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DISCUSSIONS

Correlated systems, surfaces and catalysis; nanoscale and bio imaging: general discussion

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(403:[81]81) **Kai Rossnagel** opened the discussion of the paper by **Martin Wolf**: I find the observation of two CDW amplitude modes very intriguing. In the standard mean-field theory of the CDW transition, upon lowering the temperature across the transition temperature, a single phonon mode goes soft and a single CDW amplitude mode emerges. Could you explain the two-mode scenario in a little more detail?

Martin Wolf responded: In our ARPES work on TbTe3 we have developed a 3 pulse (pump-repopulate-probe) scheme which allows us to analyze the periodic oscillations of the CDW gap size (*i.e.* the order parameter) oven an extended the time range. For these measurements it is clear that at least two frequencies (associated with optical phonon modes) modulate the gap size. We believe the this directly shows that the lattice motion associated with the amplitude mode is more complex than in a simple (quasi 1D) Peierls picture. In fact any (normal state) phonon at the CDW wave vector which is strongly coupled to the electronic structure at the Fermi Level will modulate the band structure and in TbTe3 the two modes at 1.77 THz and 2.23 THz are most prominent. Demsar and coworkers have described this scenario of phonon softening in a time dependent Ginzburg–Landau model and could reproduce the observed phonon softening and anti-crossing of the 1.77 THz and 2.23 THz modes by time resolved optical reflectivity measurements (see *Phys. Rev. B*, **89**, 045106 (2014) and references therein). However, there is non complete softening observed. Note that in optical spectroscopy as well as in time resolved ARPES we excite $q = 0$ phonons, which do not exhibit complete softening, whereas the neutron diffraction work by Frank Weber (KIT, Karlsruhe, Germany) shows that the phonon softening is most pronounced at non-zero q (CDW wave vector). Interestingly, we observe for the photoexcited state similar amplitudes for gap coupling for the gap modulation by the 1.77 THz and 2.23 THz modes, which is quite different from the findings for the thermal induced transition in *Phys. Rev. B*, **89**, 045106. This indicates that the photoinduced transition is different from the thermal equilibrium transition. In the latter case the CDW gap completely closes while in the photoinduced transition the gap remains finite and does not close even at higher excitation fluence.

(406:[82]82) **Martin Wolf** opened the discussion of the paper by **Isabella Gierz**: In your work you compare scattering rates obtained by time-resolved ARPES with

the measured self energy obtained from the linewidth in static ARPES measurements. Both quantities show the same energy dependence (as has been predicted by the theoretic work by Tom Devereaux and coworkers in Stanford). However, quantitatively there is a large difference. What could be the origin? I would also like to remark that in a system like graphene, where you have cooling of photoexcited non equilibrium electrons by phonon emission and presumably even carrier multiplication, the relaxation rate which you measure is not the intrinsic lifetime of a carrier at that particular energy. In fact you are measuring the population dynamics in an energy interval which results from the balance of filling from higher lying states and the depletion by energy relaxation to lower lying states. As such it would be surprising if the data would agree quantitatively with the self energy in the static case.

Isabella Gierz answered: I agree that the equilibrium self-energy and the non-equilibrium scattering rate measure two different quantities. As indicated by Martin Wolf, the equilibrium self-energy is related to the lifetime of the photohole, whereas the non-equilibrium scattering rate is determined by a complex interplay of state filling and depletion. However, in *Phys. Rev. X*, **3**, 041033 (2013), Sentef *et al.* have shown that for their photoexcited electron–phonon model system there is a good agreement between non-equilibrium relaxation rates and the equilibrium self-energy. The purpose of Fig. 6 in our paper is to test this statement on an actual data set. The figure compares the energy-dependent scattering rate determined by tr-ARPES with the MDC line width from high-resolution static ARPES experiments. The scattering rate continuously increases from ~0.5 THz at the Fermi level ($E = 0$) to ~4 THz at $|E| = 1$ eV. The MDC line width rises from ~0.01 A^{-1} at $E = 0$ to ~0.035 A^{-1} at $|E| = 1$ eV in agreement with *Nat. Phys.*, **3**, 36 (2007). After multiplying the MDC line width with the Fermi velocity ($v_F \approx$ 6.6 eV A) this corresponds to an increase from 16 to 56 THz. Overall, the scattering rate and the MDC line width show a qualitatively similar energy dependence. However, the values extracted from static ARPES measurements are about one order of magnitude larger than the non-equilibrium scattering rates. The most likely reason for this discrepancy is that static MDC line widths are broadened by the experimental resolution, suggesting higher scattering rates. This results in a considerable over-estimation of the electron–phonon coupling constant in graphene (see *Nat. Phys.*, **3**, 36). Therefore, Sentef *et al.* suggested the extraction of the electron–phonon coupling constant from tr-ARPES scattering rates instead. Nevertheless, as the equilibrium self-energy and the non-equilibrium scattering rate measure different quantities, the validity of this approach may be restricted to particular systems.

(409:[95]83) **Kai Rossnagel** asked: Could you comment a little bit more on why a system that has been excited rather strongly into a non-equilibrium state should relax back to equilibrium at scattering rates determined from the equilibrium state?

