitive to the electric field. In general, the instantaneous polarization can be represented as

$$P(t) = \epsilon_0(\chi^1 E^1(t) + \chi^2 E^2(t) + \chi^3 E^3(t) + \dots), \quad (4.1)$$

where $P(t)$ is the polarization, ϵ_0 is the dielectric of free space, χ^n is the n th order susceptibility in terms of the electric field $E(t)$. χ^n is usually a tensor of rank $n+1$ that is sensitive to the polarization and symmetry of the system. A second order process such as second harmonic generation would have a χ^2 consisting of a rank 3 tensor, and the higher order terms are not necessary in that case. There are many varieties of nonlinear optical effects that have been observed experimentally. Some of them are listed in Table 4.1 with characteristic information. It is worth mentioning that some nonlinear optical phenomena, such as multiple ionization or saturable absorption, have also been observed with a linear response of the polarization with a linear susceptibility, χ^1 . Such optical events themselves are “nonlinear” but the equation defines them as “linear”. These examples are given in Table 4.2 and the description is given in the section 4.3.

Table 4.1: A list of nonlinear optical phenomena with nonlinear susceptibility, optical properties, and representative references.

Optical Phenomena	Nonlinear Susceptibility	Notes on the Phenomena	Selected References	
			For soft Experiment Section in chapter	X-ray and this
Second Harmonic Generation (SHG) $2\omega_1 \rightarrow \omega_2$	$\chi^{(2)}$	Sensitive to symmetry breaking as an even order process. Generates a photon at twice the input photon energy.	[6,7] § 4. 4. 5	
Third Harmonic Generation (THG) $3\omega_1 \rightarrow \omega_3$	$\chi^{(3)}$	Generates a photon with three times the input energy. Has been used in the optical regime as a form of microscopy.	Not yet demonstrated in the X-ray regime. See [8] for more discussion from the optical regime.	
Sum Frequency Generation (SFG) $\omega_1 + \omega_2 \rightarrow \omega_3$	$\chi^{(2)}$	Similar selection rules to SHG, but with input photons of different energy.	A variation with 3 input photons is shown in [9] § 4. 4. 5	

Difference Frequency Generation (DFG) $\omega_1 - \omega_2 \rightarrow \omega_3$	$\chi^{(2)}$	Similar selection rules to SHG and SFG.	Has been discussed theoretically in the hard X-ray regime, but not yet demonstrated. [10]
High Harmonic Generation (HHG)	Varies	Used in the optical regime to generate X-ray pulses.	[11, 12] § 4. 2
Optical Parametric Amplification (OPA)	$\chi^{(2)}$	Used in the optical regime to tune laser frequencies.	Similar technique used in the hard X-ray regime as X-ray Parametric Down Conversion [38, 39].
Optical Parametric Oscillation (OPO)	$\chi^{(2)}$	Can be thought of as a way to improve the focus and power of light generated with an OPA.	Not demonstrated in the X-ray regime.
4-wave Mixing	$\chi^{(3)}$	A series of related techniques where 3 waves interact to generate a 4 th wave. Amongst the most common is transient grating.	[13,14] § 4. 4. 4
Raman Amplification	Can vary	Method of amplifying a Raman signal	Not demonstrated in the X-ray regime.

Optical Kerr Effect	Can vary	A variety of related techniques where the refractive index of a material varies with the input electric field.	Not generated in the X-ray regime
Two Photon Absorption (TPA)	$\chi^{(3)}$	Two (or in certain cases more) photons are absorbed, allowing the probing of different selection rules.	[15,16] § 4. 4. 1
Stimulated Emission	N/A	Drives a population inversion which then undergoes a stimulated emission process, like lasing.	[17,18]
Superfluorescence	N/A	Ensemble of emitters coupling to emit an intense burst of light.	[19, 20] § 4. 4. 2
Stimulated Raman	$\chi^{(3)}$	A process where a species is driven into a higher excited state before being driven back down into a lower state and emitting a photon	[21,22]

Table 4.2: A list of nonlinear optical phenomena with linear susceptibility, optical properties and representative references.

Technique Name	Nonlinear Susceptibility	Notes on the Technique	Selected References And Section in this chapter
Multiple Ionization	$\chi^{(1)}$	Multiple electrons are removed from a bound system simultaneously or nearly simultaneously	[15] § 4. 3
Saturable Absorption	$\chi^{(1)}$	At high fluxes, absorption saturates	[17,18] § 4. 3

The case of wave mixing (where two or more photons are combined to generate a single photon) has shown use in both the generation of tailored light and the study of materials, as it enables generation of light at different wavelengths. [23,24] A whole host of related techniques can be used to mix multiple photons. The mixing of two degenerate photons is SHG, as mentioned above, and mixing three degenerate photons to generate a 4th is called third harmonic generation (THG). Mixing two photons of different energy, where the resultant photon is the sum of the energies of the input photons, is called sum frequency generation (SFG), and mixing two photons where the resultant photon energy is the difference between the input photon energies is called difference frequency generation (DFG). The mixing of an even number of photons (generally two) has the special property of requiring symmetry breaking in a material for signal to occur, which requires either a noncentrosymmetric material, or an interface. This is not true with an odd number of photons which is bulk sensitive, as will be the case in four wave mixing, which provides similar information to third harmonic generation - both probe χ^3 , described below - but have different phase matching conditions. Combining larger numbers of photons is just generally termed high harmonic generation (HHG). [5,25] These techniques have shown a host of applications in the study of materials and in preparing tailored laser light to probe other materials through the generation of specific frequencies. This idea of generating different frequencies to probe matter is frequently used with other wave mixing techniques such as optical parametric amplification (OPA), optical parametric oscillation (OPO) and optical parametric generation (OPG). [26–28] Indeed, much of modern laser spectroscopy would not be possible without these techniques. The

details of performing these techniques have been reviewed extensively before and the reader is encouraged to seek out those manuscripts if more detailed knowledge is necessary. [4,24]

Nonlinear optics, however, is not limited to wave mixing and includes a host of other processes that are only possible as the field becomes strong enough to lead to nonlinear effects. These include but are not limited to: transient grating (i.e. 4-wave mixing), where diffusional processes can be mapped spectroscopically; Raman amplification which enhances the Raman signal under large fields; the optical Kerr effect which leads to a change in the refractive index with field; and multiphoton absorption (i.e. two-photon absorption), wherein multiple (two) photons are absorbed simultaneously, among many other techniques. [2,29–32] Many of these processes provide ways of probing matter in a manner for which there are either no available alternatives or no options with all the benefits of these methods. It is important to note that just because an effect can require a strong field to occur, does not mean the process is nonlinear – the signal must change nonlinearly with respect to the electric field. For instance, pump-probe spectroscopy where an initial pump prepares an excited state which is then probed by a second pulse is not necessarily a nonlinear phenomenon even though typically somewhat large fields are required to drive a noticeable fraction of the system into an excited state. [25]

To use nonlinear optics experimentally, a variety of complications must be carefully understood and potentially optimized to maximize signal. One example is phase matching. The phase of light must be considered because the index of refraction of a material generally changes as a function of wavelength, meaning the angle of the crystal being studied where the incoming and outgoing waves interfere will have a large effect on the signal. For a second order process such as SFG, at position x in a crystal system, the second order polarization is

$$P^2(x, t) \propto E_1^{n_1} E_2^{n_2} e^{i[(k_1+k_2)x - \omega_3 t]} + (\text{complex conjugate}), \quad (4.2)$$

where E_1 and E_2 are two components of the electric field at frequencies ω_a and indices n_a , with the wave vector $k_a = n_a(\omega_a) \omega_a/c$ where c is the speed of light, and $n_a(\omega_a)$ is the index of refraction at frequency ω_a . For SFG, definitionally $\omega_1 + \omega_2 = \omega_3$. Therefore, phase matching, which requires constructive interference, can only be true if the output wave vector ($\vec{k}_3$) is equal to the input wave vectors ($\vec{k}_1, \vec{k}_2$).

$$\vec{k}_3 = \vec{k}_1 + \vec{k}_2. \quad (4.3)$$

This statement can be generalized for a system of $n-1$ input vectors such that

$$\vec{k}_n = \vec{k}_1 + \dots + \vec{k}_{n-1}. \quad (4.4)$$

This is known as the phase matching conditions, albeit in certain cases the vectors may subtract instead of adding, as is the case for difference frequency generation. For certain systems, for instance those with geometric constraints, such matching is not always possible, making measurements challenging. [5] Perhaps the largest challenge in general, is that the demands on the light sources are quite high, requiring an intense light source of monochromatic and coherent light. Even today, these sources simply do not exist for every frequency range, and even when they do exist they can be quite expensive to use and maintain. It is almost a certainty that the quality and availability sources will continue to improve in the future, as they have for the past 50 years.

The key to development of nonlinear optics has been the development of powerful light sources. [5] The development of bright X-ray light sources has lagged significantly behind those in the visible, leading to a similar lag in the development of X-ray nonlinear optics. The current state of the art is significantly less advanced than that in the visible. In addition, X-rays are generally harder to work with than visible light, as they are harder to focus and reflect, and require

specialized and expensive optics for these purposes. [33] Only the recent rise of X-ray free electron lasers, with their high peak photon flux, has enabled significant work and development in the field of X-ray nonlinear optics. [34] These light sources are discussed in more detail in the next section.

