A proposal for fs-electron microscopy experiments on high-energy excitations in solids

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**A B S T R A C T**

Recent advances in ultrafast technology enable both the study and the control of materials properties thanks to the ability to record high temporal resolution movies of their transformations, or the ability to generate new states of matter by selecting ad hoc an excitation to drive the system out of equilibrium. The holy grail of this type of experiments is to combine a high tuneability of the excitation with a wide observation window. For example, this is achieved in multidimensional optical spectroscopy where the response to several excitation energies is monitored in a broad energy range by a large bandwidth optical pulse. In this article, the possibility to combine the chemical sensitivity of intense tuneable X-rays pulses from a free electron laser, with the wide range of observables available in an ultrafast transmission electron microscope is discussed. The requirements for such experiments are quantified via estimates based on state of the art experiments and simulations, and it is proposed that ultrafast electron imaging, diffraction and spectroscopy experiments can be performed in combination with a chemically selective X-ray excitation of materials.

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1. Introduction

The development of fs lasers opened the possibility to investigate the temporal evolution of photoexcitation in solids and molecules. The research field of transient states in molecules has been referred to as femtochemistry (Zewail, 1994), and ultrafast spectroscopy has been successfully applied to several domains including solid state and biological physics (Chergui and Zewail, 2009). Despite the huge potential and the evident success of these techniques, some limitations to their applicability persisted over the years, confining them to specific situations. In a nutshell, while it is often possible to measure the value of a given physical quantity by a large choice of static techniques, the out-of-equilibrium nature of time-resolved techniques makes their output more specific and its theoretical modeling more challenging and less direct. This is due to the need of referencing in time the observable, which is typically done via photoexcitation, and therefore is an intimate characteristic of such experiments. There has to be a well-defined excitation in time to be able to probe the temporal evolution of a system. Naturally, when the ground state properties are already elusive, the description of its excitations and its out-of-equilibrium state is a further complication. In molecules, this issue has proven less severe than in solids because electronic excitations are more univocally described and have smaller coupling with the other degrees of freedom, allowing for a better description of the pump excitation process. On the contrary, if one considers strongly correlated systems, many-body effects induce a broad spectrum of complex electronic states extending all the way to the visible-light region (Maldague, 1977; Stephan and Horsch, 1990), often making the description of the photoexcitation challenging.

Recent advances in ultrafast technology provided a large variety of observables. Depending on the phenomenon investigated, nowadays time resolution between ms and as can be achieved with X-rays and electrons, giving direct information on both the structure and the chemistry of materials via either diffraction or spectroscopy (Carbone et al., 2012). Free-electron laser facilities guarantee a unique X-ray flux in a highly transversally coherent beam, capable of few fs time resolution (Chapman et al., 2006; Rosenzweig et al., 2008; Ding et al., 2009), while state of the art electron-beamlines and transmission electron microscopes offer higher sensitivity and versatility at the cost of coherence and to a less extent time resolution (Fulvia Mancini et al., 2012; Siwick et al., 2003; Raman et al., 2008; Aidelsburger et al., 2010; Van Oudheusden et al., 2010; Musumeci et al., 2010; Hastings et al.,...
2006; Eichberger et al., 2013). Despite this, transverse coherence can be increased using larger beam sizes.

In short, current ultrafast techniques allow the direct observation of the out-of-equilibrium properties of materials via both structural probes and broad-band spectroscopy. The need for photoexcitation and consequently the observation of a perturbed system is a key aspect, especially for the study of complex materials, where a great challenge lies in the understanding and description of the lowest energy excitations of the ground state, which would seem logical to observe by the least perturbing possible probes. This said, a great potential hides in time-resolved experiments: if the excitation is carefully prepared (Fausti et al., 2011; Mansart et al., 2013), it can decay on a well-defined final state, and the real-time observation of the latter can have major advantages: (i) not only the amplitude, but also the phase of the wave-function describing such a state can be obtained, (ii) the temporal evolution of different many-body objects, i.e. their consequentiability, can also be obtained and therefore the evolution of a system through a phase transition can be described in much more detail (Mansart et al., 2012). The following two examples can clarify this point:

- **Graphite:** the phonon spectrum of graphite has been known for almost a century. Despite this, only recently it was discovered that some of the vibrational modes couple to the electronic structure in a particular sequence, giving rise to photoinduced structural changes that can even turn graphite into diamond during a few fs, a process that takes ages under extreme conditions in nature (Raman et al., 2008; Carbone et al., 2008; Harb et al., 2011; Carbone et al., 2009; Kanasaki et al., 2009; Acocella et al., 2010). These results shed new light on the dynamics of the structure of graphite which could not be inferred by the knowledge of its equilibrium properties.