Isabella Gierz replied: Please also refer to my previous answer. It is quite counterintuitive that a system far from equilibrium relaxes at the equilibrium scattering rate. Nevertheless, this is the result of the model calculation in *Phys. Rev. X*, **3**, 041033 (2013). There, the authors argue that (in the framework of the

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double-time Green's function methodology employed in their work) changes in the occupation of the band structure occur in the first order for small deviations from equilibrium, while actual changes in the dispersion are in the second order. As long as the self-energy does not depend too strongly on the electronic distribution function, the non-equilibrium system is supposed to relax *via* the equilibrium scattering rate. We wanted to test this hypothesis on actual (not simulated) data. For photo-excited graphene, we found that the equilibrium self-energy and the non-equilibrium scattering rate are qualitatively similar, in the sense that they show a similar energy dependence. However, they differ quantitatively by about one order of magnitude. The static MDC line widths suggest much shorter lifetimes than those measured by tr-ARPES (see figure). This discrepancy can be, at least partly, attributed to the limited momentum and energy resolution of the static ARPES results.

(408:[83]84) **Katherine Reid** asked: Have measurements similar to those that you have performed on graphene been performed on a graphite surface, and if so can you comment on the differences that are observed in the two cases?

Isabella Gierz responded: There is a one time-resolved photoemission study on graphite from 2001 (*Phys. Rev. Lett.*, **87**, 267402, (2001)). In that work, the authors combined a visible pump at 2.3 eV with 4.6 eV probe pulses, just exceeding the work function of the sample. The small photon energy only allowed for photo-emitted electrons from the vicinity of the Γ-point, and the spectra were recorded in angle-integrated mode. Despite these technical differences, the 2001 work obtained similar results for the energy dependence of the relaxation time and identified two different decay times that have been attributed to the internal equilibration of the electronic system (~250 fs) and the interaction with phonons (~1 ps). The interpretation of the two decay times has slightly changed since 2001, the main results of the graphite paper, however, remain valid. On the level of the observed decay channels and associated relaxation times graphite and graphene are very similar.

(410:[84]85) **Gwyn Williams** addressed Martin Wolf: What other tools would you like to have at your disposal to extend these experiments? Think about FELs in particular, with tunable THz and IR pumps, and higher photon energies, and 100 MHz repetition rates.

Martin Wolf responded: In almost all time-resolved pump–probe experiments we would like to have more specific tools for excitation. A promising avenue is IR or THz pumping to induce low energy excitations (*e.g.* just above the band gap of a superconductor or phonon pumping of solids). IR pumping is currently slowly penetrating in the field of tr-ARPES. THz pumping is yet to be applied, but we should keep in mind that combining THz pumping and ARPES will lead to the streaking of the outgoing electrons for light polarization with components normal to the surface. As Robert Moshammer has pointed out this may be useful to fully characterize the THz pulse. For pumping of the sample in plane polarization appears most promising (and could induce spin currents, dressing of Bloch states, *etc.*). I would propose that most ARPES work will be done with laboratory based sources and that there are currently important developments

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opening new areas by high rep-rate HHG, which may allow also for spin-resoved ARPES using new detectors. This will allow to study both ultrafast dynamics in ferromagnets as well as spin textures (*e.g.* in topological insulators) in great detail. In the field of X-ray science time resolved RIXS has great potential (see comment above)

Isabella Gierz answered: The biggest drawback of our lab-based tr-ARPES setup is the low repetition rate of 1 kHz (resulting in low signal-to-noise ratios) and the maximum achievable pump wavelength of 15 μm. We are currently considering the following upgrades:

(1) combine carrier envelope phase (CEP) stable mid-infrared pump pulses with few femtosecond HHG probe pulses to follow pump-induced coherent dynamics in real time

(2) go to higher repetition rates

(3) develop a narrow band THz pump source

Some of these aspects can be met at FELs, however, the use of FELs will also cause additional problems such as timing jitter.

(411:[85]86) **Kai Rossnagel** remarked: Regarding the persistence of the CDW gap even after rather strong photoexcitation, it could be interesting to compare the absorbed energy density to the electronic condensation energy, as given by equation (3.40) in Grüner's book, and to the energy density required to heat up the excited sample volume to above the CDW transition temperature (see, *e.g.* A. Tomeljak *et al.*, *Phys. Rev. Lett.* , **102**, 066404 (2009)). If the absorbed energy density used in the experiment lied in between these two values, the persistent gap would reflect a non-equilibrium CDW state in which the electronic order is quenched, while the lattice order persists. Have you estimated these two values?

Martin Wolf responded: In our experiments on TbTe3 we used an absorbed laser fluence between 0.5 mJ cm^{-2} and 1.5 mJ cm^{-2}. For a fluence of 0.75 cm^2 the CDW gap collapses to about half of its equilibrium value and for higher fluences no further decrease of the CDW gap is observed. For a fluence of 1.0 mJ cm^{-2} we estimate an absorbed energy density of approx. 1eV per unit cell or 250 meV per RTe3 unit. With a Debye temperature of 180 K this energy corresponds to a lattice temperature of 350 K which is just above the transition temperature of the CDW transition. Note that the CDW gap does not collapse even at the 50% higher excitation fluence of 1.5 mJ cm^{-2}. The condensation energy according to equation (3.40) in Grüner's book is estimated to be 75 meV for $\Delta = 250$ meV. We are thus clearly exciting both electronic and lattice temperature values exceeding the equilibrium CDW transition temperature, but still see only a partial collapse of the gap. However, on should keep in mind that a mean field model may not be correct for TbTe3. We speculate that other mechanisms (like spatial inhomogeneities) may play a role in stabilizing the CDW order. Without doubt the observations of "persisting pseudogaps" and "persisting order" needs further analysis.

