Martin Centurion opened a discussion of the paper by Shaul Mukamel: There seems to be an issue of two different time scales. The resonant cavity will have a long lifetime, while the excited molecules will evolve on a much faster time, which can change their absorption spectrum and thus the strength of interaction with the cavity. Will this be a problem for the method that you are proposing?

Shaul Mukamel replied: This is not a problem in the applications I presented. The cavity field is stationary and its only role is static: It dresses the bare molecular states to create joint molecule/field (polariton) states. Time dependent polaritons in multimode cavities is an interesting issue which was not addressed in the present studies.

Jon Marangos said: You include no decay of the photon field, will this be a good approximation for the dynamics you model?

Shaul Mukamel replied: Decay of the photon field like loss in mirrors may limit the spectral resolution and may limit the observation time. Chemical reactions and nonadiabatic dynamics in cavities are typically affected by other broadening effects so that the photon decay may be neglected.

Martin Centurion remarked: If the cavity has a high Q, and the absorption of the molecules changes, what will be the effect on the cavity fields?

Shaul Mukamel replied: In our applications the cavity field is given, and is unaffected by the molecule. This assumption is valid in many cases. It is made in
all classical treatments of spectroscopy. It is an open interesting question when should a self consistent treatment of the cavity field and molecule be required. This could lead to interesting new effects.

Misha Ivanov commented: Coupling a molecule to a cavity field modifies the potential energy surfaces of a molecule in a way that is controlled by the strength of the interaction and the frequency of the cavity mode. However, it is often assumed that a cavity supports a spectrally narrow range of modes. Does it affect or limit the control, especially if we are interested in ultrafast approaches to control?

Shaul Mukamel responded: The cavity polariton effect is static. It affects the zero-order Hamiltonian by dressing the molecular states with photons. This is a very powerful but limited degree of control. Dynamical control using shaped pulses is different and may not be achieved in cavities. It is a different control regime.

Misha Ivanov said: What is the advantage of using a cavity field, as opposed to a laser pulse, for modifying the potential energy surfaces of the molecule? And is there an aspect of the molecule–cavity field interaction where the quantum nature of the cavity field is important, as opposed to the classical treatment of the laser field?

Shaul Mukamel responded: These are two excellent questions. Placing a molecule in a cavity subjects it to strong coupling with a single field mode. This is formally identical to subjecting the molecule to a strong field (without a cavity). Under certain conditions the two techniques may yield the same information. However strong fields can cause many other processes such as multiphoton absorption and photodissociation. These are interesting in their own right but compete with and complicate the analysis of spectroscopy. Cavity strong coupling can be realized even by the vacuum field and does not suffer from these complications.

Some aspects of polaritons can be fully understood with classical fields. The celebrated work of Hopfield (who coined the term polariton) used an equation of motion for coupled field and exciton modes and only involves a classical field. The linear response of polaritons is thus purely classical. However, multipolariton states that are accessible by nonlinear spectroscopy may require taking the quantum nature of the field into account.

Jon Marangos remarked: In the molecular dynamics calculation – what defines $t_0$ and is it some initial excitation of the molecule and/or the cavity field included?

Shaul Mukamel answered: This is correct. The process is initiated by a preparation (actinic) pulse which defines the zero time. We assumed that the cavity plays no role in this step. It only affects the subsequent nonadiabatic dynamics

Ágnes Vibók addressed Markus Kowalewski and Shaul Mukamel: Would it be possible to take into account the rotation in the cavity (without any external field) so as to describe properly the LICI (for diatomics)?
Markus Kowalewski answered: The coupling of a dipole to a cavity mode is formally very similar to the coupling to a laser field. Both cases can be described with a molecular dressed states (Jaynes–Cummings) model.¹

The angle $\theta$, which serves as a second coordinate for the LICI, is then defined by the angle between the molecular axis and the cavity axis. A subtle difference here is that, depending on the cavity geometry, the polarization of the vacuum state might be undefined.


Shaul Mukamel answered: yes, this is a very interesting application that could potentially lead to the experimental observation of the Berry phase. Such an observation has attracted considerable attention but no clear evidence has been achieved so far.

Ágnes Vibók asked: Do you include a 2nd degree of freedom in the dynamical calculations? It would be necessary to establish a branching space in order to obtain the proper conditions for a light induced conical intersection situation. What is your opinion: Should there be any difference between the dynamical results of the numerical simulations obtained by classically or by QED description of the light?

Shaul Mukamel replied: yes, conical intersections require at least two nuclear coordinates; our simulation includes both a one dimensional model that can represent an avoided crossing and a two dimensional model of conical intersection.

The presented applications are equivalent to placing the molecule in a strong classical field. The quantum nature of the field does not play a role. However, they may be required in other measurements say photon coincidence statistics.

Jon Marangos addressed Shaul Mukamel and Markus Kowalewski: Is this a step towards a model for nanophotonic catalysis – or in general why would one want to do this? Nanostructured materials are after all used already in catalysis but won’t in practice there be limits due to the cavity field resonance (width, control over and variability)?

Markus Kowalewski replied: We agree that this is a step towards nanophotonic catalysis. In contrast to a conventional catalyst it acts via vacuum field modifications rather than chemical interactions. This opens up a whole new field of possibilities. The intended use would be to modify the outcome of a photochemical reaction under the influence of sun light. Here, the catalyst would have to be tailor made to match a substance specific resonance frequency. The question about its limits, like collective enhancement will be part of future work.

Shaul Mukamel responded: That is correct. One can view the cavity role as a novel nanocatalyst. It offers a different control space that is not available through conventional catalysts. Its control over the potential landscape is unique and can be easily varied by cavity parameters.
Misha Ivanov said: It would be interesting to extend these schemes to several atoms or molecules inside a cavity, where one could possibly think of controlling the interaction of these molecules via the cavity-induced dipoles. The quantum nature of the cavity field, with just a single photon in the cavity, could make this molecule–molecule interaction rather interesting.

Markus Kowalewski said: A subtle difference between a classical and a quantised electromagnetic field mode is the back action of the field mode on the molecule. Assuming the field mode is initially in the vacuum state, then a change in photon number introduces a large relative change in the intra-cavity intensity (or cavity coupling). The field intensity scales like $0.5I_0$, $1.5I_0$, $2.5I_0$, etc. In a classical laser field with a very large photon number this relative change of intensity becomes irrelevant.

Shaul Mukamel responded: Note that quantum optical fields offer numerous new opportunities for spectroscopy. Parameters of the photon field wavefunction may be varied to reveal matter information that is not accessible by classical light. This includes high temporal and spectral resolution and kinetics information imprinted in photon statistics. Entangled photons may be used to create entanglement in matter and control energy transfer in aggregates.

R. J. Dwayne Miller opened a general discussion of the paper by Fillipo Bencivenga: These are really remarkable experiments in that you were able to get such stable amplitude and spatial mode quality with seeding your XFEL source. The use of soft X-ray excitation in 4-wave mixing geometries is new territory. However, you are interpreting your signals in terms of carrier dynamics in SiN. How do you explain the nonlinearity in the dynamics while you show the excitation is within linear response? (I understand you are considering Auger processes. Do the estimated carrier density and observed decays make sense relative to previous studies which have extensively examined Auger?)

Filippo Bencivenga replied: The estimated carrier density is in the order of $10^{20}$ cm$^{-3}$, which is enough high to have a significant Auger contribution on sub-ps timescales (see, e.g., the case of Si, extensively discussed in ref. 1 or 2, Fig. 3). We carried out some calculations, following the approach outlined in these papers and considering the range of parameters of the present experiment. We found a qualitative agreement [the larger is the fluence and the faster is the decay: see Fig. 1 (A. Calvi et al., unpublished)] and we found that the decay is essentially dominated by the Auger. However, our calculations are very preliminary and don’t consider other effects (e.g. surface fields, see question N. 215) nor the spatial modulation of the transient grating. The fact that we are in the weak field regime (signal intensity proportional to the product of the intensities of the three input beams) is reasonable in light of the relatively low input field strength, not larger than in many optical TG experiments.

Jon Marangos asked: As in essence you’re creating an electron density grating – is the fact the recombination rate due to two body interactions the reason that the decay rate is proportional to electron density?

Filippo Bencivena responded: We found that the proportionality between the decay rate and the (average) electron density can be ascribed to a term (accounting for Auger decay) proportional to the cube of the electron density in the rate equations describing the energy transfer from photo-excited electrons and the lattice (see, e.g. ref. 1). However, other effects could play a role. We are working on that.

R. J. Dwayne Miller asked: I understand that the carrier dynamics can be nonlinear if you have carrier densities in the Auger regime (>10^{19} \text{ cm}^{-3}). However, the electrons will undergo photoemission at the surface region at your excitation wavelength. Your penetration depth is on the order of a few 10s of nm and the electron mean free path is on the few nm to 10 nm range. The photoemission creates a surface field, which for mj cm^{-2} excitation conditions could translate into a very large surface field that would affect your carrier dynamics. This near surface region of free electrons becomes trapped by the resulting charged surface potential with the electrons recombining with the surface on a time scale very similar to your observations (see work of C. Hebeisen et al.\textsuperscript{1} in imaging surface emitted photoelectrons using fs electron imaging of the charge distribution). This is just a suggestion that other processes may be involved that are unique to the soft X-ray excitation conditions employed.

Filippo Bencivenga replied: Thank you very much for your suggestion! To be honest, we didn’t consider this mechanism, but it is very likely that it is of relevance for data interpretation. We will look thoroughly into this point.

Jon Marangos asked: In principle could you write a transient grating with a non-seeded FEL?

Filippo Bencivenga answered: It depends on the longitudinal coherence length and the experimental geometry (the lower the crossing angle is the better it is). In general I’m a bit sceptical of the effectiveness of non-seeded FEL and nobody has tried it up to now.

Jon Marangos asked: How close to transform limited are the seeded pulses? What are the current limits on the photon energy range for seeded operation?