Visible nonlinear optics and X-ray nonlinear optics in the so-called hard X-ray regime (photon energies greater than 3,000 eV) are fundamentally different. In the visible the spectroscopies are dipole selected, but in the hard X-ray regime the dipole approximation breaks down leading to different effects, such as SHG being bulk sensitive in centrosymmetric media, and more accessibility of the nonlinear Compton effect. [35–37] It appears, however, that in the soft X-ray regime (photon energy less than 1,000 eV) nonlinear optics can be described well by the dipole approximation and the previous equations can be readily applied, and as such visible nonlinear optics can be used to guide the development of soft X-ray nonlinear optics. The region below approximately 150 eV is sometimes referred to as extreme ultraviolet (XUV), although the cutoff between XUV and soft X-ray is not well defined. We wish to note the description of the development of visible nonlinear optics and its detailed uses are covered only in a cursory fashion here. For a more thorough treatment, the reader is encouraged to read the several books that have been published on the topic. [5,25]

4.2 Ultrafast X-ray light sources

In almost all cases, to observe nonlinear effects one needs a strong field. (The case of X-ray parametric down-conversion is skipped here, but it is a hard X-ray phenomenon and not relevant at the energies discussed in this chapter [38,39]). The original X-ray sources, dating back to their invention by Roentgen in 1895, were based on X-ray tubes. While these were improved over the course of decades by developing rotating anodes which allowed for increased load, the continuous nature of the X-ray emission and the relatively low flux precludes their use in generating the large fields necessary to perform nonlinear optics. Additionally, these sources are not generally and readily tunable in terms of the strongest energy available. [40]

The next step in the development of X-ray sources was the development of synchrotron light sources. These machines were discovered by Vladimir Veksler in 1944, [41] built by Edwin McMillan in 1945 [42] and the observation of synchrotron radiation was made in 1947 by General Electric. [43] These machines move electrons at relativistic speeds around a ring, and as the electrons are accelerated, they emit radiation, a phenomenon which was not initially expected. Following this discovery, synchrotron light sources have undergone continuous improvements, from their early use being run parasitically from early synchrotron particle accelerators, to their current designs which approach the diffraction limit. Synchrotron light sources may now be close to their ultimate performance limits, [44] having become the workhorses of X-ray science. They deliver stable X-ray light with a high average flux, but their design is not optimized for high field science. This is because while the machines generally run at a high enough pulse rate to approach a continuous source (MHz), their peak power (or equivalently their power per shot) is quite low, with pulse lengths typically in the hundreds of picoseconds and the number of monochromatic photons per pulse often approaching 10^6 . [45] While this is many orders of magnitude higher than an X-ray tube (depending on how this is counted, 15 orders of magnitude may be a conservative estimate for the increase in monochromatic flux), the field strength is still much too low to perform most nonlinear optical experiments.

The advent of X-ray free electron lasers (FELs), however, brought even more intense X-ray sources with the potential to drive nonlinear optical phenomena. These lasers use unbound ('free') electrons as the lasing medium. [46] Because the X-ray radiation they generate does not reflect well, a reflection based lasing cavity has not yet been built and the radiation must be generated on a single pass of the electron beam, leading these machines to be large (European XFEL is 3.4 km long), and therefore quite expensive. Despite the cost of these machines, their tremendous power (up to mJ per pulse), short pulse length (as short as hundreds of attoseconds), and relatively high repetition rate (now approaching MHz), makes these machines ideal for performing nonlinear optics. Indeed, the vast majority of nonlinear X-ray experiments that have ever been performed have been performed with these machines. [47–49] They are not without their drawbacks, however, as the typical lasing method, self-amplified spontaneous emission (SASE), in essence amplifies noise and leads to a broad and non-Gaussian spectral and temporal profile. [50] There has been work to improve this by performing self-seeding, which has shown improved spectral quality and has seen rapid improvements recently. [48,49] Perhaps the optimal solution would be to use external seeding, where an initial laser pulse is amplified, as is done at FERMI in Italy. [51] While this provides a very coherent and monochromatic source, it does so at the cost of laser power, which is lower than SASE FELs. Additionally, as amplifying an external laser source amplifies the noise, using this technique to develop pulses into the hard X-ray regime and maintaining decent quality pulses has proved challenging so far and will require the developments of several new technologies. [52] The details of how X-rays from X-ray tubes, synchrotrons and FELs are generated has been handled elsewhere. [44]

The overall progress can be seen in a graph plotting photon energy versus peak brilliance – which is roughly proportional to monochromatic photon flux. [45] As shown in Figure 4.3, conventional lasers can be quite intense in terms of photon power, but struggle to produce high energy photons. This is contrasted with synchrotrons which are quite good at generating high energy photons but struggle to produce high peak flux. With synchrotrons near their performance limits, free electron lasers are opening entirely new fields of study by enabling high flux and high photon energy. An example of a modern X-ray free electron laser is shown in Figure 4.2, taken at the soft X-ray FEL at SACLA in Japan.



Fig. 4.2 A photo of soft XFEL at SACLA. By permission of RIKEN.

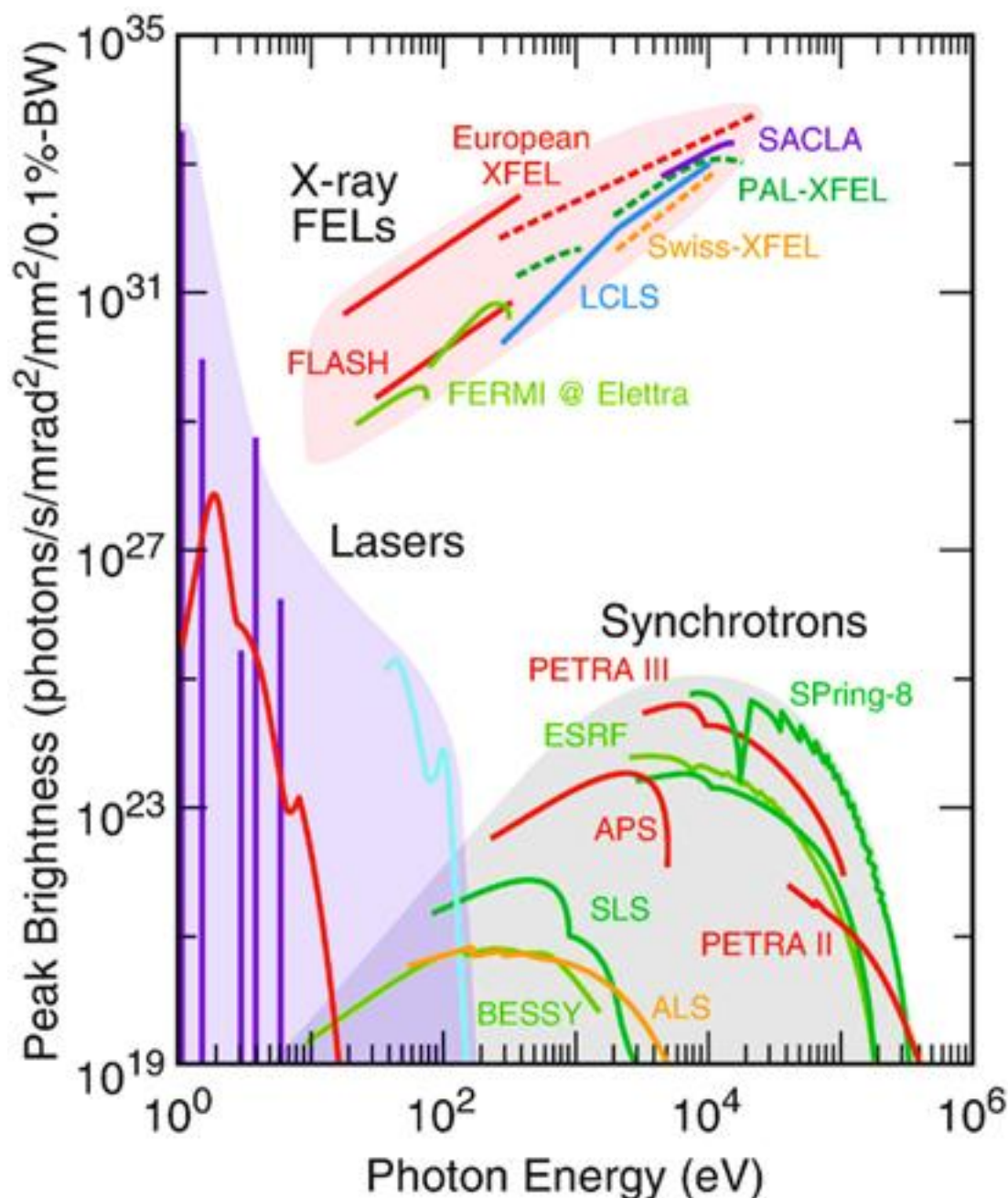


Figure 4.3 – Plot of photon energy vs peak brilliance, roughly proportional to peak photon flux. Conventional lasers are high flux but low photon energy whereas synchrotrons are high energy but low flux. The X-ray free electron laser is uniquely high flux and high energy. X-ray tubes can produce high energy X-rays, but their flux is so low it is off the scale of the plot. HHG sources are at present above synchrotron peak brightness (up to $\sim 10^{25}$ photons/s/mrad²/mm²/0.1%/-BW at 100 eV). The pace of their improvement is significantly faster than that of synchrotrons, however. Taken from [45]. Reprinted with permission from S. Boutet and M. Yabashi, X-Ray Free Electron Lasers and Their Applications, in X-Ray Free Electron Lasers: A Revolution in Structural Biology, edited by S. Boutet, P. Fromme, and M. S. Hunter (Springer International Publishing, Cham, 2018). Copyright by Springer Nature.