(412:[86]87) **Gwyn Williams** asked: Do you consider that the system is not left in the ground state?

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Martin Wolf replied: Your question addresses some fundamental issues of our understanding of the photoemission process. In photoemission and in particular in time resolved photoemission from a photoexcited sample we deal with an excited system and Koopman's theorem as well as the sudden approximation may not be valid. However, we might be in a favorable situation if we consider energy differences, *e.g* when we measure simultaneously the binding energy from a normally occupied an a transiently populated, but normally unocculied band, to evaluate the magnitude of a band gap. In this case we can assume that the energy difference is not affected by a breakdown of the sudden approximation. In general, fundamental studies of the photoemission process by time resolved methods are an important field and topic of attosecond spectroscopy from solids.

(413:[87]88) **Katherine Reid** addressed Martin Wolf, Isabella Gierz, Christian Bressler and Majed Chergui: Many talks have referred to time and angle-resolved photoemission. Can this be viewed as an "ultimate" dynamical probe, or are there other probes that would provide complementary or superior information in certain cases?

Martin Wolf replied: Time-resolved ARPES has its main advantage in studies of the valence electronic band structure of periodic solids and allows us in particular to access directly the momentum and energy resolved scattering rates of photo-excited electrons. In systems exhibiting photoinduced transitions or coherent lattice vibrations the transient evolution of the electronic band structure con be followed and we had two papers on the dynamics of gap closing and coherent modulation of binding energies mediated by coherent lattice vibrations (*e.g.* amplitude modes). When looking at the electronic structure near the Fermi level time-resolved ARPES is the method of choice, but it is limited by space charge effects to rather modest pump fluences (depending on the system and laser parameters like polarization). Most experiments on time-resolved ARPES will be done with lab based laser sources and currently different schemes (high-rep rate HHG, 80 MHz 6-7 eV ARPES and kHz HHG systems with IR/THz pumping) are implemented. There are of course many other time resolved probes which lead to complementary information on dynamics properties of the valence electronic structure. In the area of X-ray science XPE, XAS and XES provide element specific information about the chemical state and valence electronic structure. In the field of surface science and catalysis a first demonstration of element specific probing of a chemical reaction has been demonstrated using time-resolved RIXS (*Science*, **339**, 1302 (2013)). This provides information about chemical bond formation and breaking. As a core level spectroscopy tr-RIXS provides local information which is complementary/different to the electronic band structure in a well ordered periodic system. Important information about the electronic properties can be obtained also by time domain THz spectroscopy, which allows us to measure the complex conductivity as well as low energy modes (phonons, magnons) of solids after photoexcitation. This may provide important valuable information about the dynamics of the electric system. Also important are various structural probes. In particular, time resolved electron diffraction has made remarkable progress in the last few years, but is still limited in time resolution. X-ray diffraction is thus a promising tool.

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Majed Chergui answered: I do not think there is an ultimate dynamical probe. The probe depends on the scientific question you want to answer. It is true that ARPES is a very powerful tool, but: (a) it is starting to be increasingly used and still has to show the full range of its capabilities; (b) it is valid only for solid systems, that are single crystals, therefore, you can immediately imagine that it cannot be used for any sample, least of all disordered ones; (c) it is not a structural tool in the sense that it does not provide you with geometric structure. Of course you can infer it indirectly, as with many other spectroscopic techniques. However, you do get an extremely fine and detailed electronic structure. In summary, just as with other methods, it is their combination (if you can afford it) that is the best strategy.

Isabella Gierz replied: Tr-ARPES is the technique of choice to measure the response of the momentum-resolved valence electronic structure in the time domain after excitation at various different wavelengths. There is, at present, no better technique for that purpose. However, tr-ARPES could be nicely complemented with time-resolved electron diffraction (to obtain structural information with similar surface sensitivity), time-resolved STM (for spatial resolution), or spin- and time-resolved ARPES (to address spin dynamics).

Christian Bressler answered: I am convinced there will never be one single probe which will answer all scientific questions around chemical reaction dynamics. X-ray tools are also quite advantageous, as they can likewise deliver electronic, spin and geometric structural information. Guest–host interactions are extremely difficult to study due to the many-bodies involved, but X-ray scattering may deliver useful information. Photoemission studies are limited in their penetration depth, while hard X-ray tools (X-ray absorption XAS, X-ray emission XES, X-ray diffuse scattering XDS) can look several (tens of) microns inside the sample.

(414:[88]89) **Gwyn Williams** addressed Martin Wolf and Isabella Gierz: Are there any other experiments, such as Auger resonant emission or inverse photoemission or spin-resolved photoemission that might shed insight into the phenomena you are studying?