Filippo Bencivenga responded: The time-bandwidth product is ~1.5 and essentially reflects the degradation of the time-bandwidth product of the seed laser pulse when it travels through the optical transport line (several 10s of meters from the seed laser room to the undulator hall). It is very likely that the FEL pulse is as transform limited as the optical seeding laser. The larger photon energy achievable at FERMI (with pulse energy >1 μJ) is 310 eV, the facility is evaluating plans to extend this limit to ~600 eV. Larger photon energies are unlikely with optical seeding.

Daniel Neumark asked: Can you explain the different decay dynamics in the transient gratings formed in the two materials, silicon nitride and silicon oxide?

Filippo Bencivenga answered: We think that we generate an electron density grating in both materials, but in silicon oxide the decay rate is faster than our time resolution (~100 fs). This may be connected to the different bandgap of the two materials (~9 eV in silicon oxide vs. ~4 eV in silicon nitride).

Chris Milne enquired: What are your plans for extending the transient-grating set-up beyond semiconductor samples and into perhaps thin films of molecular samples or even liquids?

Filippo Bencivenga answered: We recently tested a set-up for the detection of the transient grating signal in reflection geometry. In this configuration we are not limited by the sample absorption (that is very strong at XUV/soft X-ray wavelengths). Using this set-up it is possible to probe thin samples deposited onto a substrate as well as bulk opaque samples. Liquid samples are already possible (in principle) using injectors and we are going to design a container for liquid samples with a thin Si₃N₄ window (a single window is enough by exploiting the TG detection in reflection geometry).

Jon Marangos asked: A technical question, you have a low rep rate 10 Hz – how long do you have to integrate to get your signals?
Filippo Bencivenga answered: An appreciable signal can be seen in a single shot (at the time coincidence), typical integration time is 600 shot/delay point, then we have some death times (~30%) in the acquisition system. Let’s say that a typical transient-grating measurement can take 2–6 hours.

Jon Marangos asked: Another technical question on the effect of seeding on the FEL field. Does it reduce the energy fluctuations?

Filippo Bencivenga answered: Yes, dramatically!

Hans Jakob Wörner asked: What is the diffraction efficiency of the XUV-induced grating? Can you conclude from this whether it is a pure amplitude grating or whether a phase grating is also involved?

Filippo Bencivenga replied: It is in the $10^{-5}$ to $10^{-8}$ range, depending on the sample. Up to now we worked with the field polarization perpendicular to the plane of the crossed FEL beams, so we have a pure amplitude grating. One of our planned next steps is to play with the FEL polarization to generate a mixed amplitude-phase grating (in plane polarization) and a pure polarization grating (crossed FEL polarizations); the latter may be possible with a special configuration of the FEL.

Jon Marangos asked: What is the minimum pulse duration you can go down to with the seeded FEL? Can it get to a few fs?

Filippo Bencivenga replied: In principle, yes. In the present configuration of FERMI the FEL pulse duration ($\Delta t_{\text{FEL}}$) is related to that of the seed laser ($\Delta t_{\text{seed}}$) by the relation: $\Delta t_{\text{FEL}} = (7/6) \times \Delta t_{\text{seed}}/N^{1/3}$, where $N$ is the harmonic number. At present $\Delta t_{\text{seed}} \sim 100$ fs and $N$ is in the 4–60 range, hence $\Delta t_{\text{FEL}} \sim 60–25$ fs. However, by reducing $\Delta t_{\text{seed}}$ down to ~20 fs $\Delta t_{\text{FEL}}$ can be reduced by a factor 5 (shorter seed pulses will not be effective in light of the FEL hardware of FERMI). More effective schemes are in principle possible, e.g.: (i) superradiance (FEL pulses ~10 fs with the present hardware but a large pedestal in the spectrum); (ii) coherent undulator emission (in this case $\Delta t_{\text{FEL}} = \Delta t_{\text{seed}}/\sqrt{N} \rightarrow \Delta t_{\text{FEL}} = 50–13$ fs with the present hardware but <1 $\mu$J pulse$^{-1}$); (iii) chirped pulse amplification (in this case $\Delta t_{\text{FEL}} = \Delta t_{\text{seed}}/\sqrt{N^{2/3}} \rightarrow \Delta t_{\text{FEL}}$ down to ~1 fs using $\Delta t_{\text{seed}} = 20$ fs, but an XUV/soft X-ray compressor downstream of the FEL is required).

Shaul Mukamel opened a general discussion of the paper by Victor Kimberg: Could you elaborate more on the merits and the sensitivity of your covariance technique? Which aspects of the stochastic nature of the field does it overcome?

Victor Kimberg answered: The covariance technique allows, in general, to take full advantage of the stochastic SASE radiation, widely available from present XFEL facilities. In a recent theoretical study$^1$ we showed the possibility for ultra-high (vibrational) resolution using two-color SASE pulses by means of statistical analysis in a stimulated X-ray Raman scheme. Indeed, the broad band spectrum of the SASE pulse (~5 eV) allows us to cover a wide vibrational excitation range for all electronic states involved in the X-ray Raman scattering. On the other hand,
narrow spectral width of an individual spike (~0.05 eV) of the SASE pulse is smaller than the typical vibrational spacing. Applying the covariance technique allows us to overcome the stochastic nature of the SASE radiation and to obtain vibrationally resolved RIXS maps for a broad frequency range.

However, the experimental situation is more complicated: The stochasticity of SASE radiation is often “contaminated” by some XFEL-related correlations, which should be excluded from the statistical analysis. For example, due to the instability of the XFEL source, the central energy of the X-ray beam varied in a rather broad range (+/− 3 eV) from shot to shot, while the energy spacing between the two X-ray frequency components is rather stable. This results in large XFEL-related features in the RIXS covariance map which mask completely the low-intensity fine vibrational structure related to the studied system. One can overcome this obstacle by recording the pulse energy for each XFEL shot and performing a partial covariance analysis over a sub-ensemble of XFEL shots with a small deviation of the SASE central frequencies and intensities (see also my reply to Jon Marangos regarding the ideal pulse to do simulated Raman). More sophisticated experimental schemes, such as self-seeding pump radiation considered in the present paper, brings about more complex spectral features of XFEL-related shot-to-shot covariance.

1 Struct. Dyn., 2016, 3, 34101.

Alvaro Sanchez-Gonzalez remarked: In relation to the use of covariance analysis in the case of a self-seeded pump SASE dump scheme, the main factor limiting covariance analysis to detect SRIXS was a strong correlation between the intensity of the seeded pump pulse and the depth of a hole appearing in the spectrum of the dump pulse for the particular FEL settings used. As a result of this, the covariance maps show a strong negative covariance peak exactly in the region where the positive SRIXS peak should appear. As a consequence, the background signal in the region of interest is really large, making it very difficult to observe a small SRIXS signal.

Peter Weber remarked: In laser spectroscopy, stimulated Raman experiments benefit greatly from heterodyne detection, where one looks at radiofrequency side bands. Is it possible to devise a similar method for X-ray stimulated Raman experiments?

Victor Kimberg replied: Indeed, heterodyne detection looks in general applicable for the case of nonlinear X-ray Raman processes, by using optical and X-ray frequencies. Recently, four-wave mixing of X-ray and optical frequencies in a crystal was reported,1 opening the gateway to new types of nonlinear optical-X-ray spectroscopy. However, the heterodyne detection method is rather difficult to implement at the present stage of the nonlinear X-ray Raman experiments due to limited longitudinal coherence of the currently available soft X-ray pulses and the complexity to design soft X-ray optics that would allow for splitting the X-ray beam in several beams and combining them at the sample with different angles of incidence. A discussion of “dream experiments” of stimulated Raman scattering can be found in several papers by the group of Shaul Mukamel. Although at the moment not quite implementable, I however believe that stimulated coherent
X-ray Raman spectroscopy will have a strong impact and will soon be accessible with development of X-ray sources in terms of their stability and coherence.

1 Steven Chu and Majumdar, *Nature*, 2012, **488**, 603.

Daniel Neumark asked: What is the lifetime of the final CO state produced by the stimulated X-ray Raman process? Is it long enough for the product to be directly detected via ionization, absorption, impact on a microchannel plate, or some other “flop-in” experiment that might be more sensitive than measuring gain in the X-ray emission?

Victor Kimberg answered: The final states of the stimulated X-ray Raman process are the valence excited states of the neural molecule (CO). The lifetimes of these states are rather large (varying from nanoseconds to microseconds) allowing in principle their direct measurement. At the present experimental settings of stimulated RIXS within a gas cell the direct measurement of the products is impossible. Indeed, we need to use rather high gas pressures (100–700 mbar pressure was used in our experiments) and a long gas-cell (up to 1 cm) in order to obtain high gain and high amplification for the nonlinear X-ray scattering. Moreover, as we have shown in our paper with the help of X-ray absorption analysis, strong XFEL radiation opens up many additional non-resonant absorption and ionization channels forming highly core- and valence-excited cations. These unstable products decay via various cascades with pico- to femtosecond timescales and thus can be hardly registered directly. In my opinion, the fingerprints of these intermediate products can be traced effectively from the advanced analysis of the stimulated RIXS measurements. Development of the theoretical framework for such analysis is one of the important future tasks.

Jon Marangos remarked: In response to the suggestion of detecting molecular products (rather than the stimulated field). I commented that in the latter case a high gas density is needed – but wouldn’t you need to go to a low gas density (i.e. a different experimental configuration) to collect the products with high fidelity?

Victor Kimberg answered: I agree, that this will be the main problem for direct measurements of the products, along with the non-resonant multi-channel excitation and decay processes in strong XFEL radiation.