Finally, it is worth acknowledging recent advances in lab-based X-ray sources. Beyond X-ray tubes, X-rays can be generated in a variety of ways, such as by impacting a metal with an intense laser pulse, but this provides inadequate photon flux for nonlinear experiments. [53] Perhaps more likely to be of use for X-ray nonlinear optics in the future is HHG based sources, which upconvert a laser pulse into the soft X-ray region. [11,12] While at present these sources provide inadequate peak power for nonlinear optics, they are very attractive in that they maintain excellent pulse quality and are significantly smaller financial investments than FELs. Current work has largely focused on increasing the average power of the machine by increasing the repetition rate, increasing the photon energy to hundreds of eV and decreasing the pulse length of these sources, but perhaps if more work is performed to optimize peak flux performing nonlinear optical experiments at soft X-ray energies will be possible with HHG sources. [54]

4.3 Family of soft X-ray nonlinear spectroscopy

Well established linear spectroscopies-

Before describing nonlinear X-ray spectroscopies already developed, it is perhaps beneficial to briefly describe the uses of linear X-ray spectroscopy. X-ray spectroscopy uses a high energy photon to excite core or semi-core electrons in an atom, molecule, or material system. These core or semi-core electrons are generally well separated in energy for each element, allowing X-ray spectroscopy to probe different elements in a system individually. [55] This contrasts with visible spectroscopy, which typically probes a delocalized state which can extend over an entire system. [56] Also as the excitation is high energy, the spectroscopy is often sensitive to neighboring molecules as the excited state is often quite diffuse spatially. It therefore can be a very sensitive probe; for instance the X-ray spectrum of water is significantly more feature rich than the infrared (IR) spectrum of water. [57]

X-ray spectroscopy generally takes one of several forms. In X-ray absorption spectroscopy (XAS), the input energy is scanned and the amount of photons absorbed by the sample is measured. [55] The absorption transition can be described (as was detailed in chapter 2) by Fermi's golden rule as –

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \rho(E_f), \quad (4.5)$$

Where the transition probability from the initial state (i) to the final state (f) is given by $\Gamma_{i \rightarrow f}$. H' is the Hamiltonian describing the transition from initial to final, $\rho(E_f)$ is the density of states, and $\hbar$ is Planck's constant divided by 2π . In the case of XAS, the transition is from a relaxed state (i) to a core excited state (f). As this is a single photon process, there must be a single unit of angular momentum difference between i and f , often meaning a transition from an s to a p type orbital. As f is unoccupied, this provides a sensitive probe of the unoccupied projected density of states (for instance K-shell excitations are from the 1s shell into unoccupied p-type states). In X-ray emission spectroscopy (XES), the input energy is well above the core or semi-core electron binding energy, and the emitted photons are measured as a function of energy. Many of these are elastic, emitted when the excited electron relaxes directly back to its original core or semi-core state. But there is also inelastic emission, from electrons transitioning from valence states into the empty core hole

left by the X-ray excitation. This provides a measure of the projected density of states of the occupied density of states. [58,59] In terms of Fermi's golden rule, i is a core hole state and f is the relaxed state it transitions into. As the process is single photon, the same selection rules a XAS apply. X-ray emission spectra can also be measured when the input X-rays are resonant with an excitation to a specific final state, known as resonant inelastic X-ray scattering (RIXS). This in essence combines X-ray absorption and X-ray emission spectroscopy. [60]

It is also possible to examine the electrons emitted from a system. X-ray photoelectron spectroscopy probes the energies of the initial occupied electronic states by measuring the energy of the photoelectrons excited from these states by an incident X-ray photon. Introducing incident electrons of constant energy and measuring the emitted photon energy is called inverse photoemission and is sensitive to the unoccupied states. [61] All of these techniques would be classified as linear, but all nonlinear soft X-ray spectroscopy are built upon linear techniques in some way. Linear X-ray spectroscopy is described in detail in Chapter 2.

High field linear soft X-ray spectroscopies-

Beyond measurements that can be made at synchrotrons, there are other linear effects that can be observed at FELs. The most common of these are discussed briefly here. Among the first papers to be produced from an X-ray free electron laser (XFEL) was a demonstration of the multiple ionization of neon. [62] In terms of Fermi's golden rule, this means it goes through a series of excitations from the ground state, where after the first excitation the ground state has become some ionized state. It was shown that the highly intense X-ray pulses would drive the formation of core holes by removing the inner core electrons through direct excitation; the valence electrons would then fall into the core within the duration of the X-ray pulse, which then removed these formerly valence electrons as well. This meant the way to maximize the ionization - as was demonstrated for both an atom (Ne) and a molecule (N₂) - was to increase the length of the laser pulse, not the field strength. [62,63] So while this is an interesting high field phenomenon, it is not an example of nonlinear optics.

Other related high field phenomena in the soft X-ray (and demonstrated as well in the hard X-ray regime on Fe) include the phenomena of saturable absorption (SA) and X-ray induced transparency. [64,65] In SA, the amount of absorption is so high that the final states are filled and absorption is saturated, manifesting as a decreasing amount of the rate of absorption with increasing laser power. When the ground state is fully depopulated by a phenomenon such as SA, this will give rise to the related phenomenon of X-ray induced transparency, wherein X-rays which would normally be absorbed by the material are instead fully transmitted, because all the core electrons have been depopulated. This may have use in futuristic advanced materials where X-ray transparency can be turned on and off. This has been demonstrated at the L-edge of solid Al, [66] and the N-edge of tin. [67] While both these phenomenon are dependent on the pulse power per area, the effect is not nonlinear with respect to the electric field, so here we will not consider it a nonlinear optical effect, although such a term is used elsewhere.

4.4 Nonlinear soft X-ray optics and spectroscopies

Section 4.4 will deal primarily with various soft X-ray nonlinear optical techniques. These include multi-photon absorption, stimulated phenomena, stimulated Raman, four wave mixing,

and second harmonic generation. Some of the key results are summarized in Table 4.1 listing nonlinear susceptibility and a few representative papers.

4.4.1 Multiphoton absorption

One of the most used nonlinear optical techniques in the visible is two photon absorption (TPA). [68] With this technique, rather than a single photon being absorbed, followed by another photon, two photons (generally of the same energy for practical reasons) are absorbed simultaneously. This has shown use in the visible as a method of photolithography for generating narrow etched lines, as only the most intense part of the laser pulse will have the requisite intensity for two photon absorption, ultimately leading to higher resolution linewidths. [69,70]

TPA also has different selection rules, and can therefore access states that are not normally allowed. [71] Fermi's golden rule to the first order (as shown previously in Eq.(4.5)) is inadequate for this two photon process. This is because the simultaneous absorption of two photons allows for transitions to states that are dipole forbidden with a single photon, or that require a change of two units of angular momentum. In the X-ray region, TPA forbids s->p transitions but allows (for instance) s->d transitions, or s->s transitions (allowed angular momentum changes for two photons are 0, ± 2) generating an entirely different spectrum than the low field single photon absorption spectrum. [72] This allows for matter to be characterized in a way that is not possible at lower fields; these otherwise inaccessible states can have interesting properties such as different symmetry and different lifetimes. TPA also has a different absorption rate compared to linear absorption. Linear absorption allows transmission proportional to Beer-Lambert law, corresponding to an exponential decay in intensity with regards to sample thickness-

$$I(x) = I_0 e^{-\alpha x}, \quad (4.6)$$

where $I(x)$ is the intensity, I_0 is the input intensity, α is the single photon absorption coefficient and x is the sample thickness. By contrast two photon absorption is described by

$$I(x) = \frac{I_0}{1 + \beta x I_0}, \quad (4.7)$$

with β being the two photon absorption coefficient and the other terms the same as in the single photon absorption case. The linear intensity is dominant at low field strength, but this is not always true. In the limit of incredibly high fields, two photon absorption and other multiple photon absorption processes can become dominant.

Indeed, this is how the evidence of TPA in the soft X-ray regime was noticed. The production of Ne^{9+} was observed at lower photon energies than what was required for Ne^{8+} . [15] Following careful theoretical analysis, Doumy et. al assigned it to two photon absorption; they cleverly changed the input energy for ionization and showed that the absorption rate was different as the energy was moved from 1110 eV to 1225 eV, going from a quadratic scaling factor with respect to pulse power to one that was roughly linear (exponent of 2.0 versus 1.1 respectively). 1110 eV should not be enough energy to ionize Ne^{8+} into Ne^{9+} , allowing for TPA without the possibility of single photon absorption. The reason the scaling factor is not 1.0 for the case of 1225 eV is probably related to other processes beyond simple absorption occurring, including TPA amongst many other possible effects, as shown in Figure 4.4. The cross section of TPA in the case of Ne^{9+} was many orders of magnitude higher than what had been expected, which is likely why it was observable.

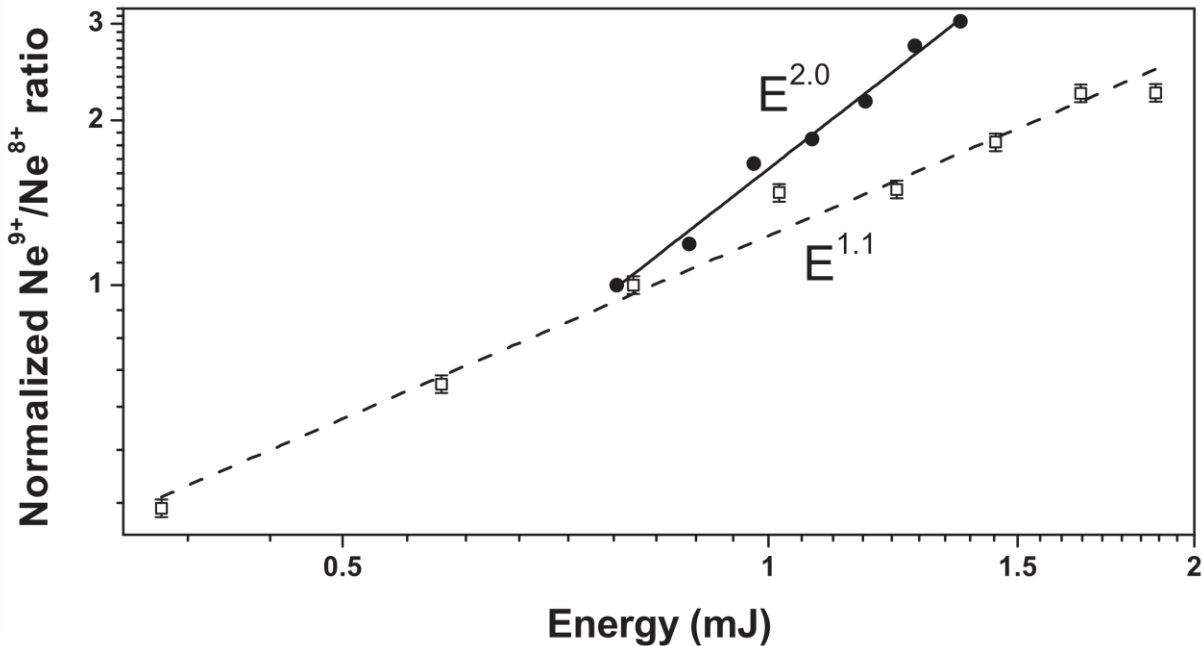


Figure 4.4 – Normalized ratio of Ne^{9+} to Ne^{8+} for excitation with 1110 eV (filled circles) and 1225 eV (open squares). The fit for the 1110 eV showed a quadratic dependence with flux ($E^{2.0}$) whereas the fit for 1225 eV showed a roughly linear dependence ($E^{1.1}$) [15]. Reprinted with permission from G. Doumy *et al.*, Nonlinear Atomic Response to Intense Ultrashort X Rays, *Phys. Rev. Lett.* **106**, 083002 (2011). Copyright (2011) by the American Physical Society.