Martin Wolf replied: Auger resonant emission may be an interesting probe which has not yet been explored in detail. Spin resolved photoemission will greatly benefit from new detector development with a 100 times better sensitivity compared to current schemes. These will be combined with spatial resolution and imaging to allow for multi parallel detection.

Isabella Gierz answered: Tr-ARPES is the tool of choice to follow the evolution of the valence electronic structure in the time domain. Time- and spin-resolved ARPES as well as time-resolved (photo-)electron diffraction would provide useful complementary information.

(415:[89]90) **Elaine Seddon** said: There have already been a couple of questions relating to future developments, especially in terms of techniques and observables. Electron spin is one such observable that has not been discussed in detail. I

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would therefore appreciate your views on potential future developments that involve electron spin.

Martin Wolf responded: There are currently important developments to open new areas by XUV pulse generation *via* high repetition rate high harmonic generation (100 kHz to several MHz OPCPA HHG) sources, which may allow also spin-resoved ARPES using new detectors with an enhanced sensitivity. This will allow us to study both ultrafast dynamics in ferromagnets as well as spin textures (*e.g.* in topological insulators) in great detail. In the field of X-ray science time resolved RIXS has a great potential.

(418:[90]91) **Katherine Reid** addressed Isabella Gierz and Martin Wolf :You mentioned time-resolved STM as a possible technique; what would be the achievable time-resolution?

Martin Wolf replied: There have been numerous attempts to achieve femtosecond time resolutions using STM. A promising attempt is the electronic pump probe STM using short voltage pulses developed by the Almaden group (S. Loth *et al.*, *Science*, **329**, 1628 (2010)), which is currently improved to obtain a high sub-ns resolution. Another idea is to use THz pulses in an STM junction as an "ulrafast switch" of the bias voltage. There is also the ongoing development of time resolved low-electron electron diffraction (LEED) to study ultrafast structural phase transitions at surfaces. Thereby an ultrashort electron pulse is emitted from an STM tip. In transmission experiments (*e.g.* on freestanding graphs covered with adsorbed surfactants, *Science*, **345**, 200 (2014)) time-resolved LEED has been already demonstrated. In back reflection mode there is the challenge to control the electron imaging in LEED using an STM tip close to the surface.

Isabella Gierz responded: Time-resolved STM using voltage pulses from a pulse generator is limited to a time resolution of about 1 ns with atomic spatial resolution (*Science*, **329**, 1628 (2010)). Recently, the technique has been combined with THz light fields (*Nat. Photon.*, **7**, 620 (2013)), achieving subpicosecond times and 2 nm spatial resolutions.

(401:[91]92) **Michael Woerner** asked Isabella Gierz: As you mentioned in your talk, one expects an anisotropic carrier distribution after photo-excitation. Did you see any dependence of the photoemission data on the laser polarization ?

Isabella Gierz replied: We have not checked yet. However, there is clear evidence for an initially anisotropic charge carrier distribution from all-optical pump–probe experiments (*Nano Lett.*, **14**, 1504 (2014)).

(402:[92]93) **Majed Chergui** asked: Regarding the carrier multiplication, have you done any fluence dependence studies?

Isabella Gierz answered: According to *Nano Lett.*, **10**, 4839 (2010) and *Phys. Rev. B*, **85**, 241404(R) (2012) carrier multiplication is supposed to occur at low pump fluences, high pump photon energies, and low sample temperatures. We systematically varied pump fluence (between 0.6 and 6 mJ cm^{-2}) and sample

temperature (20 K, 77 K, and room temperature) and determined the number of carriers in the conduction band as a function of the pump–probe delay. We found that the rise time is always longer than the pulse duration. However, we also observed a thermal distribution of hot electrons at all times. As carrier multiplication is not expected to occur for a thermalized electronic distribution we rather attribute the increased rise time to the anisotropy of the initial carrier distribution in momentum space as predicted in *Phys. Rev. B*, **84**, 205406 (2011). In conclusion, we found no carrier multiplication in the experimentally accessible parameter range. However, at the lowest pump fluence of 0.6 mJ cm^{-2}, we are severely restricted by our signal-to-noise ratio due to the 1 kHz repetition rate. Therefore, carrier multiplication may occur at even lower fluences in agreement with *Phys. Rev. Lett.*, **111**, 027403 (2013) and *Nat. Commun.*, **4**, 1987 (2013).

(404:[93]94) **Majed Chergui** remarked: There is a debate about the occurrence of band gap renormalization in graphene, can you comment on it and whether it shows up in your studies?

Isabella Gierz replied: Monolayer graphene on SiC(0001) does not have a band gap at equilibrium. Nevertheless, it is conceivable that photoexcitation might induce a band gap or renormalize the electronic structure due to the screening of electronic correlations by the presence of photoexcited carriers. However, within our experimental resolution we do not find indications for a transient band gap renormalization. Our pump–probe signal is completely dominated by the effect of an elevated electronic temperature.

(405:[94]95) **Katherine Reid** asked: At the end of your talk you referred to an alternative explanation; would you be able to elaborate on this?