Filippo Bencivenga asked: A possibility to implement heterodyne detection in the EUV/soft X-ray is to exploit the directionality of the signal in four-wave-mixing schemes. For instance by recording the interference between the (time-independent) diffraction from a physical grating and the (time-dependent) diffraction from a transient grating, as performed by E. Sistrunk et al. 1


Jon Marangos said: What would be the ideal pulse to do simulated Raman? Comment: Given the stability, possibility to reach the carbon edge, and two colour operation being developed maybe the Trieste seeded FEL is more like the ideal source.
Victor Kimberg replied: In fact, we would be rather satisfied with narrow-band (self-seeded) pump and broad-band (SASE) dump pulses, as it was used in our last experiment (July 2015), if the pump flux is strong and stable enough to launch the SRIXS. Use of the broad-band SASE pulse on the dump channel allows us to avoid a dump-energy scan, which would be necessary in the case of narrow-band dump radiation. We have shown theoretically\(^1\) that with the help of covariance analysis, applied to a large statistical ensemble of individual XFEL shots, high resolution (\(\sim 0.1\) eV) spectra can be obtained even in the case of broad-band SASE (\(\sim 5\) eV) pulses used in the SRIXS scheme.

In reality, however, the covariance analysis can be complicated due to strong XFEL-related correlations observed in the spectra. For example, in the two-color XFEL regime, the energy difference between the two X-ray components is kept constant at each XFEL shot, while the shot-to-shot variation of the central frequency is rather large (+/− 3 eV around 530 eV). As a result, XFEL-related features in the covariance map completely mask the fine low-scale structure of the SRIXS-related correlations. This problem can be solved by increasing the XFEL stability, or simply by using a partial covariance analysis for a sub-ensemble of XFEL shots with small deviation of the SASE central frequency and intensity. Partial covariance analysis however requires a much larger data set. (See also my reply to Daniel Neumark’s regarding the lifetime of the final CO state.) The suggested use of the two narrow band X-ray pulses would require a scan of both the frequency components in order to obtain a complete SRIXS map (2D function of the pump and dump frequencies), which is rather difficult to realize experimentally.

On the other hand, the use of a coherent X-ray radiation source is absolutely necessary for the study of nonlinear optical effects that require a stable phase relation, such as for example for four-wave mixing. We therefore would be looking forward to seeing a wavelength extension of seeded XFELs, for example an extension up to the carbon K-edge at the FERMI FEL. (See also my reply to Jon Marangos regarding the requirements of the synchronization of pump and probe pulses).

1 Struct. Dyn., 2016, 3, 34101.

Jon Marangos asked: What are the advantages of your scheme with respect to the impulsive Raman excitation – as you are in the “transient limit”, neither adiabatic or impulsive limit – what are the pros and cons of this?

Victor Kimberg replied: The main advantage of our “transient limit”, is its possible applications for nonlinear X-ray spectroscopic methods to study the nuclear dynamics in molecular systems. We apply our scheme to the soft X-ray range excitation, which has potential applications for the study of larger organic molecules, for which C, N, O K-edges, as well as many metal L-edges (vibrational energy transfer in bio-molecules, in metal-to-ligand transfer systems, etc.) can be addressed. Let us also note, that our scheme is fully adapted to presently available realistic parameters of XFELs operating in the soft X-ray range. Presently available X-ray pulses are still far from the ultrashort and coherent realization required for the impulsive Raman scheme. The adiabatic regime, on the other hand, would not allow for stimulated emission and other X-ray nonlinear processes, due to
pulse durations much longer than the typical lifetime of core–hole states. This would not allow the creation of a sufficient population of the core-excited state due to the strong non-radiative Auger decay channel in the soft X-ray energy range.

**Jon Marangos** asked: If you had a larger coherent bandwidth you could work in the impulsive regime. Not only would this give access to faster processes but it would ensure the phase coherence of the different spectral components of the field driving the Raman transition.

**Victor Kimberg** responded: The impulsive X-ray Raman scheme, developed theoretically in more details by the group of Prof. Shaul Mukamel, uses ultra-short (attosecond range) X-ray pulses with a rather broad bandwidth of a few eVs. This scheme addresses the dynamics of the electronic wave packet, since several electronic states can be core-excited coherently thanks to a broad-band transform-limited attosecond X-ray pulse. The nuclear dynamics is usually ignored in this scheme, since the scattering duration and the pulse duration are typically much shorter than the typical time scale for nuclear motion.

The main goal of our study was, however, to address the vibrational dynamics and nuclear wave packets by nonlinear X-ray processes. In this case, using the broadband spectrum of a short (below 1 fs) coherent pulse would not allow us to resolve the vibrational structure. In that sense, the use of a SASE pulse on the dump transition is even advantageous: the broadband SASE spectrum covers a broad range of the emission energies at each single shot, while the spectral coherence (average width of an individual spectral SASE spike) can be smaller than the vibrational level spacing. For this, we need to use rather long SASE pulses (~100 fs), since the spectral coherence is inversely proportional to the pulse duration. The high spectral resolution can then be achieved with the help of statistical analysis of a large ensemble of SASE shots, as explained in the reply to the question regarding the ideal pulse.

**Shaul Mukamel** remarked: The combination of a narrowband (picosecond) and a broadband (femtosecond) optical pulse is a powerful tool in stimulated Raman spectroscopy of molecular vibrations which yields a good optimal combination of spectral and temporal resolutions. This idea can be imported to the X-ray pump/probe technique by using a combination of a femtosecond and an attosecond pulse to study electron motion in a similar fashion. One possibility is to use an FEL femtosecond pulse and a HHG attosecond pulse.¹


**Markus Kowalewski** presented a comment:

**DETECTION OF CONICAL INTERSECTIONS THROUGH ELECTRONIC COHERENCES**

We want to point out three theoretically proposed experimental techniques, which allow for monitoring the nonadiabatic dynamics in the vicinity of conical intersections (CIs) (see Fig. 2). The first method is the Transient Redistribution
A nuclear wavepacket is photo-excited to a higher electronic potential surface where it then evolves towards a CI. At the CI, the wavepacket splits and a coherent oscillation is created. We then use a linear, hybrid narrowband–broadband (femtosecond–attosecond) Raman process to connect the two wavepackets (i.e., the upper (lower) wavepacket can be de-excited (excited) via a single off-resonant Raman interaction). In the absence of electronic coherences (or if the nuclear wavepackets no longer overlap) this linear Raman signal vanishes:

$$S(\omega, T) = 2\delta \int_{-\infty}^{+\infty} dt e^{i\omega(t-T)} e_0^*(\omega) e_1(t-T) \langle \psi(t) | \tilde{\alpha} | \psi(t) \rangle$$  \quad (1)$$

where $\delta$ is the imaginary part, $e_0$ ($e_1$) is the broad (narrow) band field, $T$ is the pump–probe time delay, and $\tilde{\alpha}$ is the molecular polarizability. Through its frequency dispersed, linear detection TRUECARS provides a direct and background free measurement of the electronic energy gap between the electronic states. The second method is time resolved photo electron spectroscopy (TRPES). It can be shown that with sufficiently short ionization pulses the created electronic coherence can be detected in the form of coherent oscillations on top of the population dominated TRPES signal. The third method is the streaking of photo electrons, which can be viewed as an extension of TRPES. Here, a strong infrared laser field is superimposed on the XUV ionization field, allowing to “time stamp” the released photo electrons. With the streaking technique adding the streaking
delay to the detection scheme, the Fourier limitation of the TPRES method is lifted and the time resolution is enhanced.


**Daniel Rolles** asked: Please give us a few more details about the results of the time-resolved photoelectron spectroscopy. What are the advantages and disadvantages of doing time-resolved photoelectron spectroscopy vs. Raman?

**Markus Kowalewski** answered: The major difference between time resolved photoelectrons (TRPES) and Raman is the fact that the TRUECARS scheme is background free, *i.e.* the signal contains only contributions from the electronic coherences. The TRPES signal is mainly composed from the population contributions with the oscillating coherence contribution on top of it. TRPES is thus not a background free detection method.

From an experimental point of view a TRPES measurement might be easier to realize nowadays with technology, possibly with an HHG based light source. The off-resonant Raman scheme requires intense attosecond laser pulses.

**Jon Marangos** asked: What are the requirements on the synchronization of pump and probe pulses?

Comment: A high degree of synchronization is achievable with a HHG source, but there the fields are weak. The alternative is a seeded FEL scheme.

**Markus Kowalewski** responded: In the TRUECARS detection scheme there is no requirement for phase synchronisation between UV pump pulse and the pulses in the probe sequence. However, the broadband and narrowband Raman pulses in the probe need to be phase stable with respect to each other.

**Filippo Bencivenga** said: The possibility to scale down the “ps-narrowband and fs-broadband” approach, by coupling (fs) FEL and (as) HHG sources is a very exciting idea! The synchronization issue is very demanding, in this respect laser-seeded FEL’s offer the advantage that the same optical laser may drive both FEL and HHG sources.

**Daniel Neumark** addressed Shaul Mukamel and Markus Kowalewski: Would it be possible to observe similar effects to those predicted in your calculations using transient X-ray absorption to monitor signals associated with Br and Br*?

**Markus Kowalewski** answered: If you prepare an electronic coherence between the Br and Br* state, the Raman detection would show up, given there is a non vanishing transition polarization matrix element between the two states.

**Shaul Mukamel** responded: In principle, transient X-ray absorption carries information about specific oxidation states of various species. However, stimulated Raman signals are much better resolved spectrally since they are not
broadened by the core lifetime, and the broad bandwidth gives a snapshot of many valence states in the vicinity of the selected atom. The technique is thus much more selective and sensitive than transient absorption.

Jon Marangos addressed Shaul Mukamel and Markus Kowalewski: In the schemes for Raman experiments with a broad band probe and a narrow band pump do the broad and narrow band fields have to be coincident in time?

Markus Kowalewski answered: The TRUECARS Raman detection technique we showed is supposed to be an off-resonant detection. The two components of the hybrid pulse must be temporally coincident. It is noteworthy that the purpose of utilizing a hybrid pulse is to exploit the dependence of the TRUECARS signal on the relative phase of the two components of the pulse (e.g., to distinguish it from the transient absorption signal). In practice, there is no spectro-temporal resolution gain achieved by employing a hybrid pulse specifically composed of broadband and narrowband components. This is due to the signal being defined as the frequency-dispersed transmission of the broadband component.