Two photon absorption had previously been seen for helium at 41.5 eV. [73,74] In this case, light generated from an HHG source was incident upon helium, generating a variety of ions. [16] Because the spectra of helium are so well understood and the quality of the data was so high, the research team was able to determine the cross section and compare it to theory, with reasonable agreement, although there is some error related to unknown amounts of 83.0 eV contamination from the source. While the importance of this specific result is perhaps limited, the ability to do these measurements in a lab setting is a significant achievement and opens the possibility of future nonlinear measurements in lab settings.

Finally, there have been two sets of measurements on graphite. The first measurement [75] showed two photon absorption near the carbon K-edge. However, this view has been revised with more recent data and is now ascribed to shifting in the edge energy over the finite length of the pulse. [65] In the newer work, it is found that TPA is fundamentally competing with SA, described in section 4.3. What is seen is that at relatively low fluences SA occurs, and at higher fluences the importance of TPA is observable. In solids the processes occur at different rates than in the case of gases, due to the very different local environment when comparing a gas to condensed matter.

This all indicates that spectroscopy at very high fluences will need to be carefully considered going forward, as multiple effects can occur. This complexity inherently grows as the systems grow more complicated. However, it ultimately provides unique insight into materials and offers unique abilities to control light and matter in ways that are otherwise not possible.

4.4.2 Stimulated emission / forward scattering

While the generation of laser light from a material via stimulated (rather than spontaneous) emission is generally not considered a nonlinear optical technique as the high fields do not drive the process, the process requires intense X-ray sources and leads to a significant nonlinear enhancement in the number of photons generated as compared to spontaneous emission. In the case of Ne, an X-ray laser was made by pumping a gas with very intense X-ray pulses which causes a population inversion of the neon single excited ion. This transition to stimulated emission from spontaneous emission for 960 eV input photons occurred at roughly 0.15 mJ power. [76] For an infinitesimally thin sample with interaction length dx , the emission probabilities P can be described as

$$P = \sigma \rho_{atom} dx, \quad (4.8)$$

and

$$P = \sigma \rho_{ch} dx, \quad (4.9)$$

Where σ is the cross section of either absorption or stimulation, ρ_{atom} and ρ_{ch} are the number density of absorbing atoms and core holes respectively. As such, more core holes linearly increase the probability of stimulated emission. In the limit where stimulated emission is large ($P \sim 1$), the ratio of densities can be expressed as

$$\frac{\rho_{ch}}{\rho_{atom}} = \frac{\lambda}{dx}, \quad (4.10)$$

where λ is the absorption length. For high efficiency, the absorption length relative to the interaction length has to be similar to the ratio of excited atoms. For comparable interaction and absorption lengths it would require full excitation of the system, that is to say a population inversion will be required, i.e. lasing will occur. The ability to drive this type of lasing phenomenon should open the way to future nonlinear X-ray studies. This was later extended to show that in certain situations superfluorescence, a quantum effect leading to the collective emission of fluorescent light, similar to but distinct from amplified stimulated emission, could also occur. [19,20] There has been a variety of work expanding upon this in the hard X-ray regime with potential spectroscopic applications. [77–79]

The demonstration of stimulated emission for materials science with soft X-rays was made in 2013. [17] This work was motivated by X-ray emission generally being an isotropic process with the efficiency for low energy excitations often below one percent. [80] This means that sample damage from nonradiative decay, such as Auger decay, limits the ability to make measurements on samples that are sensitive to radiation damage, notably including biological and organic molecules. Using stimulated emission instead allows for a higher conversion efficiency and thus less sample damage by mitigating processes such as Auger decay.

This is identical to what drove the lasing phenomenon seen in neon. Beye *et al.*, propose that stimulated emission can be used with nonlinear optical techniques to enable measurements such as X-ray emission on samples that are highly susceptible to damage.

This work was expanded upon more recently by studying the emission from Co/Pd multilayers. Through careful design of the X-ray pulses, Stöhr and coworkers were able to observe an enhancement of 10^6 for stimulated versus spontaneous emission. [81] This large enhancement was found for both inelastic X-ray scattering as well as elastic X-ray scattering. [81] However, they also found that there were effects caused by the temporally spiky nature of the SASE radiation used in this study, as the electrons would diffuse between spikes within a pulse causing unwanted spectral effects. Thus, they suggest that the ultimate way to minimize the unwanted effect and enhance the stimulated RIXS spectrum would be for a single short (possibly hundreds of

attosecond) spike. This would enable linear spectroscopy efficiently in the high photon flux regime often associated with nonlinear optics.

On the same Co/Pd system at the Co L-edge, differences in the absorption and the magnetic circular dichroism spectra were observed when comparing XFEL measurements to synchrotron measurements. It appears that over the intensity range available at XFELs near absorption edges, the intense X-ray pulse changes the valence electronic structure, which can then be observed by differences in absorption. [18] This paper also saw enhancement in elastic X-ray scattering. Such an enhancement has been observed previously in a series of manuscripts. It was first proposed that this would occur in high intensity coherent X-ray pulses leading to a deviation from the Beer-Lambert law. [82] The results verifying this theory showed up only a year later, when high fluence led to a loss of diffraction signal in Co/Pd systems. [83] This was definitively shown two years later by a loss of diffraction signal with a simultaneous rise in forward elastic scattering for the same system. [84] Stöhr and coworkers were able to explain how the ratio of stimulated to spontaneous emission affected transmission and diffraction contrast as a function of intensity.

4.4.3 Stimulated Raman scattering

A critical milestone in the development of 2D X-ray spectroscopy is a demonstration of the ability to control the electronic state of molecules as well as control the motion of the constituent atoms such that they can be driven in specific relative motion. This can in principle be used to drive highly specific reactions as well as understand the motion of atoms. While this was theorized for a long time with X-rays, [85] the cutting-edge experiment to coherently drive matter from an excited state to another excited state is relatively recent, using stimulated electronic X-ray Raman scattering. [21] In normal Raman scattering, a single pump photon is input ω_{pump} , and some of the energy is lost (or gained) inelastically, corresponding to a difference of ω_{signal} . In contrast, in stimulated Raman, two photons are input, the pump photon ω_{pump} and the Stokes photon ω_{Stokes} . When the difference between the two photons ($\omega_{pump} - \omega_{Stokes}$) corresponds to a Raman transition ω_{signal} , a large enhancement is seen due to stimulated Raman scattering. In the frontier X-ray experiment of stimulated Raman scattering, an X-ray pulse pumped Ne gas into an excited state and then resonantly deexcited the atom into a lower energy state accompanied by photon emission. This is possible due to the wide energies available in a SASE pulse and its finite pulse length, ultimately leading to an emission band in this case, slightly lower than the input photon energy. In this case the input energy was roughly 870 eV and the emitted energy was roughly 850 eV. This pushing of an atom from a strongly excited state into a less excited state by resonant deexcitation is a demonstration of control of an excited state. This type of exquisite experimental control will be necessary for the ultimate realization of 2D X-ray spectroscopy. Unfortunately, despite substantial effort to extend this technique, [86] advances have been slow due to a range of experimental challenges. One pulse schema suffer from the inherent jitter and irreproducibility of individual shots, making data analysis and definitive proof hard at SASE beamlines, and the spectral width of seeded lasers are too low to easily observe Raman deexcitation in a single pulse. More advanced techniques require two pulses with well tuned parameters and high power. This is the kind of problem which is challenging for current FELs as the FELs with excellent spectral properties have limited energy tunability for two pulses and lower power, and the FELs with tunability for a second pulse and high power produce noisy pulses. It does seem inevitable that newer machines will enable these measurements eventually.

In 2020 while studying nitric oxide, researchers were able to drive NO into a core hole excited state, before pushing another electron back down into the core hole leaving the element in a relatively stable excited state. [87] This excited state could be used to drive chemical reactions and otherwise prepare molecules into specifically chosen states and extends upon the previous work by demonstration atomic control in a molecular system. It also provides the opportunity to track the motion of electrons within a molecule with higher spatial and temporal resolution than can be obtained with direct excitation of the same energetic states. This technique requires fast pulses and high fields, so the increasing availability of higher intensity X-ray pulses should make such experiments more accessible.

Finally, it was noticed that when exciting neon in a particularly strong resonant X-ray field, it was possible to drive it from an excited state (hundreds of eV) into a slightly excited yet stable neutral state (few eV) which does not undergo recoil after excitation due to no emission of an electron. [22] This is done by exciting the electron and then driving it back down into a neutral but excited ground state that is below the binding energy of neon, preventing the possibility of the of emission an electron. When imaging an atomic beam of xenon, it is quite apparent that these excited atoms exist, as the excited xenon molecules show up as a solid line on the 2-dimensional imaging detector, tracking the path of the beam of atoms which was inserted. Interestingly, this phenomenon is seen only at 855 eV excitation, not 860 eV excitation, indicating it is sensitive to the specific nature of the excited state. Regardless, such exquisite control is a demonstrative step towards 2D spectroscopy of neon atoms. This is shown in detail in Figure 4.5.