Isabella Gierz responded: The question refers to the fact that the observed rise time of the pump–probe signal is longer than the pulse duration, which might indicate the occurrence of carrier multiplication by impact ionization. However, we also observe a thermal Fermi–Dirac distribution of electrons at all times. This distribution does not allow for carrier multiplication to occur. Hence, the enhanced rise time of the signal must have a different origin. We propose, that the reason for the enhanced rise time is the gradual relaxation of the initially anisotropic carrier distribution. The matrix element for photo-excitation is anisotropic, resulting in an anisotropic charge carrier distribution in the conduction band with nodes along the direction of light polarization. This distribution becomes isotropic *via* the emission of optical phonons within ~200 fs. In the present experiment the photocurrent was measured along the nodes of the initially anisotropic contribution. Hence, the maximum pump–probe signal is reached only after the excited electrons have scattered into the field of view of the analyzer, which takes about ~200 fs.

(501:[96]96) **Martin McCoustra** opened the discussion of the paper by Chris Jacobsen by asking: We have heard many comment on the idea of molecular movies in this Discussion. What likelihood have we of what might be referred to as biomolecular movies showing the temporal evolution of biomolecules in a living organism?

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Chris Jacobsen communicated in reply: The challenge here involves radiation damage. For repeatable phenomena in measurements that involve statistical measures of systems, one avoids radiation damage by measuring at a variety of time points after a stimulus (repeatability) with the irradiation hitting a number of biomolecules so that the dose to each individual biomolecule is reduced (statistical measures). This might apply for example to small angle scattering. When it comes to imaging larger and thus non-identical objects such as organelles and whole cells where there is considerable overall structural variation (no two cells look alike), so direct real-space statistical averaging seems difficult to apply. Also, when one is doing even 20 nm resolution imaging, the radiation dose is in the $1e^8$ Gray range which is sufficient to break about one bond per molecule so the movie is far more likely to show the biomolecule being damaged rather than undergoing a "normal" temporal evolution. Of course, pump–probe crystallography can be used for stroboscopic (repeatable sample) and ensemble-averaged (crystal with many identical unit cells) measurements of the time evolution of a photostimulable biomolecule –which in the case of proteins represents a very small though important subset of all known proteins.

(502:[97]97) **Henry Chapman** asked: Would it be possible to use some sort of dynamic response in a pixel of an STXM scan as a contrast mechanism, for example to map the distribution of chemical activity in a sample?

Chris Jacobsen responded: Interesting thought. Of course X-ray photon correlation spectroscopy (XPCS) involves using the rearrangement of the coherently scattered intensity distribution to tell one about the timescale of rearrangements of optical phases of the material within the coherently illuminated beam spot. The challenge of course is one of radiation damage, in that when one goes from a large-beam-spot XPCS experiment to a nano focus scanning transmission X-ray microscope (STXM) beam spot, the number of photons per area goes up to very high levels and one is as likely to see a dynamic response caused by beam damage as a dynamic response caused by a more "natural" process in a pixel. The per pixel dose in 20–50 nm resolution STXMs is in the $1e^6$-$1e^8$ Gray range, and at around $1e^8$ Gray one has broken about one bond per molecule. At the same time, there are some indications that chemical damage takes on the order of a millisecond or so to be made manifest in diffraction patterns, so maybe there is some hope? Interesting question.

(511:[98]98) **Grigory Smolentsev** remarked: You use the regularization method to include *a priori* knowledge into your model. Are there any other methods that allows you to include *a priori* knowledge into the model, for example, those based on the linear combination of components obtained using principal component analysis? Could you compare your method with the alternative algorithms?

Chris Jacobsen replied: In fact the spectra arising from cluster analysis (which we include as the "cluster similarity" regularizer in eqn. 10–13 in our Faraday Discussion paper) are exactly what you suggest: a linear combination of components obtained from principal component analysis (PCA). As described in our earlier paper (Lerotic *et al.*, *Ultramicroscopy*, **100**, 35 (2004)), we use PCA to obtain a basis set with desirable properties like orthogonality and noise-supression. We

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then find weightings among these components by seeking clusters of pixels (independent spectral measurements) in this component space, yielding spectra that are linear combinations of PCA spectra. However, as explained in Section 2 of this Faraday Discussion paper, the resulting set of cluster spectra can be incomplete as a basis set and can lead to errors in analysis. What NNMA gives us is a way to use the cluster spectra as one part of the cost function (one regularizer). However, it is used in combination with the data-matching cost of eqn. 3, and the sparseness regularizer of eqn. 7–9, to yield an improved solution as shown by the lack of unphysical "negative absorption" values in the NNMA solutions shown in Fig. 6 of our paper.

(515:[99]99) **Jonathan Underwood** communicated: The regularization method presented in your paper bares some similarity to other widely used strategies such as Tikhonov regularization and particularly Projected Landweber regularization in terms of the non-negativity constraint. The convergence properties of these strategies are reasonably well studied and understood (*e.g. Num. Funct. Anal. Opt.*, **13**, 413 (1992)). Is anything known about the convergence properties of your regularization strategy?