Shaul Mukamel responded: This is an interesting and subtle issue. If the molecule is stationary, the Raman process is instantaneous and the two photons are time coincident (within the electronic dephasing time). Time resolution is not an issue in that case since no dynamical process takes place. However when the molecule undergoes a process such as nonadiabatic dynamics, the signal does not simply depend on the temporal overlap of the two pulses since the two photon process is convoluted with the dynamics. This is clearly seen from the expressions for the signal.

Jan Marcus Dahlström asked: I have two questions about the use of short and long pulses to obtain simultaneous resolution in both time and frequency. Recently, I was involved in a theoretical study of photoionization by one short pump pulse and two “monochromatic” probe fields. In our work, we found that the effective two-photon interaction was limited to the short duration of overlap between the pump pulse and the probe fields (in a resonance free region). In practice this means that only a small fraction of the probe field energy is used efficiently. Are the processes your study also suffering from this overlap issue? How high would the probe pulse energies need to be to reach a meaningful signal without complete ionization of the target during pump ramp up?


Shaul Mukamel responded: The temporal and spectral resolutions in nonlinear optical signals are not fully controlled by experimental knobs and depend on the molecular response as well. The molecule decides which spectral components of the pulses are relevant in a given measurement which affects the resolutions. This is discussed in ref. 1 and 2.

Stimulated Raman signals have been measured in atoms (Ne) using the LCLS. This demonstrates their ability to compete with Auger and other ionization processes.
Morgane Vacher commented: In your Raman simulations, the nuclear wave packet initially on one electronic state approaches the conical intersection and then splits on the two electronic states, leading to coherent oscillations in the simulated spectra. As time goes by, the nuclear wave packet moves back and forth, crosses several times the conical intersection and the coherent oscillations seems to survive for a long time.

However, the harmonic potentials used look very similar, just slightly shifted in position. The energies of the two electronic states may be more realistically described by potentials of different frequencies and shifted both in energy (along the vertical axis, i.e. minima at different energies) and in position (along the horizontal axis, i.e. minima at different nuclear geometries). I would then expect the nuclear motion on the two potentials to be quite different. As the overlap between the nuclear wave packets on the two electronic states decreases with time, don’t you anticipate that the coherences should disappear with time in this more realistic case?

Markus Kowalewski replied: The harmonic system is suitable to clearly demonstrate the features of the signal. As you already pointed out this is not a realistic system, because the coherences, i.e. the wave packet overlap is too long lived. In ref. 1 we also show a simulation for a more realistic 2D system with non-harmonic potential energy surfaces and a conical intersection. The decay of the signal and the electronic coherence depend on the gradient difference between the surfaces. The TRUECARS signal thus contains not only information about the electronic energy gap but indirectly also information about the gradient difference.

Hans Jakob Wörner opened a general discussion of the paper by Dane Austin: In your article, you are discussing the importance of the asymptotic part of the Dyson orbitals in defining the properties of the continuum wave packets in high-harmonic spectroscopy. In a recent study of high-harmonic spectroscopy of the methyl halides,1 we have found that the existence of a permanent dipole moment can qualitatively change the shape of Dyson orbitals, when the Stark shift becomes larger than the separation of the electronic states (which were degenerate in our case). Can you explain which role this effect plays in your work?

Dane Austin answered: In principle, laser-induced coupling of the cation states is included in our calculation for through equation (4) in the paper, which describes the coupled evolution of the phases of the cation states in the field-free basis. One could derive the laser-induced shape change of the Dyson orbitals by diagonalizing the matrix \( |T_p - E(t)\cdot \Delta H| \) that appears in (4), and forming
appropriate linear combinations of the orbitals. Figure 3 shows the result of such a calculation for benzene and o-xylene with a static field corresponding to $0.3 \times 10^{14} \text{ W cm}^{-2}$ along the x-axis.

The Dyson orbitals of the field-dressed states are indeed significantly distorted with this particular field direction. This occurs even in benzene, which has no permanent dipole. However, we find that the overall effect on the angular dependence of the harmonic emission is small. Figure 4 (which is the same as Fig. 2 of the paper) shows the orientation-resolved emission from toluene. Figure 5 shows the same simulation with the laser-induced coupling switched off. The change in the relative amplitude of the emission from the different orientations is of order 10%, and the phase flip between the upper and lower half-planes is still present.

**Albert Stolow** stated: The dynamic polarizability of the ion core can have a big effect on strong field ionization processes. As an example, it is remarkable that, in the same laser field, transition metal atoms (I.P. around 7 eV) can have ionization rates comparable to Xenon atoms (I.P$>$ around 12 eV).\(^1\) This is due to dynamic screening in the core which reduces the field applied to the departing electron. Have you considered the polarizability of the ion core in your modelling?


**Dane Austin** replied: The polarizability is not included. Including such effects in HHG molecular calculations is beyond the capability of current models. We agree it is likely to significantly alter the orientation-independent part of the ionization rate. Indeed, the saturation intensities of benzene and toluene were shown in 2000,\(^1\) to be much higher than that expected from ADK. Regarding the
Fig. 4  Spectral amplitude (a) and phase (b) of the attosecond burst from a single laser half-cycle in toluene with the laser field in the HOMO symmetry plane; the radial direction corresponds to photon energy and the angle $\theta$ is between the ring carbon–methyl carbon bond and the direction of electron motion at ionization. The phase is plotted relative to the average over all angles (removing the angle-independent attochirp), and its color is set to grey where the amplitude is less than 1% of its maximum value. (c) Amplitude (blue, left $y$-axis) and phase (red, right $y$-axis) at 20 eV. Both $y$-axes have the same scale as the respective color scales in (a) and (b).

orientation dependence, some indication of the anisotropy is given by the measured polarizabilities along the principal axes of the molecule.$^2$ Of the molecules considered in this study, the most anisotropic is $p$-xylene, which is 50% more polarizable along its major axis than perpendicular to the molecular plane. Connecting this bulk effective medium polarizability to the dynamic screening relevant to tunnel ionization requires more theory however. We note that the
effect of a linear polarizability possesses inversion symmetry, and hence will not affect the asymmetries caused by the substituent groups.


**Jon Marangos** asked: Dane looked at a number of different cation channels, he found that the different channels had different dependencies on alignment. To what extent in a given experiment should we consider an individual molecule in a coherent superposition state and when should we regard the system as a statistical mixture?
Dane Austin replied: The different channels do indeed have completely different dependencies on alignment. The plot (Fig. 6) shows the intensities (left column) and phases (right column) of the emission at 20 eV, resolved by orbital (rows) and molecular orientation (horizontal and vertical axes of each subplot).

The intensity distributions of the different orbitals are nearly orthogonal. Therefore, to a good approximation the system is a statistical mixture, with the participating orbital determined by the molecular orientation. That said, there are particular angles where the X and A states contribute similarly to the emission, but these are a small fraction of the total.

Morgane Vacher addressed Dane Austin: In atoms or small molecules, orbitals may have well-defined symmetry and potentially (perpendicular) nodal planes. Therefore, different electric field polarisations (or rather different orientations of the molecule with respect to the electric field polarisation) would open different ionisation channels i.e. lead to ionisation from different orbitals. An important consequence seems indeed to be the population of a single, but different, electronic state in each molecule across an ensemble of unaligned molecules, rather than the population of a coherent electronic wave packet in each molecule of the sample. The magnitude of this effect depends on the molecular system and especially on the structure of the molecular orbitals. As we go to larger and less symmetric molecules, this effect may be less important which suggests we would “recover” the population of coherent superpositions in each molecule.

**Fig. 6** Plot showing the intensities (left column) and phases (right column) of the emission at 20 eV, resolved by orbital (rows) and molecular orientation (horizontal and vertical axes of each subplot).
Dane Austin answered: I agree, and Figure 6 in this discussion in my earlier response illustrates this.

Hans Jakob Wörner addressed Dane Austin and Misha Ivanov: I would like to comment about the role of electron-ion entanglement in reconstructing ionic dynamics from high-harmonic spectroscopy. Let us consider two electronic states of the cation ($\psi_X$ and $\psi_A$) and their associated electronic continua $\psi_X$ and $\psi_A$. When these two continua are orthogonal to each other and laser-induced transitions in the ion (real or virtual) are neglected, the ion-electron wavefunction is fully entangled, i.e. it must be written as $\psi = c_X^* \psi_X + c_A^* \psi_A$, where $c_X$ and $c_A$ are complex coefficients and cannot be factorized into a product of the ionic and continuum wavefunctions. In this case, nothing can be said about the electronic state of the cation and no dynamics can be reconstructed. If, in contrast the continua $\psi_X$ and $\psi_A$ have partial overlap, then partial information about the ionic state can – in principle – be extracted from a high-harmonic measurement.

Dane Austin responded: I basically agree, but would express it slightly differently. Regardless of the number of participating electronic states, HHG is only sensitive to the component of the ion-electron wavefunction in which the continuum electron has appropriate momentum for recollision (i.e. zero transverse momentum in a linearly polarized laser). Whenever one speaks of reconstructing dynamics with HHG, one is always – implicitly or explicitly – referring to this component of the wavefunction. Regardless of the orthogonality of the wavefunctions or the degree of entanglement, this component is at least well-defined, although as you point out it may not be the full picture.

Misha Ivanov responded: This comment is absolutely correct. Of course, in the presence of the laser field, dynamics in the ion occurs even when the continua are orthogonal, and the interferometric nature of high harmonic measurement allows one to capture such dynamics: the whole process starts and ends in the same state (the neutral ground state). Moreover, for sufficiently high continuum energies, the continua correlated to different cationic states have very substantial overlap, so the degree of entanglement is low and the degree of coherence is high.