- **High temperature superconductors:** In recent ultrafast experiments on high-temperature superconductors (Mansart et al., 2013), 1.5 eV photons were used to induce a direct transition between the ground state of the material and higher energy electronic states, ascribed to the excitation of charge stripes and the Cu-O charge transfer bands (Lorenzana and Seibold, 2003; Uchida et al., 1991), see schematics in Fig. 1B. In a conventional static Raman experiment, as depicted in Fig. 1A, one can excite the system with a continuous wave (CW) photon beam at 1.5 eV and analyze the Raman-shifted outgoing photons, obtaining the energy spectrum of the low-energy excitations, structural and electronic. In a pump-probe experiment, the final state after impulsive excitation at 1.5 eV is the same as in a static Raman experiment. Only this time, instead of analyzing the outgoing photon, one probes the system with weak non-perturbing fs pulses while the excited state still survives (few ps after excitation). As a result, an equivalent of the Raman spectrum is obtained in the time domain, Fig. 1C and D, via the Impulsive Stimulated Raman Scattering mechanism (ISRS). This scenario is confirmed by the agreement between the data (FFT) and conventional Raman experiments (Sugai et al., 2003), in Fig. 1E and F. These results provided the first observation of the coherent oscillation of the Cooper pair condensate in the time domain.

The aim of this article is to propose a new class of experiments that can exploit the ISRS mechanism to provide a selective population of the different excited states and at the same time combine the advantages of pulsed X-rays and electron beams for the investigation of solids. Particular emphasis is put in the discussion on the advantages of a chemically selective excitation, as achievable via X-rays. In what follows, the technical requirements and the feasibility of experiments based on an X-ray photoexcitation and an EM probe will be discussed. A quantitative discussion of what type of excitations and physics can be probed in solids by such a technique is proposed. These ideas borrow concepts from the community of ultrafast technology, electron microscopy and condensed matter physics, and provide an interdisciplinary challenge aimed at exploiting the most recent technologies made available worldwide.

### 2. The role of the excitation in time-resolved experiments

As was briefly introduced above, a key ingredient of this discussion is the preparation of the excited state via the photoexciting pulse. In fact, not only are X-rays a unique tool for probing materials and molecules, they also provide the possibility to create chemically selective excitations. Typically, ultrashort laser pulses in the visible light region are used as a pump because of their easy availability. In this energy range, temperature jumps, charge transfers, and phase transitions can be triggered. However, at these energies, the strong orbital hybridization makes the chemical selectivity of the pump absent in many systems, and in some cases like strongly correlated solids, it is often very hard to decipher the effect of light excitation in the sample, since a thorough description of the static optical absorption can be lacking or be model dependent. Very novel and interesting experiments have been put forward where a more precise selectivity of the excitation has been obtained via the use of THz pump pulses (Fausti et al., 2011). In the low energy region of the infrared spectrum, light can excite selectively atomic motions, providing a way to distort “ad hoc” the structure of a system for probing its consequent dynamics. This approach takes advantage of the interaction between light and low-energy many-body bosonic excitations and allows a direct manipulation of collective modes in materials. However, because of the way THz pulses are generated and their intrinsic characteristics, sub-ps temporal resolution is often challenging. Another possibility to achieve selectivity, although local, in the excitation would be to use X-ray pulses tuned to specific core levels while monitoring the consequent dynamics with another photon or an electron pulse.