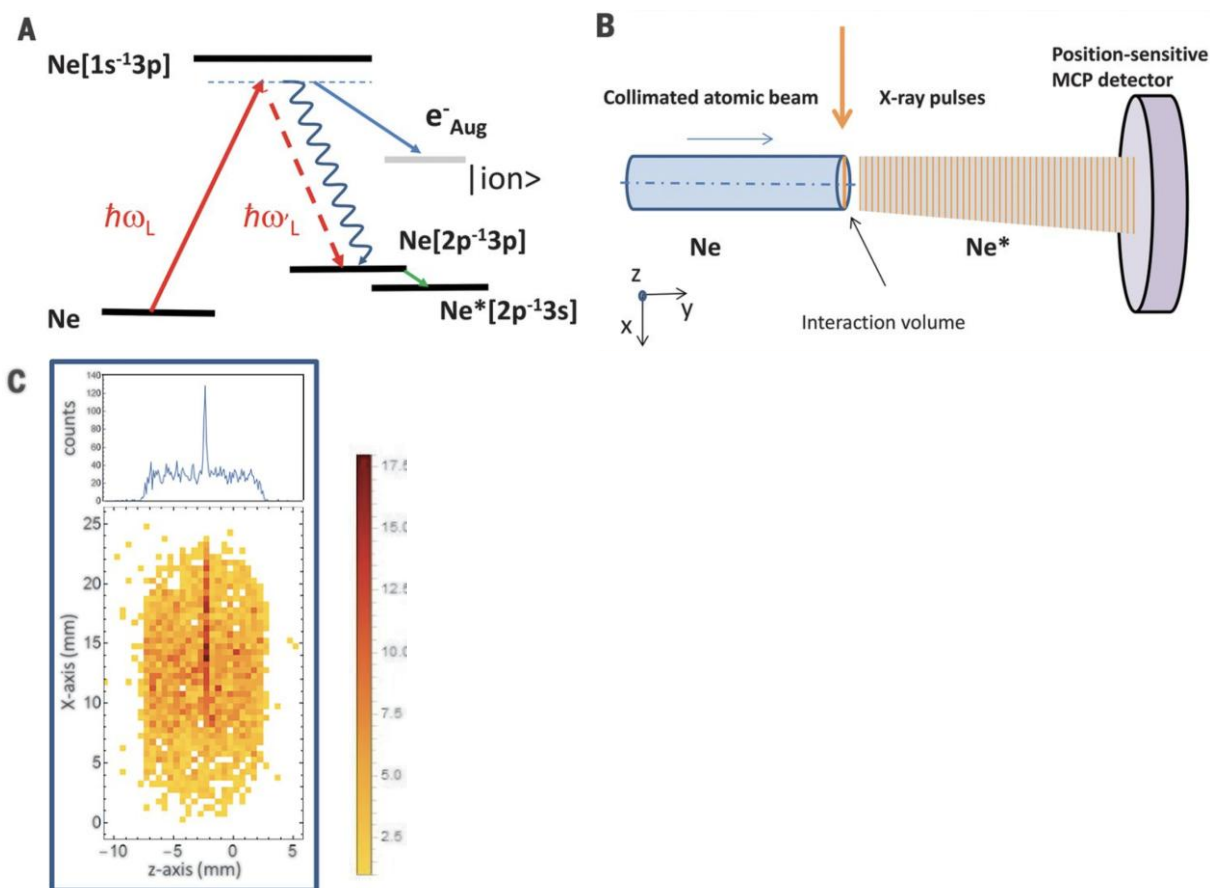


Figure 4.5 – A – Excitation and decay pathway in neon for X-ray scattering near 855 eV. The initial pulse excited the laser into a state Ne[1s⁻¹3p] state, followed by either Raman emission to the Ne[2p⁻¹3p] state or Auger emission (blue line to grey horizontal line). The Ne[2p⁻¹3p] state can decay to a long lived metastable Ne[2p⁻¹3s] state which can be detected. B – Experimental setup for this experiment including position-sensitive MCP detector to observe excited Ne atoms. C – Distribution of excited neon atoms deflected as a result of spontaneous x-ray scattering leading to momentum transfer with an incident photon energy of 855 eV. The narrow vertical line is not seen when excited at 860 eV and is due to the mechanism described in A. Adapted from [22]. Reprinted with permission from U. Eichmann et al., Photon-Recoil Imaging: Expanding the View of Nonlinear x-Ray Physics, Science 369, 1630 (2020). Copyright by Science AAAS.

4.4.4 Four-wave mixing

There is only a single beamline in the world dedicated to the study of nonlinear phenomena: TIMER at FERMI. That beamline is dedicated specifically to the four wave mixing (4WM) technique, a powerful method demonstrated with optical pulses before its more recent push into the X-ray regime. [88] In this technique, two (typically degenerate) pulses are incident upon a surface with some angle relative to each other. The positive and negative interference between the two waves generate areas which are excited and other areas which are not excited in the form of a transient grating. This allows for time scale of properties from attoseconds (if the initial pulses are

fast enough) to dynamics of hundreds of picoseconds as the system returns to initial conditions. Over time this energy will diffuse, and it can be used to study various dynamic properties such as thermal transport, coherent phonon diffusion, and ultrafast magnetism by probing it with a third wave, which scatters off the transient grating and in the process generates a fourth wave which is then detected. [29] This technique is quite important in the visible and has been used to study a variety of materials such as radiation materials, quantum materials and magnetic materials. [89–91] It is important that phase matching conditions be met such that the total momentum of the four pulses cancels out. In the case of the geometry used in typical transient grating experiments

$$\vec{k}_{FWM} = \vec{k}_1 - \vec{k}_2 + \vec{k}_3. \quad (4.11)$$

where $\vec{k}_{FWM}$ is the signal, $\vec{k}_1$ and $\vec{k}_2$ form the grating, and $\vec{k}_3$ is the probe pulse. In the general case where the grating is made up 1 frequency, $\vec{k}_1$ and $\vec{k}_2$ will be the same energy. The signal is generally time dependent due to both a long term exponential decay of the signal and the sinusoidal ‘beating’ of the signal. This generally takes the form of

$$Signal \propto |e^{-\Delta t/\tau_i} \sin 2\pi v_i \Delta t|^2, \quad (4.12)$$

where Signal is the signal, Δt is the time delay, and τ_i and v_i are the frequencies and damping times of the impulsive stimulated mode. There are a variety of prefactors which can be dependent on the specific nature of the measurement and will otherwise affect the absolute signal but not the general shape.

A higher frequency grating, and thus a higher momentum transfer and energy, allows one to go from studying molecular excitations to studying electronic excitations, in addition to the thermal and acoustic modes. This means that properties on a smaller length scale, approaching the size of a unit cell can be studied. If pulses as high energy as hard X-ray pulses were used as a grating the length scales that could be studied approach nanometers and would allow for determination of phenomena like thermal diffusion on an unprecedentedly small length scale. The length scale is limited by the wavelength of the pulses that make up the grating, so shorter wavelength allows for more microscopic information. Specifically, the spacing of the grating is given by

$$L = \lambda/2 \sin \theta, \quad (4.13)$$

where L is the spatial periodicity, λ is the frequency of light used in the grating and θ is the angle between the two pulses that make up the grating. For that reason, there has been tremendous effort put into the development of soft X-ray 4WM and thus lower λ , as soft X-rays have significantly shorter wavelengths than the UV wavelengths used previously, and is a necessary step to shorter frequencies, as well as allowing for the study of phenomena on the tens of nanometers length scale. The key to these measurements is that the transient grating must be made from relatively coherent light, as otherwise the grating will be of insufficiently high quality. Thus a seeded FEL with a beam splitter was key to making the cutting-edge measurements. [13]

The measurements were therefore conducted at FERMI, an externally seeded FEL, on SiO₂, likely chosen because it is easy to work with and made for a strong demonstration. [13] Part of the challenge is overlapping two XFEL pulses in space and time while also meeting the phase matching conditions. In this demonstration, the probe pulse used was an optical pulse, which allows for high intensity and a frequency that exploits an optical resonance, allowing for one to examine the destruction of a specific state due to the existence of the grating. The experimental and conceptual setup is shown in Figure 4.6. The phase matching conditions are also shown in Figure 4.6. Because the FEL is inherently ultrafast, it is quite simple to demonstrate the time

dependent nature of the technique. The ultrafast beating as the transient grating sinusoidally oscillates was readily detected even in these initial measurements.

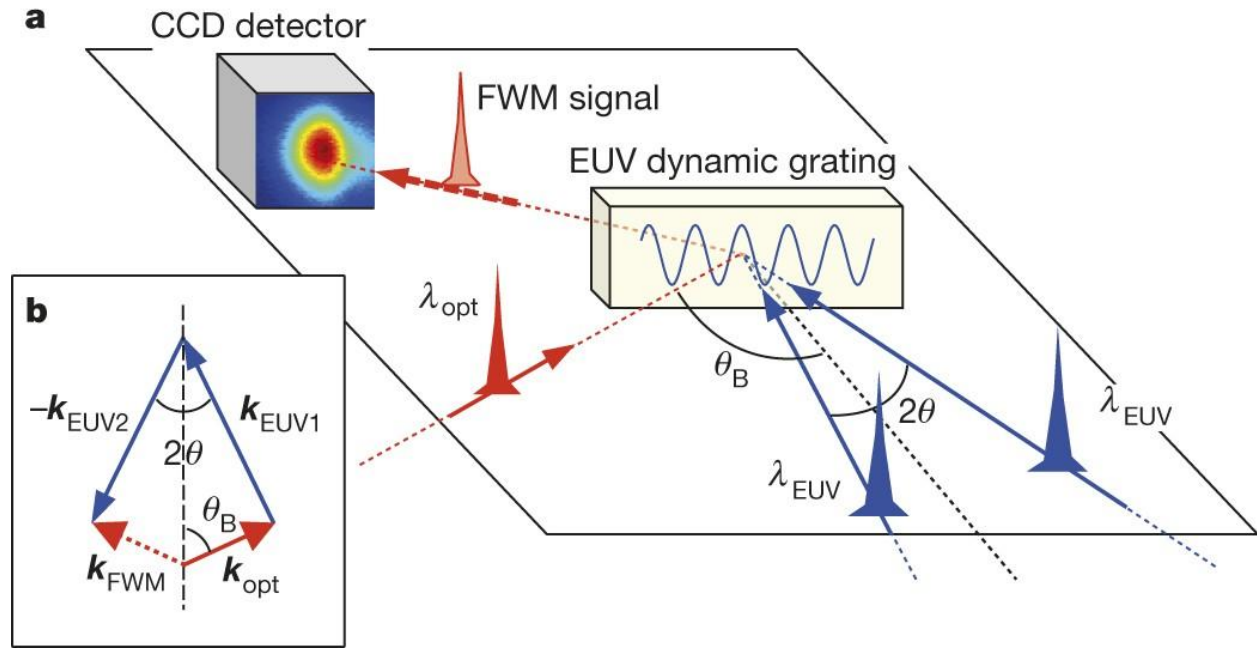


Figure 4.6 – a – Experimental schematic of FWM experiment. $\Lambda_{EUV} = 27.6$ nm and $\lambda_{opt} = 392.8$ nm were used here. The CCD is placed in the expected direction of the FWM signal beam (k_{FWM}), as determined by the phase matching conditions. B – Phase matching conditions used here where k_{opt} , k_{EUV1} and k_{EUV2} are the wavevectors of the optical and of the two FEL pulses, respectively [13]. Reprinted with permission from F. Bencivenga et al., Four-Wave Mixing Experiments with Extreme Ultraviolet Transient Gratings, Nature 520, 7546 (2015). Copyright by Springer Nature.