Hans Hakob Wörner remarked: In situations where the electronic states of the cation have a different electronic parity (e.g. X vs. B in CO$_2^+$), electron and ion are maximally entangled, which prevents the definition of a unique time-dependent electronic wavefunction for the cation. Does the perpendicular two-color HHG scheme used here fundamentally change this situation?

Nirit Dudovich and Misha Ivanov replied: The two-color scheme does not change the situation, but the situation is somewhat different from how you have described it. In fact, the assumption of maximum electron-core entanglement for different electronic parities of the cationic states is not straightforward. Consider, for example, the case of X and B states of CO$_2^+$. Had the molecule been perfectly aligned along the laser polarization, the outgoing continuum electron wavepackets would have been, indeed, orthogonal to each other. The wavepacket originating from the X state would have had a node along the laser polarization, while the wavepacket emerging from the B state would have had no node. However, there are
no perfectly aligned molecules. In our experiments, the characteristic alignment angle is about $30^\circ$. In this case the nodal structure of the continuum wavepacket correlated to the X state of the cation is gone, and the wavepacket is very similar to the continuum wavepacket correlated to the cation in the B state. Of course, none of this changes the analysis of the high harmonic emission itself, since in this process the initial and the final states of the system are the same and the interference of different pathways proceeding \textit{via} different ionic states is not affected by entanglement. Specifically, the reconstruction procedure for the amplitudes of different ionization channels correlated to different ionic states is not affected by the degree of electron–core entanglement.

Kiyoshi Ueda addressed Dane Austin and Misha Ivanov: Let us consider the case when HOMO is doubly degenerate, like benzene (or CO$_2$). I suppose field ionization may be regarded to occur from one of the HOMO orbitals, or a linear combination of them from which the ionization rate is maximal. Then, the returning electron wavepacket sees the polarized ion (the ion part would not have time evolution in this case) and so the recombination takes place for the polarized ion. Does theory take account of such a polarization effect of the ion or can the effect be negligible?

Dane Austin replied: The theory takes into account ionization occurring from all of the included orbitals (5 in this study). Linear combinations are certainly possible, depending on the relative ionization potentials of the orbitals and the orientation of the molecule. My previous answer to Jon Marangos on coherent superposition state illustrates this – there are some angles at which emission from only one orbital dominates, and others were multiple orbitals participate equally. In the model, the electron can only recombine into the orbital with which it is correlated. Transitions of the ion between different orbital vacancy states driven by the laser are possible, but do not appear to play a large role.

Misha Ivanov answered: Yes, our theory takes this into account fully. This is one of the key aspects of the paper: we include both real and virtual excitations of the ion between ionization and recombination, which leads to coherent addition of multiple recombination pathways \textit{via} different ionic channels.

Kiyoshi Ueda addressed Dane Austin and Misha Ivanov: If two orbitals participating in the tunnel ionization are not degenerate, does the coupling between the two hole states \textit{via} the IR field play any role? Are such effects included in theory?

Dane Austin responded: The orbitals are degenerate in all the molecules except benzene. The coupling is included in the theory, but does not play a large role in our study because (i) for the most part (all results except Fig. 5 and Fig. 6 in the paper) the electric field is restricted to a nodal plane of the HOMO-1, so that it does not participate, and (ii) the coupling is fairly small.

Misha Ivanov responded: Yes, this coupling is included, both due to the IR field and due to the returning electron. The IR-induced coupling is incorporated by solving the Schrödinger equation for the ion in the IR field. The electron-
induced coupling of the ionic states is naturally included via multi-channel R-matrix calculations of the recombination dipole.

**Hans Jakob Wörner** addressed Misha Ivanov: I understand from your article that you have calculated the dynamics of the cation during the “propagation step” by solving the TDSE in the basis of the lowest four electronic states of the cation. Is such a calculation really converged for CO$_2^+$ with only four states and without including the ionization continuum of the cation?

**Misha Ivanov** replied: Given the intensity and the mid-IR wavelength of the driving field, yes. Most of the dynamics in the mid-IR field is due to laser-induced polarization of the core. We have checked that the four states were sufficient to represent the relative Stark shifts of the cationic states. In fact, the important role of the C state was a bit of a surprise, given how far it lies above the ground state of the cation – the reason turned out to be the strong coupling between the C and B states. Of course, a lot more states are needed to converge the recombination step due to the high energy of the returning electron – up to 300 states where used, including representation of the double continuum.

**Albert Stolow** opened a general discussion of the paper by Nirit Dudovich: Field-driven non-adiabatic interchannel coupling, also termed Nonadiabatic Multi-Electron (NME) ionization, can induce sub-cycle transitions in the field, particularly when the field is changing most rapidly.$^{1,2}$ This is expected to be near the zero crossing of the field, leading to the expectation of a quarter-cycle phase shift between adiabatic multi-channel strong field ionization and these field-induced non-adiabatic processes. Have you seen evidence of such processes in your results or analyses.


**Nirit Dudovich** answered: In our previous study$^1$ using a perturbative field in parallel polarization we observed a signature of nonadiabatic dynamics in tunneling. Indeed as you suggest, nonadiabatic dynamics leads to a shift in the two color phase, compared with the adiabatic picture.


**Danielle Dowek** remarked: The method presented in the paper “Multidimensional HHS of polyatomic molecules” provides a means to characterize the multielectron dynamics induced by strong field ionization in molecules (first step of the HHG process), featured by the contribution of different ionization channels and their coupling during ionization. The question is about the ability, with the support of the AZUR method presented, to disentangle the coupling between different ionic states (here of the CO$_2^+$ molecular ion) induced by the IR laser field from that driven by electron correlation dynamics, also evidenced in weak field photoionization, and to determine the relative weighting due to both types of interaction.
Misha Ivanov responded: Disentangling the two contributions is a very important point. We believe this becomes possible when mid-IR drivers are used, so that the electron excursion is much larger than the characteristic size of the “inner region”, where ion-electron correlation cannot be ignored. In this regime, one cannot disentangle the role of the tunneling electron and the laser field in the inner region, and this complex dynamics creates the target of reconstruction: the unknown amplitudes and phases of the cationic states created when the electron leaves the vicinity of the molecule. In the AZUR method, we treat these as unknowns and aim at reconstructing them from the best possible calculation of the remaining two steps of the three-step HHG process: electron propagation far away from the laser-driven core, and electron recombination with the laser polarized core characterized by IR-induced amplitudes in the different cationic states.

Danielle Dowek asked: Would the polarization analysis of the HHG radiation constitute an interesting additional dimension to the multidimensional high harmonic spectroscopy study presented in this work?

Nirit Dudovich answered: Polarization analysis holds the potential of adding valuable information. When the molecule is aligned at 0 or 90° such an analysis does not require a polarizer. Due to symmetry odd harmonics are polarized along the fundamental field’s polarization while even harmonics are polarized along the SH field’s polarization. The polarization vector is dictated by the recollision angle and the polarization of the dipole moment. Extracting the modification of the recollision angle provides an additional signature of strong field’s trajectories that participate the interaction.


Allan Johnson asked: Given that the two-colour method functions by disturbing the phase of the recolliding electron, this must also change the phase of the HHG emission, which should change the phase matching conditions as well as the single emitter response. What effect do you expect this to have upon the macroscopic signal, and how do you take this into account for comparisons with single emitter theory calculations?

Nirit Dudovich answered: Phase matching conditions are modified when the propagation length is sufficiently long. Our setup minimizes modifications of the phase matching conditions, by generating HHG in a thin jet and low gas pressure. We verify that phase matching does not play an important role by performing a systematic study. We perform the two color scan for different pressure values and focusing geometry. Our experiment is invariant to these modifications, demonstrating that they reflect the single molecule response.

Allan Johnson remarked: When would you expect your phase matching controls to fail? For instance, I can imagine in a system with many absorption resonances the phase matching conditions becoming too complicated to simply isolate the single emitter response.
Nirit Dudovich answered: The single molecule response approximation can fail in the case of long propagation distances, or in case of multiple absorption lines. In this case the 1D HHG spectrum will reflect the macroscopic response. This is a general limitation of HHG spectroscopy which is not unique to the two color measurement.

Hans Jakob Wörner said: In his article, Fernando Martín has shown that in single-photon ionization, the leaving photoelectron can perturb the dynamics over the first 0.5 fs. Whereas the exact length of the relevant time span will depend on the velocity of the electron, this raises a question about the possible influence of the continuum electron on the ionic dynamics during the “electron propagation step” of high-harmonic spectroscopy. I understand that the influence of the continuum electron is accounted for in properly correlated multi-channel calculations for recombination and it is accounted for in the ionization step by adjusting the relevant populations and phases of the ionic-state coefficients, as also performed in our recent work.1

1 P. M. Kraus et al., Science, 2015, 350, 790.

Misha Ivanov replied: The complex dynamics associated with the interaction between the outgoing electron and the core is one of the key reasons for nontrivial ionization phases and amplitudes. Reconstructing these phases and amplitudes is the key aspect of the paper. In fact, excitation of the ionic core driven by the outgoing electron on its way out are the source of the surprisingly large probability of ionic excitation during tunneling.1,2 The real question here is whether one can split the whole high harmonic generation process into three steps (ionization, propagation, recombination) and treat the “propagation” step separately. The short answer is “yes”, for sufficiently long driving wavelengths. Indeed, the influence of the outgoing electron on the core is determined not by the time (say, 0.5 fs), but by the distance between the electron and the core. The characteristic distance we should worry about in this context is about 10 Bohr or so – the inner region in the R-matrix approach. As long as the electron excursion in the intense, mid-IR laser field is large compared to this distance, the “simple” propagation step can still be factored out, relegating all complexity to the “ionization” step.2


Artem Rudenko addressed Misha Ivanov: The pulse duration used in the experiment is comparable to the vibrational period. Does the vibrational motion disturb the reported reconstruction of the phases for different ionization channels?