In the case of pump–probe experiments in high-temperature superconductors, it is clear that in certain circumstances one can regard a pump–probe optical experiment as a resonant Raman experiment. The main difference is that instead of detecting the outgoing photon and its polarization, to obtain the low-energy excitations spectrum, information is obtained directly in the time domain via an appropriate ultrafast probe. In the end, by Fourier transforming the time-domain probe signal, one ends up with a Raman spectrum. In addition, the time domain observation yields the phase of the probed state and its temporal evolution through phase transitions. In this context, as much as Resonant Inelastic X-ray Scattering (RIXS) provides additional information with respect to low-energy Raman experiments (Ament et al., 2011) thanks to chemical and orbital selectivity, an (X-ray pump)-(time resolved probe) experiment would take advantage of the same benefits. In RIXS, resonance with certain core-levels can greatly enhance the inelastic cross-section, i.e. the population of excited states; X-ray photons can also probe the dispersion of low-energy excitations and can even differentiate between different sites occupied by the same element, if they have distinguishable absorption features. In the energy range of the L-edge of transition metals, X-rays have a penetration depth of few hundreds of nm, matching both the penetration depth of high energy electrons and infrared light. One of the main challenges of a RIXS experiment is the presence of a relatively broad elastic peak whose tail hides the lowest energy excitations (in the THz, meV regime). On the contrary, the technique is very effective for energy losses in the region of a fraction of an eV to a few eV. This behavior is complementary to the performance of time-resolved experiments, because in this case, the lowest energy (meV, THz) excitations translate into slower oscillations requiring few tens to few hundreds of fs time resolution. The high energy
Fig. 1. (A) Schematics of a Raman experiment (left), and static Raman spectrum in a La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) high temperature superconductor. (B) Scheme of the Raman process involved in an ultrafast ISRS experiment. (C and D) Temporal evolution of the optical susceptibility of LSCO in different Raman geometries, B$_{14}$ and B$_{2}$, respectively. (E and F) Fourier transform of the temporal traces and comparison with the static Raman spectra of the superconducting gap in LSCO.

Adapted from Mansart et al. (2013) and Sugai et al. (2003).

features like charge transfers instead are found in the eV region, requiring a temporal resolution within the single fs regime. This concept is depicted in Fig. 2, where we show the typical excitations observed via RIXS; the graph is adapted from Ament et al. (2011), and a temporal scale was added to the top of the panel, making the correspondence between the energy of the electronic states and its consequent time-period. In one example, the low-lying orbital excitations (orbitons) which are speculated to be in sight within the elastic peak of a conventional RIXS experiment may be visible in a time-resolved measurement as a hundreds of fs oscillation of the probed quantity. Moreover, looking at the example of the ultrafast response of LSCO, the THz Raman spectrum of a high-temperature superconductor was obtained through a time domain experiment, with no information on the dispersion of the observed features. Tuning the photoexcitation to an appropriate core-level and taking advantage of matrix elements and selection rules, one could perform an experiment that is sensitive also to the dispersion of the electronic states and, more importantly, will have a better chemical and orbital sensitivity. Chemical selectivity of X-rays has been also proposed to induce photodoping in materials through cascade decay processes of the electron hole pairs, or by directly promoting itinerant carriers in valence band orbitals (Campi et al., 2003). This said, in any pump-probe experiment, a certain amount of unwanted excitations will be present. For example, ultrafast excitation of perovskites often results in strong coherent phonons being excited together with the electronic excitations (see the La vibration mode observed in Mansart et al. (2013) for example). However, the ability of an EM to combine diffraction, EELS, (Piazza et al., 2013a) and imaging would give further ability to disentangle the different excitations during the probing.
3. Quantitative analysis of an X-ray pump-TEM probe experiment

3.1. The fs-TEM probe

Currently, fs-resolved TEMs operate in the regime of 1–10 electrons per pulse at repetition rates between 200 kHz and 2 MHz (Piazza et al., 2013b; Zewail, 2010). Overall, the number of particles per second ranges from $10^3$ to $10^7$, of which only 10% are detected by the most common cameras. Since the temporal resolution is obtained by simple modification of commercial TEM columns, these machines preserve the versatility characteristics of TEMs and can operate in a variety of modes including imaging, diffraction and analytical microscopy. XFEL sources can on the other hand provide repetition rates between few Hz (Elettra, 2014) and tens of kHz (xfel, 2014). Therefore, to retain the same signal per second in the TEM probe, the electron pulses should contain between $10^3$ and $10^4$ particles each. To have such an amount of charge in a sub-ps pulse and yet retain the energy spread within few eV and the spatial coherence required for imaging and diffraction, a careful design of the TEM source and column is needed.