Chris Jacobsen responded: To our understanding, the cited paper deals with the problem of determining A in $Af=g$ when f and g are known, subject to constraints; it shows good convergence properties. In our case we know neither A (the set of spectra) or f (the thickness maps) in advance; we only know the measured data g. We are not aware of analyses on convergence rates for global solutions, though the steepest-descent type approach we have used (based on derivatives of cost functions) at least aides in finding local solutions. We have carried out some work on the optimization of the regularizing parameter λ; we will report on that in a separate paper.

(516:[100]100) **Henry Chapman** addressed Chris Jacobsen and Jasper van Thor: I noticed that the update algorithm you present in your paper (eqn. 3–5) is essentially the algebraic reconstruction technique (ART) used in tomography (also called the Kaczmarz algorithm, used in Caterina Vozzi's tomographic reconstructions paper). Presumably regularisation has been applied in tomography too, or perhaps your developments could be of interest for that application. Your method is also immediately applicable to solving structural kinetics problems, and would be a big improvement upon the SVD method developed by Marius Schmidt and others for time-resolved WAXS and time-resolved crystallography, just replacing energy (in your case) for time (in theirs). I have not seen a discussion in those applications how they impose the constraint that populations are positive. It seems to me that your regularisation technique would be a big improvement, especially sparsity which will enforce populations to occur more in a sequence than a jumble, and allowing one to avoid model bias.

Jasper van Thor communicated in reply: Dear Henry, in Singular Value Decomposition or other methods of matrix factorisation, a separation is made purely on the basis of orthogonality. The fundamental assumption is one of linearity. Thus, any individual measurement, or single column, of the input matrix must then be some linear combination of the left singular vectors. The

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basis spectra, or left singular vectors in themselves, have no physical meaning: these do not represent spectra for pure species. Therefore, it is always required to apply a model or connectivity scheme that relates to the populations found in the right singular vectors (see for example reference **1**). By requiring amplitudes to be non-negative, as Chris has implemented, such a model is effectively being used.

1. L. J. G. W. van Wilderen, C. N. Lincoln, J. J. van Thor, *PLOS One*, **6**, 2011, e17373.

Chris Jacobsen answered: Good suggestions. I hasten to add that by no means did we invent regularization methods! We simply applied them to the case of spectromicroscopy analysis, where to our knowledge these methods had not been applied before (except for the PhD work of Holger Fleckenstein, who is a coauthor on the paper).

(517:[101]101) **Jasper van Thor** asked: Dear Chris, in the matrix decomposition did you perform a matrix inversion which presents the basis spectra μ_{SxN} which you show to have all the significant amplitude? Or did you perform a Singular Value Decomposition $D = \mu S t^{\mathrm{T}}$, where the singular values represent the amplitudes and also provide the statistical significance of the contributions of the basis spectra μ. The thickness maps as well as the basis spectra would need to be weighed by the respective singular value S. Does that correspond to the amplitudes which you have shown?

Chris Jacobsen replied: In the cluster analysis approach described in the first part of the paper, our procedure is as follows: (1) perform an eigenvector analysis from the covariance of the data matrix D, and then limit the vectors to those with statistical significance; and (2) carry out cluster analysis to find pixels with similar eigenspectra weightings. The spectra at those pixels are then averaged together to yield a matrix μ_{SxN} which is then inverted using singular value decomposition (SVD) as you describe. This is described in the 2004 Ultramicroscopy paper by Lerotic *et al.* cited in the manuscript. These spectral solutions are then used as just one of two regularizations in the non-negative matrix analysis (NNMA) approach described, where the main cost function is the data matching error (optical density matrix minus the product of the present guess of the set of spectra times the present guess of the weightings or thicknesses; that is, minimizing the square of $D - \mu t$). I hope this answers the question.

(519:[102]102) **Michael Woerner** communicated: I see some similarities of your method with the so called maximum entropy method (MEM). Is it possible to combine your method with the MEM?

Chris Jacobsen responded: Maximum entropy involves minimizing some norm that measures contrast or fluctuations in the solution. These can include norms such as L-1 or L-2. In our case, we used an L-1 norm on the thickness solution t, so in some sense we have included a regularization that is representative of what is used in some Maximum Entropy methods.

(512:[103]103) **Majed Chergui** opened the discussion of the paper by Michael Woerner by asking: Your set-up for fs powder diffraction is quite unique. How do you compare it with ultrafast electron diffraction where the electron beam can be focussed down to a single grain size, or also to the developments for nano-diffraction at synchrotrons, which may lead to ultrafast studies too?

Michael Woerner communicated in reply: First, I would like to mention, that table top femtosecond X-ray diffraction can be also performed using the rotation method as we have recently demonstrated (B. Freyer *et al.*, *Optics Express*, **19**, 15506 (2011)). However, the diffraction efficiency for X-rays is much smaller than that for electrons. Thus, femtosecond nanodiffraction of X-rays will be the playground of the big accelerator machines (at least in the near future). Recently, we started a collaboration with Andrius Baltuska of the TU Vienna to develop schemes for a table top femtoseond X-ray source using a long wavelength driver (*i.e.* an OPCPA system working at $\lambda = 4$ μm). Such experiments turned out to be very promising in the sense that we can expect for future table top systems a hundred times higher X-ray flux.