Misha Ivanov responded: Firstly, there is some (rather limited) effect of vibrational dynamics in the cation, between ionization and recombination. It is easily accounted for via a complex nuclear auto-correlation function between the nuclear wavepacket created at the moment of ionization and the nuclear wavepacket at the moment of recombination, see ref. 1. Secondly, there might be some
vibrational excitation of the neutral molecule, which could change the harmonic emission at the beginning and at the end of the pulse. This has not been included in the analysis.


**Raluca Cireasa** asked: In photoionisation, shape resonances lead to changes in the phase sign of the outgoing electron wavefunction. The CO$_2$ molecule has a shape resonance in the C state. This may induce a flip of the phase sign for the harmonics emitted at energies in its vicinity. Did you include in the calculations the shape resonance and if so, how does it contribute to the phase?

**Zdenek Masin** replied: The formation of the shape resonance in the C-channel has been included in the $R$-matrix modeling of the dipole matrix elements. For details of this model see ref. 1. For the purpose of this work, where we aim at describing HHG driven by mid-IR pulses, which results in extremely high energies (up to approx. 100eV) of the returning electron capable of exciting the ion, this model has been extended to include a large number of 300 cationic states and a more accurate description of the continuum wavefunction. However, these changes did not result in significant differences in the description of the shape resonance which remains in an excellent agreement with experimental data. The shape resonance appears in the partial photoionization cross section as a broad peak between approx. 30 eV and 50 eV of photon energy with a peak around 40 eV. Both the amplitude and the phase of the resonance are included in our calculations. For example, its effect on the HHG signal can be seen from Fig. 9 of the paper being discussed which shows the channel-resolved contributions to the total signal. The direct contribution of the state C, see panel (b), shows an enhancement with a peak around 40 eV whose width approximately corresponds to the width of the resonance in the partial photoionization cross section. This enhancement of the C–C contribution probably comes from the shape resonance.

Figures 12 and 14c of the paper show the relative phases between different HHG channels. Due to laser-driven dynamics in the ion between ionization and recombination, electron recombination with the C state of the ion imprints the recombination phase onto several HHG channels, such as BC, XC, CC. The phase of all channels recombining to C (BC, XC, CC) with respect to channel XX does not show specific structure-related features in the vicinity of the resonance due to the following reasons: (i) the resonant feature is quite broad in energy (ii) other contributions to harmonic phases evolve faster as a function of harmonic number.


**R. J. Dwayne Miller** asked: The use of 2 colour HHG as the first entry into multidimensional methods seems very promising with respect to extension to more complex systems. The additional information as you show helps distinguish mechanisms. In terms of chemical dynamics, the relevant time scales are nuclear (femtosecond domain). The changes in electron distribution with excitation create forces (the excited state potential energy surface is displaced from the ground state) that lead to nuclear motions and subsequent relaxation to some
minima. The attosecond methods for following the electron dynamics hold great potential for giving us information on the electron distribution during this process. The electron dynamics do, however, become rate limiting with respect to the dynamics at CI. There have been a few small molecule systems studied in which it has been possible to access this information (N₂ orbitals for example). Do you think multidimensional HHG methods are important to advancing the imaging electron distributions/dynamics at CI’s? I recognize that you are currently using VUV transitions related to core transitions and hole redistribution. I am referring to optical preparation with HHG probes.

Nirit Dudovich replied: The use of HHG to follow electronic dynamics near CI’s is indeed an exciting direction for the field. We are very interested in pursuing this direction using multidimensional HHG methods. We have already used such methods to provide full reconstructions of the electronic dipole moments in vibrating molecular dimers, see Ferre et al.¹ The concepts presented in this work could be generalized to provide a picture of the nuclear and electronic dynamics near CI’s. This would entail optical preparation of the excited state, as the questioner implies, followed by a time delayed two colour HHG probe. Since the probing takes place on attosecond time scales, the measurement can be made on sufficiently fast time scales to resolve the electronic distributions and dynamics near the CI. This measurement will be an exciting extension of the current study – we will be able to resolve how multielectron dynamics evolves while we change the potential surfaces.


Albert Stolow asked: A non-zero polarizability in the ion core means that there could be an “image charge” or “hole” in the ionic charge distribution during strong field ionization¹ which is itself driven in the field but presumably has a different effective mass. How would the non-zero polarizability of the ion core affect the interpretation and modelling of your results?


Nirit Dudovich and Misha Ivanov answered: The target of our analysis is the reconstruction of ionization amplitudes. The complexity of the ionization process does affect the reconstruction procedure. However, it will affect the outcome – the amplitudes we reconstruct.

We have found that channels B and C are a lot stronger than standard, single-channel tunneling theory would predict. This has to be related to the interaction between different cationic states, and between the cation and the outgoing electron, during the ionization process. The interaction can be induced by the laser field and by the electron–electron correlation, the latter changing the state of the cation during the departure of the tunneling electron, a process we have described previously,¹,² which can lead to substantial enhancement of the ionization amplitudes from inner orbitals. Regarding the polarization of the core described by M. Smits et al.,³ it can be viewed as the adiabatic limit of the non-adiabatic electron–core interaction during tunneling,¹,² which we think is likely to
be responsible for the enhanced ionization amplitudes from the deeper orbitals, relative to the ionization amplitude from the highest orbital.


**Jon Marangos** asked: You demonstrate the importance of good molecular alignment, how then can we apply these techniques when we have not got the controls?

**Nirit Dudovich** responded: Indeed, if the alignment angle cannot be directly controlled the measurement will reflect an averaged response only. However, in the case of a poor alignment contrast, applying a more advanced measurement scheme can be applied. Adding an XUV polarizer will isolate the weak contribution of the aligned molecules from the large signal obtained from the unaligned molecules.

**Albert Stolow** asked: Would it be possible to observe field-induced non-adiabatic interchannel coupling, which leads to a “memory” (non-periodicity) effect between one field cycle and the next, in the form of the envelope of the total high harmonic spectrum?

**Nirit Dudovich** replied: Field induced non-adiabatic interchannel coupling that leads to “memory” will leave a clear signature on the spectral response within each harmonic order. Such a memory will break the periodicity between the different cycles, leading to spectral variation of the two color phase on a sub-harmonic scale. In the experiment described in the paper such a modification has not been observed.

**Wolfgang Domcke** opened a general discussion of the paper by Raluca Cireasa:

Could you please explain the connection between your measurements and radiotherapy. Which kind of radiation is employed in radiotherapy, what are the chemical mechanisms and how is radiotherapy related to your results?

**Raluca Cireasa** answered: The most common radiotherapies employ either photon-based sources (X-, $\gamma$-radiation) or particle-based sources (proton, heavy ion beams). It is generally agreed that the mechanisms responsible for the destruction of DNA (single and double strand breaks) by the ionising radiation occur following indirect processes: interactions of the DNA with primary and secondary low energy electrons and radicals (OH, OH*,...), ions, pre- and hydrated electrons.\(^1\)\(^-\)\(^3\) The radiation produces all these species as it travels through matter (water and other biomolecules) to reach the tumour site thereby leading also to the destruction of healthy cells. In the case of the photon-based radiotherapies, the energy is distributed and attenuated along the irradiation path, while in the case of particle therapies, the energy can be delivered in
a more controlled and localised manner to the tumour site to reduce the damage of the healthy cells. In combination with radiosensitiser molecules (including 5FU), they permit to devise more efficient treatments, while reducing the radiation dosage. In the particular case of the halogenated radiosensitisers, it was suggested that the interaction with hydrated electrons or low energy electrons, generated in the radiotherapies, leads to anion formation and their subsequent dissociative electron detachment produces reactive species: halogen atom/anion and uracil anion/uracil neutral radical, respectively.\(^4\)\(^5\) Although most of the chemical studies focused on the indirect processes induced by the ionising radiation in the DNA, nevertheless, about half of the processes initiated in the DNA result from the direct interaction with the radiation.\(^3\) With the development of new therapies that target better the tumour site, perhaps these direct processes may become prevalent and their studies could reveal new mechanisms underlying the DNA damage and radiosensitivity. In our project, we investigate the direct interaction between the 5FU radiosensitiser molecules and ionising radiation. We have chosen XUV radiation to study the ionisation in the valence region where the dissociation processes occur. We have performed both time- and energy-resolved measurements. The fragmentation spectra recorded for 5FU (see the paper) and 5 BrU in our experiments have very similar relative intensities of the peaks as those obtained in 100 keV proton beam experiments.\(^6\) At such high projectile velocities only a small fraction of a few tens of eV is deposited in the molecules and the proton induced ionisation bears similarity with the photoionisation processes. Therefore, our studies have direct relevance for these experiments and our time-resolved results may be used to validate mechanisms proposed in ref. 6 to explain dissociation processes induced by proton beams. At higher XUV energies (not presented in the paper), we measured timescales for tautomerisation and isomerisation processes which were also observed through the fragments detected in the proton mass spectra. The information we obtained for the electronic states and the dynamics timescales helps us to build a picture of the photo-damage and photo-stability processes occurring in the gas-phase 5FU. Our studies relate to the studies of the interaction of gas-phase radiosensitisers with proton beams, which is the radiation employed in radiotherapies. The complementary information gained from both these studies about the intrinsic properties of 5FU radiosensitiser molecule is extremely valuable for modelling the interaction between radiosensitisers and ionising radiation, and such experiments are the first step in a bottom-up approach aimed at the investigation of the mechanisms underlying radiosensitivity (from isolated molecules to in-vitro and in-vivo).