The spatial or transverse coherence length is given by $L_\perp = \lambda / \Delta \theta$, with $\lambda$ being the de Broglie wavelength and $\Delta \theta$ the uncorrelated angular spread. In order not to waste any electrons, the beam diameter $D$ should be matched to the sample size. Then the proper figure of merit for spatial coherence (transverse beam quality) is the relative coherence length $L_\perp / D$, a conserved quantity which is inversely proportional to the normalized emittance $e_n : L_\perp / D = \lambda_c / (4e_n)$, with $\lambda_c = \hbar / mc = 2.43$ pm the Compton wavelength. For amplitude contrast imaging at 100 keV with near-atomic resolution a relative coherence length around $10^{-3}$ is ideal, i.e. $e_n = 0.5$ nm-rad. Similar numbers are required for the most demanding diffraction measurements, i.e. diffraction of micron-sized protein crystals or nano-diffraction of solid state samples. However, by properly correcting aberrations, imaging with sub-nm resolution is possible also with a completely incoherent source (Pennycook and Jesson, 1990). A normalized emittance of 0.5 nm-rad can in principle be achieved by photoemission with a micron diameter.
the bunches together with the results of GPT simulations (blue and black lines).

Using this model, we can then investigate the effect of inserting a radiofrequency cavity for beam compression in the column. A radio-frequency TM_{010} mode cavity resonant at 3 GHz was inserted at z = 60 cm from the virtual cathode source point to compress the bunch. Preliminary estimates indicate that it is possible to obtain 10^3 particles in <200 fs at the sample with comparable transverse beam quality with current designs. Since the mechanism for compression is to accelerate the particles in the back of the beam and decelerate the ones in the front, a larger beam energy spread is induced by the cavity. This does not present a major problem for diffraction and imaging, although the latter can be affected by chromatic aberrations, but it certainly hinders the possibility of high resolution spectroscopy. With a combination of multiple (not just one) longitudinal lenses then one could design a “condenser” stage for the time-energy phase space and control both the beam bunch length and energy spread at the sample. We leave this possibility as a topic for further more detailed study. In the inset of Fig. 3, the pulses duration and energy spread are displayed for an RF compressed beam.

It is important to notice at this point that the imaging performances of such an instrument will be different from those of a conventional TEM. However, when combining space and time resolution, no technique exists which is capable of reaching fs and nm resolution in time and direct space simultaneously. There is a great deal of phenomena that could be investigated successfully with a spatial resolution of tens to hundreds of nm and fs temporal resolution. To name a few, direct imaging of magnetic domains and their motion could be performed. Also, the dynamics of the vortex lattice in superconductors, or the temporal evolution of charge domains and phase separation are topics for which the ability to combine time and direct-space imaging will be a breakthrough. In a TEM, bright field and dark field images already give a contrast to morphological features of a specimen, while in out-of-focus Lorentz microscopy enhanced contrast to magnetic domains and charge patterns can be obtained (Cottet et al., 2013).

3.2. The XFEL pump

The impulsive stimulated Raman scattering effect has been exploited for the study of coherent structural and electronic excitations via the observation of changes in the optical constants.

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**Fig. 3.** Electron pulse duration and energy spread as a function of the beam charge. Inset: bunches duration and energy spread for an RF compressed beam. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)
For visible-light pumps, absorbed fluences in the range of 100 μJ/cm² per pulse have been used for photoexcitation. In typical pump-probe experiments, such an excitation is found to produce a background of linearly excited particle-hole pairs on top of the desired Raman excitations. In the example from Mansart et al. (2013), it was possible to obtain about $10^{-3}$ to $10^{-2}$ IRS excited states per site, yielding a signal in the order of $10^{-3}$ in variation of the dielectric function. In recent fs-resolved electron scattering experiments, signals of similar strength have been detected successfully.