(520:[104]104) **Jasper van Thor** asked: Dear Michael, from your presentation it is clear that you apply a maximum entropy method to find the charge density distribution from your experimental data. Firstly, could you please reiterate the phasing method that was used, and the accuracy of the structure factors in terms of crystallographic quality indicators and *R* factors. Secondly, can you show that the pumped data are truly isomorphous with the unpumped data? From the strength of the charge density which you derive and have shown is surprising that no bond length modification is apparently observed, which would likely dominate the transient structure factor amplitude differences. Further, transient difference density is present only within the duration of the pump and is not seen after. For the field driven signal, would THz pumping then retrieve the time-domain response to the field?

Michael Woerner communicated in reply: First, I would like to mention that we use the maximum entropy method (MEM) (instead of using a direct Fourier transform in the truncated *q*-space) just as a tool to derive the electron density map. Thus, the MEM has nothing to do with phase problem. How we deal with the phasing problem is detailed at the beginning of section 3 of our article. In summary, our method of analysis determines the average unit cell of the entire powder sample which has per definition the symmetry properties of the initial structure. An analysis using the Patterson method (Stingl *et al.*, *Phys. Rev. Lett.*, **109**, 147402 (2012)) shows that the latter is the dominant contribution to the change of the electron density map. In general, an excitation using a polarized electric field might also change the intensity along a particular diffraction ring in powder diffraction. Our diffraction efficiency is too low to address such questions in more detail. Within an optical cycle of the 800 nm driving pulse the change of bond lengths are negligible. Impulsive Raman excitation, however, leads to changes of the bond lengths in $LiBH_4$ at later times as evident from Fig. 3(c–f) in our article. Similar to impulsive Raman excitation THz excitation might also lead to bond length changes on the longer times scales of vibrations.

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(521:[105]105) **Martin McCoustra** commented: One wonders what might happen to the charge exchange as LiH is compressed? Would measurements in a diamond anvil cell be possible to experimentally address this question?

Michael Woerner responded: In the literature one finds stationary X-ray diffraction experiments on compressed LiH up to 250 GPa (Lazicki *et al.*, *Phys. Rev. B*, **85**, 054103 (2012)) using a diamond anvil cell. Thus, in principle femtosecond X-ray diffraction under pressure should be possible. In practice, however, one expects additional problems in time-resolved experiments due to both X-ray absorption and dispersion of pump light in the anvil cell itself. So far, I did not find an analysis of stationary diffraction experiments concerning a pressure dependent ionicity of LiH. Depending on the ionicity of the pressure dependent ground state of LiH I expect a field induced change of the ionicity as discussed in our article.

(522:[106]106) **Christian Bressler** communicated: You have succeeded in extracting results *via* fs-powder diffraction in a laser-driven X-ray plasma source. Do you see the need to apply for beam-time at an XFEL source? What benefit from this source would you expect against your ample in-house beam-time? Or why did you not apply for XFEL beam-time anywhere so far?

Michael Woerner answered: I will apply for beam-time at an XFEL source once those devices provide >10 keV X-ray pulses at a repetition rate of 1 kHz or higher with a timing jitter between laser pump and X-ray probe pulses of less than 50 fs. So far the research we would like to do can be easily performed with our table top fs X-ray source (despite having much less X-ray photons per shot). The main reason I did not apply for XFEL beam-time is simply the lack of free personnel and working hours from our side. The experiments we are doing in our lab are very time consuming and personnel intensive. If this situation changes in the future (*i.e.* more personnel) we are happy to apply for beam-time at an XFEL.

(506:[107]107) **Jonathan Underwood** opened the discussion of the paper by Jochen Küpper by commenting: Prof Marangos asked what would be needed to extend the technique presented by Küpper and colleagues for diffractive imaging of ground state (static) molecular structures to the measurement of excited state structural dynamics. If one considers an experiment where a resonant pump pulse electronicly excites molecules, and then the resulting structural dynamics are probed *via* diffraction with a time delayed X-ray pulse, then the optimal situation would be that the molecular alignment is maximal at the instance of probing. So, one can imagine an approach in which a strong non-resonant laser field is applied prior to the pump pulse to create a rotational wave packet in the ground state of the molecule. By careful design of the alignment laser field parameters (pulse shape, time-dependent polarization) and time-delay between the alignment and pump laser fields it may then be possible to transfer the rotational coherence to the excited electronic state where the subsequent wave packet evolution will produce the desired alignment at the instance of probing. However, this is clearly a very challenging proposition, as one needs to understand how the rotational wave packet will evolve in the excited state which may have very different (and time-dependent) rotational constants to the ground

electronic state. Also, the alignment field parameters would need to be varied each time the pump and probe time delay was changed. There is very clearly a need to consider this problem in further detail as current understanding of what is and is not possible is currently poor.

Jochen Küpper communicated in reply: This experimental protocol suggested by Dr. Underwood is interesting and should, in principle, work. There are a few comments I wish to make below.