Using an X-ray probe pulse with an X-ray transient grating, however – a so called all X-ray transient grating experiment – would allow for one to exploit the element specific nature of X-rays as a probe, so it was perhaps inevitable that such a measurement would be accomplished. [92] By cleverly exploiting the harmonics generated at FERMI, the same group demonstrated an all X-ray experiment from both a thin and a thicker sample which allows for different experimental geometries. They were able to estimate the effective cross section for 4WM in the all XUV setup of $6 \times 10^{-24} \text{m}^2 \text{V}^{-2}$. While in this case the probe pulse was not used in a resonant scheme, this experiment clearly opens the possibility of exploiting that phenomenon.

Silicon nitride has become the most reliable standard for X-ray 4WM experiments because it's cheap, readily available, and reasonably robust. In fact, after SiO_2 , the next measurement published was on Si_3N_4 . [93] These initial measurements established that 4WM is a general technique and could be applied to a wide variety of systems, and that the systems – not surprisingly – will show different cross sections and different time constants depending on the specific material being studied. It was also discovered that these systems can have quite complicated dynamics, with Si_3N_4 displaying both a slow (extending over 100 ps) and rapid component (as fast as 100 fs can be resolved) to its time decay following excitation. The power dependence was also investigated, and the system behaved as expected indicating that four wave mixing in the X-ray

regime will behave similarly to that of optical 4WM. Perhaps the most important result of this study was showing that sample damage is going to be a problem for X-ray 4WM experiments. While certain samples can work, at present there is always a risk of sample damage before signal can be obtained and experiments must be carefully planned.

However, silicon nitride is a particularly robust sample and makes it an excellent tool for the curious scientist. Because it is so robust, Si_3N_4 was used as an example for a resonant transient grating (in this case, resonant with the Si L-edge). [94] The probe pulse remained optical, and the work was otherwise similar to the previous work on Si_3N_4 with an optical probe, the large difference being the switched pump energy. By resonantly exciting the silicon, the method of thermalization was changed dramatically as the silicon can relax by newly accessible channels involving core hole decay such as Auger and fluorescence. This led to faster dynamics when the silicon nitride is resonantly excited.

The most recent and most advanced published FEL work using 4WM concerned optimization of grating resolution. Using both Si_3N_4 and crystalline silicon as samples, the authors were able to show different dynamics between the two samples. [14] Of more significance in the long term, they used grating wavelengths of 13.3 nm spacing, producing period spacings of 28 nm. This means it is possible to observe thermal and coherent phonon dynamics on length spacings as small as tens of nanometers. At this length scale, it becomes possible to study the effects of defects in materials on phenomena such as heat flow and magnetic dynamics. It may even be possible to investigate structural effects in liquids, although for simple liquids such as water the ideal grating spacing will be even smaller, which will require using higher X-ray energies for the grating.

The most comprehensive X-ray 4WM study compared diamond, glass and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. [95] By performing Fourier analysis on the resulting spectrum, the observed signal could be assigned to Rayleigh surface waves and bulk longitudinal waves moving throughout the sample, with frequencies ranging from THz to GHz. Waves that were combinations of these waves were also observed – a combined Rayleigh and longitudinal wave for instance. $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ was found to have a coherent optical phonon mode at approximately 3 THz. The authors point out that this method can be used to generate waves of a wide variety of acoustic frequencies without the need of making a transducer. While this is true, a transducer is generally more practical and cost effective. It will be more immediately useful in explaining particularly interesting phenomena such as microscopic heat diffusion.

Finally, there has been work reported on the 4WM of silicon carbide. [96] In this case, a transient grating with a period of 84 nm was used. At these length scales the Fourier heat equations break down, but the system can be fully described by Lamb waves, elastic waves that travel along the surface. Additionally, there was a slight angular difference in the signal corresponding to the signal strength. Although not definitively shown, the authors speculate it is related to time-dependent non-isotropic changes in refractive index.

There has also been extensive work in demonstrating four wave mixing with gaseous samples using lab based HHG systems. While these sources lose the pulse power and often the energy range of FELs, they have large advantages in that the dedicated equipment is comparatively cheap and optimized for the measurements, and signal can be averaged indefinitely without needing to accommodate other measurements.

Amongst the first to make such measurements were Leone and Neumark, who led a series of measurements mixing XUV with near IR in a 4WM setup. They first demonstrated that they could drive neon into an electronically resonant state (the ns/nd state) which would then transition to the ground state. [97] They also successfully demonstrated the expected behavior with regards

to signal versus input power intensities and the expected sinusoidal decay of signal as is seen in other frequency ranges. One interesting aspect of this study was that the signal changed monotonically with increasing gas pressure, suggesting phase matching conditions are important even in these conditions. A similar result demonstrating electronic sensitivity was shown by a separate research group demonstrating ultrafast oscillations of neon. [98] The work on phase matching has been extended to really explore the detailed effects of phase matching conditions. [99]

Eventually, a noncollinear setup where the HHG pulse was offset from the two Near IR (NIR) pulses was demonstrated. [100] In this arrangement, the HHG pulse intercepts the NIR pulse, combines with two NIR photons, and generates a photon offset angularly from both the NIR and HHG pulse. This setup is highly desirable because it removes the background and also allows one to see various four wave mixing process and their different excitation pathways, and in certain cases weaker 6 wave mixing processes were observed. The research team were able to show coherent Rydberg wavepackets, which could be prepared in different ways depending upon the experimental details. They point out this is a significant step towards multidimensional spectroscopy with coherent dynamics. This would be similar to 2D-infrared but with X-ray pulses, allowing for 2D-X-ray spectroscopy. This work has now been extended to self-heterodyne, enabling even cleaner spectra, and up to eight distinct states in the case of helium. [101] The more states that can be seen, the more accurately the electronic structure of the material can be understood.

It was subsequently demonstrated that dynamics as fast as attoseconds could be probed. First, krypton was studied and dynamics as fast as 22 fs were demonstrated. [102] However, because the technique is so sensitive, multiple different decay channels with different decay times are all simultaneously accessible. Because the signal is convoluted by all these decay channels determining the ultimate time resolution is difficult, but probably was noticeably faster than 22fs. This was later proven by some of the same authors. [103] Ultimately, by working with attosecond XUV pulses in helium mixed with few cycle NIR pulses, they demonstrate that the resolution approaches hundreds of attoseconds. It is certainly better than 1.5 fs which can be determined from the higher order diffraction peaks from the transient grating and could be assigned based on excellent matching with the Maxwell-Schrodinger equation.

One clever variation of four wave mixing is to use three nondegenerate pulses. While this makes the experimental setup more difficult, it enables the effect of each individual pulse to be separated and studied in a simpler manner. This has been accomplished and was used to study lifetimes of argon as short as 200 fs. [104] Such a setup may ultimately have limited time resolution as mixing three separate pulses inherently increases jitter and uncertainty. However, this is not a theoretical limit, and subsequent work did claim substantially higher time resolution (probably approaching 10 fs). [105] The ability to have three separate pulses may prove important in the demonstration of future multidimensional measurements.

Four wave mixing has already shown uses beyond simple demonstration spectroscopy. It has been used to narrow the bandwidth of XUV pulses, and such a scheme should be extendable to the X-ray regime. [106] However, this is probably not necessary for seeded FELs which have intrinsically narrow bandwidth. Finally, we wish to note that 4WM been extended into the hard X-ray regime, albeit using a very different setup. [107] For matters requiring investigations on the truly atomic scale, hard X-ray 4WM provides a unique probe for which there are no currently existing analogous techniques.

4.4.5 Soft X-ray second harmonic generation / sum frequency generation

As discussed above, one of the most common uses of nonlinear optics is to combine waves. When one combines two waves through either SFG or SHG the signal will only be generated when there is no center of inversion, i.e. the measurement occurs at a place that lacks centrosymmetry. This is generally, although not always, surface and interfaces. This centrosymmetry argument does not hold when one combines three photons to generate a fourth, as in 4WM. Broken inversion symmetry can be shown to be essential for even order nonlinear processes by considering the expansion,

$$\vec{P} = \epsilon_0 \sum_{i=1}^n \chi^{(i)} \vec{E}^i, \quad (4.14)$$

where $\vec{P}$ is the polarization, ϵ_0 is the permittivity of free space, $\chi^{(i)}$ is the nonlinear susceptibility of order i , and $\vec{E}^i$ is the electric field associated with order i and n is the arbitrarily large polarization expansion. If the inversion is defined as $I_{inv} \vec{P} = -\vec{P}$ then it can be shown that

$$I_{inv} \vec{P} = -\vec{P} = I_{inv} (\epsilon_0 \sum_{i=1}^n \chi^{(i)} \vec{E}^i) = \epsilon_0 \sum_{i=1}^n (-1)^i \chi^{(i)} \vec{E}^i, \quad (4.15)$$

and adding the first equation to the second yields

$$\vec{P} - \vec{P} = 0 = 2\epsilon_0 \sum_{i=1}^{n/2} \chi^{(2i)} \vec{E}^{2i}, \quad (4.16)$$

Proving that the signal will be zero when the process is even order and inversion symmetry is present. This argument does not hold in the hard X-ray regime for both SFG and SHG. [36,37] This is because in this regime, as the wavelength is on the order of the density fluctuations in the electron density of a material, in essence everything becomes a surface and SFG/SHG signal is generated in the bulk causing the previous equation to break down at small wavelengths. At these particularly short wavelengths the dipole approximation can also become inadequate, as the electric field may not be constant over the length scale of the excited transition. What would happen in the soft X-ray regime, with photon wavelengths between visible and hard X-ray, was not obvious before the soft X-ray SHG measurements were made. Typically, soft X-rays processes are dipole selected, but this had not been proven for even order nonlinear processes.