**Jon Marangos** asked for a clarification of the pump–probe pulse sequence used in the experiments.
Raluca Cireasa answered: We have employed several pump–probe excitation schemes to investigate 5FU cation dynamics: XUV + 800 nm, XUV + 266 nm, 400 nm + 800 nm and 400 nm + 266 nm. The molecules are ionised and excited either by the absorption of a single XUV photon, or alternatively, of several 400 nm photons. These dynamics initiated by single photon ionisation (SPI) or multi-photon ionization (MPI), respectively, are probed either by 800 nm photons or by 266 nm photons. The corresponding transient signals appear for positive delays in Fig. 4 of the paper. For photon flux requirements, we have used all the high-order harmonics (HHs) contained in the XUV spectrum (HH3–HH9). In order to disentangle the various channels that could be excited simultaneously by different or the same HH, we employed excitation schemes based on MPI and also different probe wavelengths. The 400 nm was the driving wavelength in the high harmonic generation process and MPI provides excitation energies commensurate with individual HHs. Based on the comparison of the dynamics initiated by SPI and by MPI, we were able to identify the HH responsible for initiating particular dynamics.

Adam Kirrander asked: Looking at the transients in the XUV + 800 nm measurements (Fig. 6 in your paper), it appears that one may distinguish some periodic oscillations in the signals? Is this correct, and if so, have you attempted to fit them?

Raluca Cireasa answered: There are visible fluctuations in some of the signals that lend to associations with oscillatory behaviors. The signals for m/z = 60, 32 and 1 are low and the fluctuations reflect low S/N ratios. For m/z = 28, they seem to be on a longer time scale and have more an appearance of proper oscillations, however, there is no regular pattern and we have not attempted to fit them.

Ruaridh Forbes remarked: In Table 1 of the presented paper time constants are listed which were obtained from fitting the time-resolved ion yield data. In several of the mass channels, for example m/z 87, numerous time constants are extracted which have values significantly less than the temporal resolution of your experiment. The reported time resolution in your experiment, obtained from cross correlation signals in Ne, was 45 fs (for XUV + 800 nm). Could you comment on the reliability of fitting and the absolute values obtained from the fit?

Raluca Cireasa answered: Indeed, several time constants, corresponding to time delays and a rising time, have values in the range of 6–9 fs, which represent 15–20% of the time resolution value of 45 fs. They are non-trivial parameters that were included in the model to accurately reproduce the time dependences. The transient signals from Fig. 6 in the paper obtained with an excitation scheme: XUV (HHG in Kr) + 800 nm, exhibit significant shifts of the peak maxima from 0 fs time delay, thus indicating the necessity to account for time delays in the dynamics and in the fitting procedure. These parameters are unambiguously determined with a confidence level of 95% (1 σ = 1 fs: corresponding to 15–10% of their value of 6–9 fs). The m/z = 87 ion signal exhibits a visible step contribution. The fit yielded a time constant associated with an ultrafast rising time of 9 ± 7 fs, which is less accurately determined, but still significant at the same confidence level of 95%. Without accounting for this step contribution in the model, the data...
could not be reproduced and the time constant and the error extracted for the 
other dynamics would be affected. Consequently, all these parameters are 
physically meaningful for the fitting models employed. As for the reliability of 
the extracted values with regard to the experimental resolution, if the 0 fs time delay 
and the time resolution are well determined through an independent cross 
correlation measurement, as it was in our experiments, a fitting analysis giving 
parameter values down to about 20% of the resolution is trustworthy. Taking this 
into account, as well as, the error bars, we believe that the absolute value for the 
rising step parameter is rather the upper limit. This was confirmed by an exper-
iment in which the temporal resolution was about 7 fs.2

2 R. Cireasa, work in progress.

Sebastian Mai asked: Which of your results relates to the neutral dynamics of 
5-fluorouracil? What can be learned from these results?

Raluca Cireasa answered: We interpret the dynamics observed at positive 
delays on the parent cation transient signal (m/z = 130) as being the result of an 
interaction between a Rydberg state and a valence or another Rydberg state, where 
the former is excited by HH3. In addition, the transient signals appearing for 
some m/z at negative delays in Fig. 4 and 5 (of our paper) also correspond to 
dynamics initiated in the neutral 5FU molecules, by 266 nm or 800 nm photons 
and probed through either SPI using XUV radiation or MPI using 400 nm photons. 
Absorption of one or three pump photons, respectively, leads to the excitation of 
S2(ππ*) state as in the case of the DNA/RNA bases. A preliminary analysis indi-
cates that a primary relaxation occurs in about 50 fs, faster than for thymine and 
uracil.1 The full analysis of the data obtained for the three halogenated uracils 
(5FU, 5ClU and 5BrU) using both SPI and MPI to probe the dynamics, should help 
in solving the long-standing debate about the occurrence of population trapping 
on the S2(ππ*) state prior to the relaxation mechanisms responsible for the 
photostability of the other DNA/RNA pyrimidines.

1 R. Cireasa, work in progress.

Daniel Rolles asked: In the paper, you also show results for 266 and 400 nm as 
pump wavelengths. How are those results different from those using 800 nm as 
the pump? What was the pulse length of the 266 nm pulses?

Raluca Cireasa replied: The results recorded using 400 nm pump photons 
correspond to the excitations by three 400 nm of some Rydberg states and by four 
or five 400 nm photons of some cation states. The ensuing dynamics are similar 
with those discussed in the paper for the XUV pump excitation scheme (see Table 
1 of the paper). In turn, the absorption of one 266 nm photon or alternatively, 
three 800 nm photons results in the excitation of the S2(ππ*) state of the neutral 
5FU. This will subsequently launch the dynamics leading to relaxation back to 
the ground state. It is difficult to compare the results obtained with 266 nm photons 
with those obtained with 800 nm photons as the latter were recorded only in a very 
narrow temporal range of about 150 fs and thus, cannot be properly fitted. The 
use of 800 nm pulses was intended only as an alternative probe, not also as
a pump. We have not measured the duration of the 266 nm pulses, only their cross correlation with 400 nm pulses (in Xe), which gave a FWHM of ~ 80 fs.

**Dave Townsend** remarked: When using 267 nm, your measurements potentially provide some information on the excited state dynamics taking place in the neutral 5-fluorouracil molecule – specifically, this is shown in Fig. 4(e) and (f) of your paper. There is an extensive body of literature relating to the analogous dynamics in the bare uracil system and, in particular, the origin of a ~2 ps decay lifetime seen in this species is a matter of some contention [being assigned to either non-adiabatic crossing from the $S_2(\pi\pi^*)$ state to the $S_1(n\pi^*)$ state or, alternatively, population trapping on the $S_2(\pi\pi^*)$ state]. Are your findings in 5-fluorouracil able to say anything more about this issue? Additionally, the fragment ion transients you present are different in appearance to that of the parent ion, displaying much greater (and seemingly longer-lived) signals at extended delay times. Once again focusing specifically on the 267 nm data, what is the reason for this and does it offer any additional insight into the neutral excited state dynamics?

**Raluca Cireasa** responded: The time dependencies recorded for the $S_2(\pi\pi^*)$ state dynamics initiated by 266 nm photons in the neutral 5FU are shown in Fig. 4 e–f (of our paper) only for comparison purposes. Their analysis and interpretation are in progress and will be published elsewhere. In order to tackle the long-standing debate about the existence of a barrier on the $S_2(\pi\pi^*)$ state PES leading to population trapping dynamics in uracil and thymine, we have investigated the effect of the substituent bonded to C5, by performing measurements for three halogenated uracils ($5XU$, with $X = F, Cl, Br$). Moreover, we have employed two probe schemes: XUV SPI and 400 nm MPI, to enable some selectivity in the ionisation or dissociative ionisation of the population evolving on different regions of the PESs ($S_2, S_1$ and $S_0$ states) involved in the relaxation mechanisms responsible for the photostability. We expect that the differences observed for the transient ion signals and the associated dynamics, as a function of the substituent and probe excitation scheme, should contribute to clarifying this issue for 5-Halouracils and the other DNA/RNA pyrimidines.

**Oliver Schalk** commented: In Figure 6 of your paper, you show a transient for the $m/z$ 28 channel for the HHG pump, 800 nm probe. Your transient shows a signal at negative delays. Does that mean that you have a signal for the 800 nm pump? If yes, that means that you can have a multiphoton probe process which causes you to have an undefined number of probe photons. Does this cause problems with the interpretation of your data (e.g. because you do not know which ionization channels are open, etc.)?

**Raluca Cireasa** answered: Indeed, some of the $m/z$ transients exhibit dynamics launched following the excitation by three 800 nm photons of the $S_2(\pi\pi^*)$ state. Moreover, the mass spectra recorded with 800 nm photons (Fig. 2e of the paper) indicate that as many as 8–9 photons can be absorbed leading to ionisation and subsequent fragmentation. These observations confirm that multiphoton absorption is involved in the excitation and ionisation of the neutral molecules. That is also the case when using the 800 nm photons to probe the dynamics.
initiated in the cation. Note though that we did not observe any di-cation signal. The intensity of the 800 nm radiation was adjusted to minimise the one-colour MPI signal, while still obtaining a decent XUV pump – 800 nm probe signal. The ability to absorb several photons enables access to different dissociation limits of the cation and hence, probe the dynamics via the different fragmentation templates. As concerning the ionisation channels accessed in the pump step, we identify which HH of the XUV comb contributes to them by comparing the dynamics induced by XUV radiation with those induced by MPI with 400 nm photons. From additional spectroscopic experiments (3D coincident photoelectron–photoion momentum imaging measurements of photoionisation induced by synchrotron radiation) we gain knowledge about ionisation and dissociation energies, and thus we find out which channels are open by HH and which by 800 nm probe photons. On the signals recorded for \( m/z = 87, 60, 28 \) and \( 1 \) with a different number of probe photons, we have identified contributions occurring on a very similar timescale (within the error bars) that we have related to the same dynamics (dynamics 1). In turn, the ps dynamics was observed only on the \( m/z = 28 \) transient. For a particular \( m/z \) fragment, the absorption cross section dependence on the number of photons and the Franck–Condon factors, leads to weighting or selecting contributions of different dynamics to the total \( m/z \) signal. Actually, the multitude of fragmentation channels provides the selectivity that lacks spectroscopically: the dynamics can be revealed through different fragmentation channels. Of course, the experiments, where the pump ionises the neutral molecules and the probe reveals the dynamics occurring in the cation through its dissociation, \( i.e. \) (same) ions are produced by both pump and probe, are more difficult to interpret than those where the dynamics are recorded via chemical species that can only be accessed by the probe: dynamics initiated in the neutral and probed via ionisation of the neutral parent or fragments, and dynamics initiated in the cation and probed through double ionisation. However, our results show that as for the other two, it is possible to disentangle and interpret such experiments relying on additional experiments and/or calculations. In all cases where IR photons are used for probing, one should be careful about the possible intensity effects on the extracted dynamics and on the interpretation.