At the same time, I want to point out that we should really make big efforts to look at ground state chemistry. While there is very important electronically-excited state (photo)chemistry going on in chemistry and biology, most chemical dynamics does not happen in excited electronic states, but in the ground state. This involves almost all "classical", thermally activated chemistry and biology and comprises by far the largest part of all chemical and molecular dynamics. Therefore, we need to develop protocols to trigger and time chemical reactions on the ground state potential energy surface, and methods to investigate, image them with spatial and temporal atomic resolution. It might be possible to define the starting point of such ground-state reactions with (resonant or non-resonant) THz or IR photons. An alternative approach would be to use highly sensitive detection methods that are capable of simply observing the few, rare, reaction events in a thermally activated "soup" of reactants. While the latter is a dream, maybe solely a thought, the former approach of photo-triggering ground state reactions seems in reach. First experiments are already emerging[1,2] and need to be transferred to the ultrafast-time and structure resolved domain of imaging experiments. Regarding the suggested transfer of coherence from the electronic ground state to the electronically excited state, a few points discussed at the meeting were related to the change of the inertial tensor upon excitation, *e.g.* the changes of rotational constants and the reorientation of the principal axes of inertia. These are generally important considerations, but we might be lucky in many cases: axis tilting effects are often very small ($<1^\circ$) for valence excitations, rotational constants typically change by one to a few percent, and sometimes even the electronic properties, such as dipole moment and polarizability, change only weakly. Moreover, all these details can be derived from eigenstate resolved spectroscopies –for the prototypical molecule indole this has been shown in detail, including the details of strong vibronic cooling between different electronically excited states.[3–5] Regarding the alignment process, which is in the short pulse "impulsive" regime, I wish to point out that for the alignment to be visible in the coherent diffraction pattern, one has to obtain very strong degrees of alignment, *i.e.* $\cos^2\phi >> 0.8$.[6] This will be very hard to achieve in an impulsive alignment approach. Overall, it might be easier to implement a quasi-adiabatic alignment protocol, in which a moderately-long-pulse ac field angularly "permanently" confines the molecule – with significantly stronger degrees of alignment and independent of the molecule's electronic state. However, the presence of the field clearly has to be considered regarding the stability of the molecule in various states as well with respect to its influence onto the investigated dynamics (see also the next question for further details). Then, the truncated pulse method mentioned by Jonathan Underwood elsewhere might be a very viable compromise. Overall, I conclude by fully supporting the statements of Jonathan. Underwood that "there is very clearly a need

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to consider this problem in further detail as current understanding of what is and is not possible is currently poor". Even the *sole* development of an understanding of the right approach would yield tremendous insight into the workings of molecules.

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(507:[108]108) **Jonathan Underwood** commented: Jochen Küpper makes very good points about the need to find ways to measure structural dynamics during ground state (chemically relevant) processes in molecules. My main concern about using the approach presented by Küpper and colleagues for structural imaging of ground state molecules undergoing chemical change is that the presence of the adiabatically applied alignment laser field could well be expected to change the observed chemical processes (beyond that expected from steric/geometric considerations). The laser field intensities used for producing molecular axis alignment typically lie in the region of 10^{12} W cm^{-2} corresponding to an electric field of about 10^{9} V m^{-1}. Such high fields strengths are expected to significantly distort the electronic structure of even ground state molecules – indeed the quantum mechanical expression for the molecular polarizability expresses the field-induced mixing of electronic states. As such, I am concerned that the alignment laser field would directly influence the distribution of charge in the molecules under study, affecting their reactivity.

Jochen Küpper responded: Again, this is a very insightful and important comment by Jonathan Underwood. On the quantitative detail I wish to point out that the quantum-state-selection exploited in our work[1] not only allows for the selection of distinct molecular species,[2] but it allows the achievement of very strong alignment (and orientation) at moderated field strengths of only 10^{10} W cm^{-2}.[3] Nevertheless, while this strongly mitigated the problem, it does not solve it and one has to consider the (ac) Stark effect onto the chemical dynamics. Typical Stark energy shifts are of the order of 1 meV under the specified conditions. These shifts, clearly, could change the dynamics in a state-to-state resolved experiment where degeneracies might be lifted or induced, but it is likely not relevant in terms of the chemical energies in typical reactions, which could be of the order of 1 eV. Therefore, our current investigations of statistically averaged (over quantum states) dynamics should not be much influenced.

At the same time, one should also relate these fields (1e8 V m^{-1}) to the "internal fields" from the reactions partners, which are of the order of the atomic unit of the electric field (5e11 V m^{-1}). Again, this is a difference of more than three orders of magnitude and it will take some effort and progress to be able to see these effects. In how far the more subtle effects hinted at, such as charge redistributions, *e.g.* through the Stark-cooling of orbitals or states, are a different issue,

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is related to the discussion of the validity of the Born–Oppenheimer approximation, elsewhere in this Discussion.

Overall, the presence of an alignment laser will surely have an influence on the molecular system under investigation. Personally, I would be very happy to see this effect as it would show that we had finally arrived at the observation of intricate details of the dynamics of molecular dynamics. Under these circumstances we would first learn what this influence is and, subsequently, would surely be able to mitigate or avoid it altogether. The presented X-ray diffraction probe[4,5] should, at least, be a largely unaffected probe to observe these effects –once it is a routine tool with sufficient temporal and spatial resolution.

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