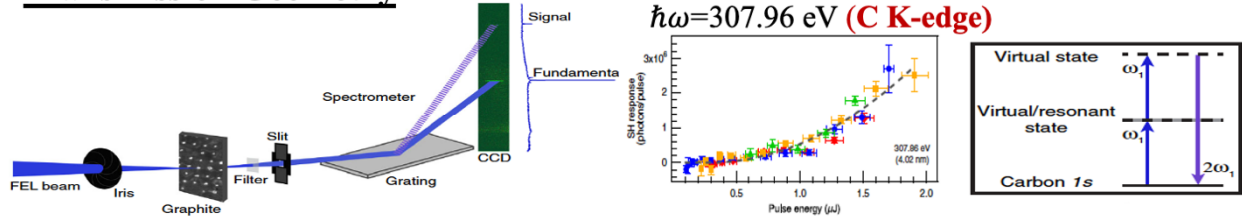
The pioneering demonstration of SHG in the soft X-ray regime used graphite samples in transmission mode, exploiting the coherence of the FERMI FEL source. [6] Signal was observed at incident photon energies below the carbon K-edge, resonant with the carbon K-edge and above the carbon K-edge, but generally close to the carbon K-edge. A quadratic power dependence in accordance with theory was seen. DFT calculations were also performed to try to simulate the spectrum, but with only three experimental energy points the simulations could not be fully validated by experiment. More significantly, both the calculations and the experiments showed that the measurements were surface sensitive. This was done theoretically by determining the signal as a function of slab thickness and noting that it saturates after about 4 atomic layers. Experimentally, SHG signal was shown to be constant for transmission samples of varying thickness, implying that signal was generated only from the front and back surfaces. This measurement was performed in a single shot mode, where the graphite films were destroyed with each shot. The experimental geometry (transmission) is detailed in Figure 4.7A.

A different research team simultaneously conducted separate SXSHG measurements at SACLA, studying a noncentrosymmetric crystal, GaFeO_3 , at the Fe M-edge. [7] This contrasts with the previous experiments at FERMI, but by using a bulk crystal these measurements were made in a reflection geometry, and perhaps most significantly, below the damage threshold, meaning the measurements can be made on rare and hard to produce samples. In this case several energy points near the Fe M-edge in double resonance were measured and with enough energetic data points to

be able to show definitively that SHG occurred. Once again the expected quadratic signal was observed. The reflection geometry and associated theory is shown in part B of Figure 4.7. These two measurements collectively demonstrated second harmonic generation at input frequencies that were resonant with the one photon transition, generating a photon at twice the resonant frequency (2ω), as well as input frequencies that are half the resonant energy of a single electron transition, generation photons at a frequency of ω .

A)

Transmission Geometry



B)

Reflection Geometry

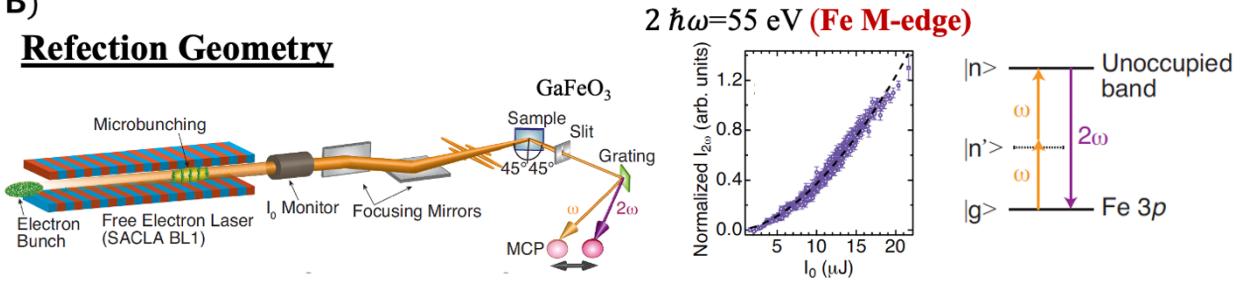


Figure 4.7 – A) Experimental setup of a transmission experiment on graphite performing SXSHG at FERMI free electron laser (left). In this experiment, pulses were transmitted through sheets of graphite at roughly resonant with the carbon K-edge (right) generating signal at roughly 600 eV and a quadratic dependence with no thickness effect was seen (middle). This suggests SXSHG is largely surface sensitive [6]. Reprinted with permission from R. K. Lam *et al.*, Soft X-Ray Second Harmonic Generation as an Interfacial Probe, Phys. Rev. Lett. **120**, 023901 (2018). Copyright (2018) by the American Physical Society. B) Experimental setup of a reflection experiment on GaFeO_3 performing SXSHG at SACLA (left). In this experiment, pulses at half resonance (right) were reflected off the sample. Once again a quadratic signal dependence on input power was observed [7]. Reprinted with permission from Sh. Yamamoto *et al.*, Element Selectivity in Second-Harmonic Generation of GaFeO_3 by a Soft-X-Ray Free-Electron Laser, Phys. Rev. Lett. **120**, 223902 (2018). Copyright (2018) by the American Physical Society.

A study of boron films covered by a thin 100 nm layer of a polymer was conducted in transmission mode. [108] This boron/polymer interface was chosen as an example of a buried interface, which are generally difficult to probe with existing experimental methods. In this case, by tuning the FEL source to the boron K-edge, the X-rays passed through the polymer which contained no boron and were thus only probing the boron layer. Distinct spectra were observed for the boron/polymer (B/P) interface compared to a bare boron control sample, and the researchers were able to determine the separation between the polymer and the boron layer to within $\sim 0.2 \text{ \AA}$.

by comparing calculations to experiments. In comparison, XAS of boron/vacuum and boron/polymer were roughly identical as shown in Figure 4.8. One of the advantages of this study over the previous carbon work was more spectral points, enabling a better interpretation of the data. This is a measurement which is only currently possible with soft X-ray SHG (SXSHG). No other techniques can both penetrate to the buried interface and offer the high sensitivity demonstrated in the SXSHG data.

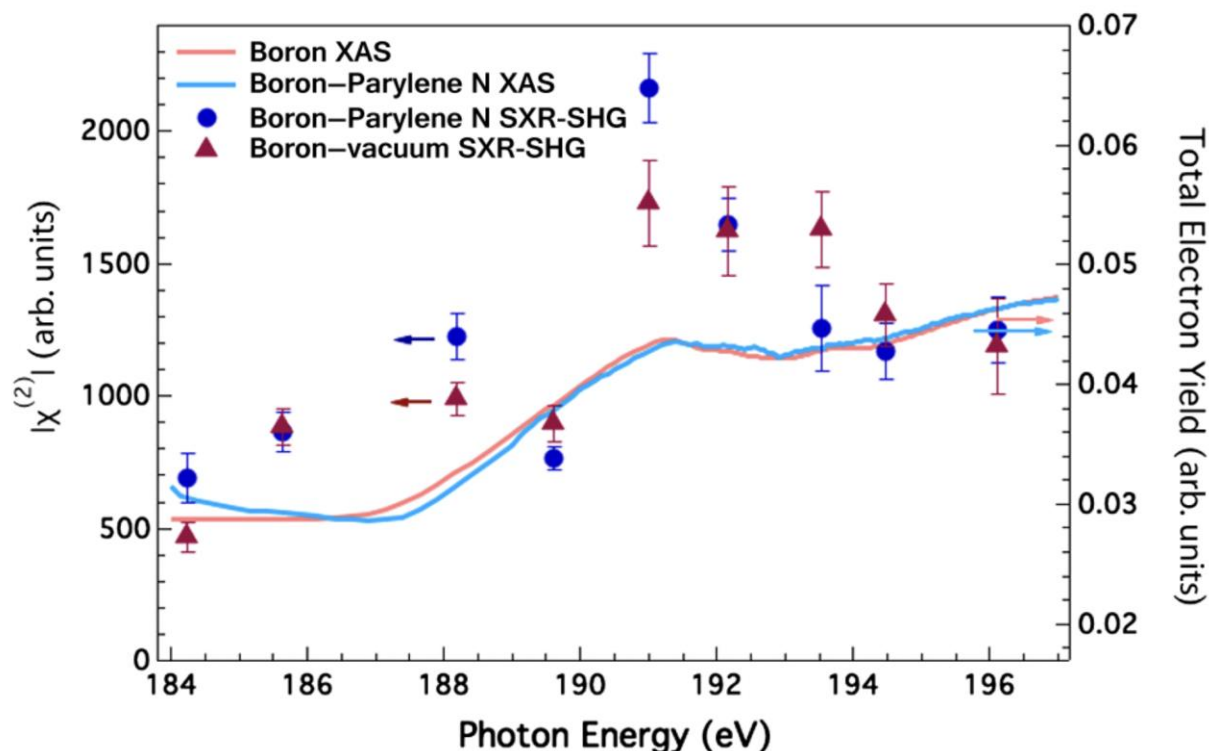


Figure 4.8 – SXSHG spectra of boron/vacuum (B/V) and boron/polymer (B/P) interfaces. B/V (dark red triangle) and B/P (dark blue circle) interfaces, shown along with the linear XAS of boron (light red line) and boron/polymer (light blue line), with arrows showing the appropriate y axis. The difference in XAS is believed to be due to differences in the background, whereas the SXSHG signal is significantly different [108]. Reprinted with permission from C. P. Schwartz *et al.*, Angstrom-Resolved Interfacial Structure in Buried Organic-Inorganic Junctions, *Phys. Rev. Lett.* **127**, 096801 (2021). Copyright (2021) by the American Physical Society.