**Fernando Martín** asked: You showed fragmentation spectra obtained by using different radiation sources but also referred to experiments in which fragmentation was induced by ion impact. How do spectra obtained with ions compare with those obtained with synchrotron radiation? Since the energy deposited in both kinds of experiments is in principle quite different, I would expect that the fragmentation spectra are also different. Could you comment on this?

**Raluca Cireasa** responded: In addition to the mass spectra presented in the paper, in Fig. 7 we show here spectra obtained with 21.5 eV synchrotron radiation (panel a) and with HH7 (21.5 eV) and HH9 (27.7 eV) (panel b).\(^1\) We have chosen a photon energy of 21.5 eV because HH9 is only 10% of the HH7. When visually comparing the signals of mass spectra recorded with synchrotron and with HH, one should take into account the shape of the peaks, \( i.e. \) the widths and the resolutions due to the detection methods. The relative ratios of the signals are very similar as expected from the photoexcitation rules. A comparison of the...
synchrotron and HH spectra with proton impact spectra published in ref. 2, Fig.1, shows that the ratios of the main ion fragment signals: 87, 60 and 28 to the parent ion signal are very similar and that some differences can be seen for \( m/z = 44, 43, 32 \) and 31. The only stark differences appear for the weaker fragments: \( m/z = 40, 39 \) and 38 which are barely visible in the synchrotron spectra and for \( m/z = 15–12 \) which are absent. The energy of the proton beam is 100 keV, but only a small fraction of a few tens of eV is deposited in the molecules.\(^2\) In principle, ionisation by proton impact in this (high) collision energy regime bears similarities with the photoionisation processes. From ref. 2, we learn that the kinetic energies of the halogen cations can be as large as 10 eV and that the double ionisation amounts about 10\% of the total events. In our experiments, no double ionisation was detected and the halogen cation (Br) exhibit extremely low kinetic energy \( \sim 100–200 \) meV. Therefore, we expect that the differences present in the mass spectra produced by proton impact would mainly arise from the excitation of electronic states lying above 21.5 eV, which are accessible in those experiments, but not in ours. This is consistent with the above observations indicating that the differences essentially concern the light fragments with higher appearance energies. The energy region above 21.5 eV corresponds to deeper inner valence states. On the one hand, these states dissociate into smaller fragments. On the other hand, for such high-lying electronic states and molecules of this size, the electronic correlation and relaxation effects are significant and may substantially

Fig. 7 Mass spectra recorded employing: (a) synchrotron radiation at 21.5 eV and 3D coincident photoelectron–photoion momentum imaging detection\(^1\) and (b) HH7 and HH9 generated in Ar and Velocity Map Imaging detection; a 100 \( \mu \)m Aluminium filter was used to remove the low harmonics: HH3 and HH5 and to keep only HH7 and HH9. The Y axis ticks were chosen to guide the eye in the comparisons. Note: in panel b \( m/z = 20 \) and 22 are due to Ne carrier gas, and \( m/z = 40 \) is due to pollution with Ar, while in panel a, \( m/z = 18, 17 \) and 16 are largely due to \( \text{H}_2\text{O} \) “pollution”.

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influence the nuclear dynamics and the ensuing fragmentation. The electron
dynamics occurring in inner valence states may be responsible for the differences
between the mass spectra obtained by proton impact and by XUV ionisation
(synchrotron or HH).

1 R. Cireasa, in preparation.

Misha Ivanov opened a general discussion of the papers by Dane Austin, Nirit
Dudovich and Raluca Ciresa: It is fair to say that there are successful techniques
for imaging subfemtosecond dynamics with both spatial and temporal resolu-
tion: these are based on electron recollision with the parent ion, driven by the
laser field. High harmonic generation spectroscopy, laser-induced electron
diffraction and electron holography are theory-intensive but have been quite
successful in unravelling electron dynamics inside the core on sub-femtosecond
time scale.

R. J. Dwayne Miller answered: I agree. These methods are most important for
following core electron dynamics on subfs timescales. The problem is connecting
the change in the spectroscopic or electron scattered signatures to the nuclear
dynamics directing the chemistry on the 10–100 fs timescale of sampling different
nuclear configurations. To date only small molecules have been demonstrated,
mostly diatomic, but recently conformational motions of benzene have been
shown as a proof of principle. It will be interesting to see how far the attosecond
methods can be pushed to larger molecules. I gather the main limitations are
separating different signal source terms to assign the scattering processes. In
conventional electron or X-ray scattering the wave source and divergence can be
well characterized so one is dealing primarily with uncertainties in phase, e.g., in
diffractive imaging. With differential detection we have shown you can solve
the phase/inversion problem for systems as large as proteins and still attain
of the order of .01 Å resolution.¹ The challenge for the conventional or free
space electron probe approach is to go to shorter timescales than a few 10s of fs;
whereas the challenge is going to larger systems to probe different chemistry for
attosec methods. There is also the problem of the strong laser fields ionizing the
molecule or perturbing the electron distribution that needs to be taken into
account in connecting attosecond methods to 1-photon photochemistry. We are
seeing a convergence from both fronts.

¹ Tadahiko Ishikawa, Stuart A. Hayes, Sercan Keskin, Gastón Corthey, Masaki Hada, Kos-
tyantyn Pichugin, Alexander Marx, Julian Hirsch, Kenta Shionuma, Ken Onda, Yoichi
Okinoto, Shin-ya Koshihara, Takashi Yamamoto, Hengbo Cui, Mitsushiro Nomura, Yugo
Oshima, Majed Abdel-Jawad, Reizo Kato and R. J. Dwayne Miller, Direct observation of
collective modes coupled to molecular orbital-driven charge transfer, Science, 2015,
350(6267), 1501–1505.

Misha Ivanov addressed Raluca Ciresa: I was wondering if using only one
harmonic, say H5, in combination with measuring photoelectrons in coincidence
with fragments would give any additional insight into the underlying dynamics.
What limits the possibility of such a measurement?
Raluca Cireasa answered: Selecting one harmonic and using 3D momentum imaging detection of coincident photoions and photoelectrons allow us to define the excitation energy and to identify the dissociative channels open in the cation. For time-resolved measurements, this approach enables disentangling energetically the temporal contributions from various orbitals/ionisation channels in order to extract their associated nuclear and electron dynamics and electronic correlations. Because of the unique association of the photoion kinetic energies with those of the photoelectrons, the energy selected photoion time dependences may reveal the effect of the electron motion and correlations on the nuclear dynamics and the electronic origin of non-adiabatic dynamics. This type of detection is particularly important for electron dynamics studies of polyatomic molecules for which the photoelectron spectra are complicated by overlapping competing contributions from many orbitals/ionisation channels, making their time dependences difficult to interpret based on the photoelectron detection only. Due to the low counting rates, time-resolved coincidence experiments are very demanding in terms of acquisition time and stability of molecular and laser sources, and of the pump–probe spatial overlap and temporal definition. Advances in optical technologies show that (time-resolved) coincidence measurements can be performed at 50 Hz for atoms and volatile molecules. Currently, these experiments are not feasible for non-volatile molecules as in our case, where the vaporisation source stability is the key limiting factor. The HH are commonly generated using lasers running at 1kHz and such a low repetition rate will imply many hours of acquisition, making thus impossible to fulfil this stability requirement. An alternative solution would be the use of covariance methods. Until now, these methods were generally applied for other types of experiments where ion–ion and electron–electron energy correlation were measured. Using covariance methods instead of the coincidence ones, could enable us to extract the information for the correlated electrons and photoions on acquisition timescales compatible with the stability requirements.


Nirit Dudovich asked: Can we extract additional information by resolving the dynamics for the different fragments?

Raluca Cireasa replied: In the paper, we show that on the signals recorded for different fragments ($m/z = 87, 60, 28$ and 1) with a different number of IR probe photons, we identified contributions occurring on a very similar timescale (within the error bars) that we have related to the same nonadiabatic dynamics (dynamics 1). We have not observed any coherent motion due to vibrational wavepackets excited by the XUV pulse, but, in principle, it could be possible to observe such dynamics. If the probe pulse projects the vibrational wavepacket on higher excited states that further dissociates, the vibrational dynamics is recorded on the ion fragment signals. If these states correlate to different dissociation limits, then the dynamics can be revealed on the time-dependence of different fragments. In
order to achieve dissociation, the vibrations of the wavepacket should correspond or couple to the vibrations of the dissociation coordinates. Information on both the nature of the vibrational wavepacket (vibration frequency and type) and the nature of the potential surface (chemical bond) excited by the pump can be extracted from the signal of different fragments.¹ Because we have not selected a single high-order harmonic (HH), but employ the whole XUV spectrum, it is possible to excite coherently and selectively different electronic states by two (consecutive) HH of the attosecond pulse train. As in the experiments performed for D₂, by adding an IR pump pulse it may be possible to create interferences of electronic wavepackets to control the excitation and the ionisation on the attosecond timescale.² Another IR pulse (probe) delayed from the XUV+IR pump pulse will lead to dissociative ionisation. Selective bond-breaking will be achieved by controlling the excitation wavelength as well as the delay time between the pump and probe pulses. Nevertheless, for a molecule of this size, it is challenging to devise and understand such control schemes due to the high density of states, multielectronic effects and numerous nonadiabatic interactions.