To estimate the yield of the Raman excited particles per site for excitation with X-rays one needs to estimate how many photons are absorbed by the material at a given energy. For the example we used, LSCO, it is well known that the Cu L-edge (930 eV) provides a very good yield for resonant Raman experiments (Ament et al., 2011). At this energy, the absorption of a 200 nm sample, ideal thickness for being transparent to 300 keV electrons, accounts for about the 70% of the impinging beam (Henke, 2014). For an XFEL pump, each pulse can be expected to contain around 10^{12} photons. If one considers these photons to be absorbed in a volume of $\pi \times 50 \times 50 \times 0.1 \mu m^3$, the number of photons absorbed per site can be as much as 10^{-1}. The fluorescence yield at the Cu L-edge is in the order of 10^{-2}, of which up to 20% can be due to inelastic events (Ament et al., 2011; Krausz, 1979), leaving a net number of IRS excitation per site in the order of 10^{-2}, in the range of the optical IRS experiments. Such an excitation yield per pulse is expected to provoke changes in the spectroscopic and diffraction properties of the material in the order of the fraction of a percent, while we cannot make an estimate of the effects of such changes observable in imaging. The visibility of such a change depends in turn on the signal to noise ratio and integration time of the experimental setup. In the optical experiments for example, these phenomena were resolved by summing as many as 1.6 million pulses at a repetition rate of 1 KHz for a total acquisition time of 20 min, having a shot to shot noise in the experimental probe at the percent level.

Based on these estimates, we argue that for a large and general class of pump-probe experiments aimed at investigating the properties of coherent modes, the combination XFEL-pump and electron-probe offers a competitive alternative to more standard optical pump-probe schemes.

### 3.3. The synchronization

Practically, X-ray pump/fs-TEM experiments would require the synchronization of a laser source to the X-ray source. The fs laser will serve as a drive for the TEM photocathode, allowing to generate electron bunches with different duration and charge via the photoemission process. Synchronization between a laser and an X-FEL source has been recently discussed, proposing different approaches that can lead to a stabilization of the relative delay between the sources in the order of the pulse duration itself (Winter, 2005; Kim et al., 2008). An alternative way to solve the problem is offered by time-stamping each image, enabling data sorting in postprocessing the images. This has been successfully demonstrated at XFEL achieving sub-10fs temporal resolution (Riedel et al., 2013). For ultrafast electron pulses time-stamping was pioneered for MeV electron diffraction setup using electro-optic sampling methods (Scoby et al., 2010). New techniques have recently been demonstrated to work also for non-relativistic electrons (Gao et al., 2013b).

In addition, a RF-fs laser synchronization technique has been developed which allows the measurement of the phase of the amplified RF field in the cavity with respect to the fs laser pulse for each individual shot with 30fs resolution (Brussaard et al., 2013). Since the main cause of arrival time jitter is due to RF phase jitter of the compression cavity, the latter technique should allow accurate time-sorting of the individual images.

In the case discussed here, an extra complication arises from the need to use an RF electron gun in the TEM. Such a device requires the synchronization between an RF cavity and the laser source, which can be done also with high accuracy using the technique described in Brussaard et al. (2013). In total, the jitter of such a time-resolved experiment will be mainly affected by two components: the laser-XFEL jittering, and the laser-TEM jittering. Each of these two components has different sources: (1) the XFEL-laser jitter originates from the laser rep-rates instabilities, mainly due to temperature drifts in the cavity, and the intrinsic noise of the XFEL source. (2) The laser-TEM jitter is mainly caused by the synchronization between the RF cavity, temperature drifts plus the noise of the RF source, and the laser itself, temperature drift of the optical cavity. These sources of non-idealty can be considered to a first approximation as independent, and therefore, summed quadratically. Based on current technology available, the overall jittering of such a set-up will be expected to be about 50% higher than the laser pulse duration.

### 4. Conclusions

In this article, we discussed the feasibility of combining ultrashort X-ray sources, currently under development, with an ultrafast TEM. The goal of these experiments is to provide a uniquely broad-band view of materials and nanostructures and their transformations happening in the fs time-scale. Such an approach would benefit from both most recent achievements in ultrafast science, i.e. time-resolved TEM and XFEL technology, and promises to deliver combined structural, spectroscopic and morphological information on an extraordinarily wide class of systems, ranging from biomolecules to strongly correlated solids.

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