Using the same setup, several more measurements have been performed that take advantage of operating below the damage threshold. Lithium osmate is a so-called polar metal below a transition temperature, [109] meaning it no longer has centrosymmetry and SHG was easily observable. However, when the temperature was raised and the crystal undergoes a phase transition into a centrosymmetric state, no signal was observable. The SHG spectra were used to determine the lithium bond distances in the crystal based upon comparison to calculations. While this information can also be obtained from other techniques like neutron scattering, performing this experiment spectroscopically allows for the possibility of studying the system following an excitation laser pulse. It should be possible to watch the system ‘recover’ into the polar metal

state, as the detailed way in which this transition occurs is not presently known. Such a measurement should now be possible with SXSHG.

Another measurement was made on lithium niobate. [110] This is a standard non-centrosymmetric crystal used in nonlinear optical measurements, for example as an optical parametric oscillator. [111] In this case, the lithium and niobium peaks overlap spectrally, so the resultant SHG spectrum was quite complicated. However, with the aid of calculations even spectra with contributions coming from more than one element can be disentangled. The most important result from this study is that, as is seen in the visible, there is a polarization dependence to the signal at a given energy. [112] This can be used to understand the symmetry of a crystal in the visible, but at X-ray energies it reveals the symmetry around a given element. By measuring a wide variety of different angles, it is possible to obtain detailed polarization analysis. It additionally confirms that SXSHG is dipole selected. This method of using a polarizer to detect SHG has potential in that it efficiently suppresses the background, but the mirrors only function within a limited spectral range. This can be mitigated using multiple sets of different mirrors. This of course increases the equipment cost, but given the expense of FEL experiments, the expense could be considered minor.

More recent studies have moved beyond fundamental physics to probe chemistry. A recent work demonstrated that in a solid-state battery system, a large spectral shift was seen between the surface SHG measurements and the bulk absorption measurements. [113] Because of the sensitivity of these measurements, the shift could be assigned to the lithium having more freedom to move (fewer librational constraints) at the surface than in the bulk. This is an important structural property for battery designs and is the cause of the previously unassigned large surface resistance seen in a variety of solid-state batteries. This implies a means of mitigating this problem through careful battery design.

There has also been a successful demonstration of two NIR photons and one XUV photon combining in a variation of SFG on LiF. [9] Working below damage required using the three photon scheme so the signal would be bulk sensitive, as the two photon transition was likely too weak to be measured at the relatively low fluences used here. The authors demonstrated both SFG (XUV + two NIR photons) and difference frequency generation (DFG) (XUV – two NIR photons). They also showed that the overlap between the NIR and XUV photon must be relatively precise, or else the signal drops to zero as is expected. Interestingly, the observed line width was sharper than the bandwidth of the FEL pulse, which suggests the spectral limit is due to the excitonic LiF state probed. This has potential use in the development of high-resolution spectroscopy at FELs, although may not be particularly useful at seeded FELs.

Finally, we should note there has been a SXSHG measurement made without an FEL. [114] Using a large laser system with a power of $\sim 10^{11}$ W/cm², which is roughly 5 orders less power density than typical from an FEL, SXSHG was successfully demonstrated in lab at the titanium M-edge. This opens the possibility of performing these types of measurements in labs going forward and hopefully one day will negate the need for a national facility such as an FEL. This particular system, however, is substantially larger than an HHG source and lacks the tunability of a FEL. However, there has been large progress in the development of lab based X-ray sources.

Thus, SXSHG represents a technique with great potential for studying surfaces and buried interfaces, dynamics of noncentrosymmetric materials, or dynamic symmetry breaking in centrosymmetric materials. It is maturing as new detection schemes become available and a variety of methods to understand the resultant spectra have been developed. New FELs such as

LCLS-II and developments in lab based light sources may make this technique a standard technique for surface studies in the future.

4.5 Theoretical calculations for the spectral analysis

It was only shortly after the laser was invented that the first nonlinear optics measurements were made. [3] This was possible because theoretical predictions made well in advance of the development of the laser had predicted the phenomena, and to some extent even how to perform such measurements. This has been true to some extent also in the field of X-ray nonlinear optics, with measurements such as hard X-ray SHG having been guided by earlier theoretical work. [37] The guiding theory has taken on a variety of forms, and the most widely used conceptual frameworks are discussed further here.

Since nonlinear optics are well established in the visible, theoretical frameworks used in the visible can be applied in the soft X-ray regime in certain cases as both are dipole selected and have similar selection rules. Perhaps the clearest example of this was the study of LiF by four wave mixing, [9] where the measured single photon X-ray absorption data was combined with reflectivity and known nonlinear optical constants to predict the sum and difference frequency generation spectra. [5] This type of technique, where well established laws of physics in the visible can be applied to a problem in the soft X-ray regime, is quite powerful when adequate information about a system is known. But well-established values and equations must exist, and this is not always, or even generally, the case.

Because of limited information in most cases in X-ray nonlinear optics, such an approach is not generally applicable. More general approaches such as those that propagate motions of atoms, electrons and fields are available, including techniques such as velocity gauge real-time time dependent density functional theory (VG-RTTDDFT). [115–117] This method is, like many used for calculations involving soft X-ray nonlinear optics, incredibly expensive, but it gives accurate results and can describe a wide variety of phenomena, including second harmonic generation, sum frequency generation and multiphoton absorption and can potentially be extended to simulate other measurements. This method works by propagating the fields, the motions of the electrons, and the motions of the atoms in a real-time formalism. This means in principle it is possible to describe the electronic structure and the resulting change in electronic structure as a function of time as fields interact with the system. There is another approach, based on the first principles calculation, that uses the Korringa-Kohn-Rostoker (KKR) method. The calculation can be made by the software, such as AkaiKKR(Machikaneyama). [118,119] In the method, the second order susceptibility for SHG is expressed with the Green's functions and the dipole matrix element that are calculated by the density functional calculation. The calculation successfully reproduced result of the soft X-ray SHG experiment. [7] The technique is highly feasible and it can easily be applied to the non-uniform system, such as impurity or superlattice. Such a technique is inherently powerful, but the computational expense means it requires large amounts of supercomputing time and is limited to relatively simple systems.

For this reason, there has been significant effort put into extending cheaper methods that exist in the visible but did not yet exist in the X-ray region, particularly using linear response. [6,120,121] While linear response techniques are almost universally cheaper than RTTDDFT, they come with their own costs. First, the formalism must be built to solve a relatively specific problem or class of problems. Secondly, the formalism must be tested to ensure that it works and provides reasonably accurate results. Since nonlinear X-ray optics is a new field, there

is often no data to test against, and the ability to perform tests at high fields is limited by FEL time which is difficult to obtain. [34] This is particularly true if the experiment is seen as risky, as may happen if it is based on highly original and possibly controversial theoretical work. There is at present no easy solution to this other than for more free electron lasers and more supercomputers to be built, but this is an expensive solution and one that will likely not be readily championed by governments around the world.

Still, some interesting and powerful methods have been developed. Perhaps some of the nicest examples of this have been in the variety of methods used to describe advanced X-ray Raman techniques. [21,85,86,122,123] These have proven very useful in the development of novel and X-ray specific forms of Raman spectroscopy, as the specific measurements appear to have been simulated in detail before they were initially attempted, leading ultimately to the initial demonstration of stimulated Raman. However, several of the suggested forms of Raman either have not been made to work yet, or may prove ultimately impossible to perform due to some yet unknown issue with the calculations. Still, attempting to develop theories which can be tested is an important aspect of development of nonlinear X-ray spectroscopy and should be encouraged.

Going beyond this, several authors, among them Mukamel and Santra, have been engaged in forward looking theory, supporting experiments that may be feasible in 10, 20 or 50 years but are not feasible currently and do not look to be feasible in the immediate future. [124–128] This can serve the purpose of inspiring long-term experiments and goals for large national and international facilities. It also promotes thinking about dream experiments and the ultimate limit of what could be achieved with X-ray nonlinear optics.

However, one opportunity for real advancement in X-ray spectroscopy in general, and in nonlinear optics in particular is the development of predictive actionable theories. While there is certainly value in predicting experiments with four rotatable, phase and mode locked attosecond, infinitely tunable Fourier-limited FEL pulses, a real opportunity for growth where new theorists could enter is in performing calculations to guide and inform currently feasible experiments. Even for problems where there exists adequate theory to calculate spectra, the methods are often too expensive to be performed in advance of the experiment. For instance, performing VG-RTTDFIT is quite expensive, and makes performing calculations of spectra in advance of an experiment, when it is still not known whether the measurement will work. In practice, the theorists who have worked on SHG as of the time of this writing have always only offered to calculate results after the experiment was completed. Thus, there certainly would be a welcome niche for potentially less accurate, but significantly cheaper and therefore more predictive calculations, because they can be used to guide experiments. Given the incredible expense of FEL time (approaching \$10,000 an hour [129]), such an investment in theory might also make sense financially even if it requires a relatively large investment in supercomputing time.

4.6 Summary

The development of high intensity X-ray sources has opened the door into a whole new field of X-ray physics. In the soft X-ray region, nonlinear optics has been shown to be quite similar conceptually to work that is already present in the visible with the added benefit of shorter wavelengths and atomic specificity. Rapid progress has been demonstrated on a wide variety of fronts, ranging from multiphoton absorption to wave mixing. As progress on both sources and experimental setups continue and are in their early stages, we expect to see rapid progress.

Theoretical efforts in certain cases have guided many of the existing experimental methods and hopefully will be even more important in the future.

The early work laying the foundations of a variety of soft X-ray nonlinear optics measurements has now largely been done, and now the community must begin the process of making more useful and less proof of principle measurements. The ability to do this will depend on a variety of experimental and theoretical developments. Of particular benefit to the experimentalists would be phase locked coherent attosecond lasers with high pulse rates and high repetition rates, beam splitters, flexible mirrors and generally anything which makes soft X-rays more flexible to work with. This will enable measurements which are not just analogous to the measurements made in the visible but can push beyond that, exploiting X-ray photons sensitivity to core excitations and the ability to control electronic structure in a novel manner.

Acknowledgements

We thank Hisazumi Akai for his comment on theoretical calculation of nonlinear spectral analysis. We appreciate Tomoaki Senoo, XingYu Su, Toshide Sumi and Iwao Matsuda for editing and revising the chapter. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC-0023397.

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