

## Structural dynamics: general discussion†

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**Hans Jakob Wörner** opened a general discussion of the paper by Artem Rudenko: The  $\text{CO}_2^+$  yield seems to be exclusively dominated by the spin-orbit frequency of the ground state of  $\text{CO}_2^+$ , whereas the  $\text{CO} + \text{O}^+$  yield exclusively the spin-orbit frequency of the first excited state. Can you explain why this is the case?

**Artem Rudenko** responded: It indicates that the dissociation to the  $\text{CO} + \text{O}^+$  channel does not proceed *via* the ground state of the  $\text{CO}_2^+$  ion, in contrast to sequential double ionization. This is consistent with the conclusions made in M. Opperman, *et al.*<sup>1</sup> The appearance of the spin-orbit frequency of the excited A-state indicates that this dissociation channel at least partly proceeds *via* the excitation to the A-state.

1 M. Opperman, *et al.*, *J. Phys. B: At., Mol. Opt. Phys.*, 2014, 47, 124025.

**Oleg Kornilov** commented: The coherent beating detected at 20 meV and corresponding to the spin-orbit splitting decays on the timescale of a few picoseconds. The authors suggest this is a dephasing due to coupling to rotational degrees of freedom. What would be the rephasing time of this feature given the known rotational constants of  $\text{CO}_2$ ?

**Artem Rudenko** replied: If there would be any rephasing time, we would expect it to be way longer than our window of observation of ~ 30 ps.

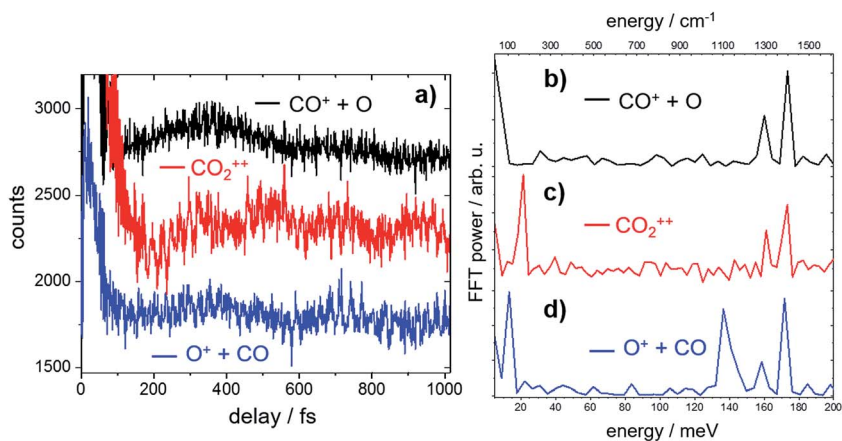
† Yann Mairesse was unable to attend the Faraday Discussion meeting to present his article and there was no discussion of this article: Y. Mairesse *et al.*, Probing ultrafast dynamics of chiral molecules using time-resolved photoelectron circular dichroism (DOI: 10.1039/C6FD00113K).

**Hans Jakob Wörner** said: Is there any evidence for the population of electronically excited states of the singly-charged ion, *i.e.* the A or B states which are known to be populated from high-harmonic spectroscopy?

**Artem Rudenko** replied: At our experimental conditions we do not populate these states very efficiently because of a rather weak pump pulse. In a recent work of the TU Vienna group<sup>1</sup> it was shown that the signature of the symmetric stretching mode of the A-state becomes very pronounced if one increases the intensity of the pump pulse. In our data we also see a signature of the dynamics in the A state, but mainly in the dissociation channel with an  $O^+ + CO$  final state, and its relative contribution becomes stronger with a weaker probe pulse. As can be seen in a Fig. 5d of our manuscript (here shown as Fig. 1), the peak at  $\sim 139$  meV reflecting the symmetric stretching in the A-state becomes very clear. In addition, the peak at  $\sim 13$  meV due to the electronic wave packet because of the spin-orbit splitting in the A-state of the  $CO_2^+$  ion also becomes rather strong. As for the B state, the difficulty there is that its symmetric stretching mode lies very close to the corresponding frequencies of the ground states of both, the ion and the neutral molecule (a peak at  $\sim 158$ – $160$  meV in our data), so it is hard to identify its contribution, especially since we expect it to be rather weak under our conditions (weak pump pulse).

<sup>1</sup> Sonia Erattupuzha, Seyedreza Larimian, Andrius Baltuška, Xinhua Xie and Markus Kitzler Erattupuzha, *J. Chem. Phys.*, 2016, **144**, 024306.

**Danielle Dowek** commented: In the reported results for strong field ionization of the  $CO_2$  molecule studied by pump-probe momentum-resolved ion spectroscopy, you do not comment on the angular distribution of the ion fragments: would the measured distributions provide any insight into the studied ionization processes? Are differences or evolutions observed for different channels and pump-probe delays?



**Fig. 1** (a) Yields of three different fragmentation pathways measured as a function of pump-probe delay between two identical 8 fs pulses at the intensity of  $1.5 \times 10^{14}$ – $3.5 \times 10^{14}$   $W\ cm^{-2}$ . (b), (c), (d): The power spectra obtained from the Fourier transforms of the ion yields shown in Fig. 1(a) for  $CO^+ + O$  (a),  $CO_2^{++}$  (b), and  $O^+ + CO$  (c) channels.

**Artem Rudenko** answered: First of all, the measured angular distribution of the Coulomb explosion fragments provides a good estimate of the time-dependent evolution of molecular alignment. The 8 fs pump pulse we used does induce noticeable (even though rather weak) alignment of the molecule, and we can trace a signature of this in the delay-dependent angular distributions for Coulomb explosion. However, since we used a linearly polarized probe pulse, this angular distribution is also convolved with the angular-dependent ionization probability for the probe step. The latter is even more important for angular distributions of other fragments (*e.g.*, those from the dissociation in the singly ionized states). In this work we focused on the delay-dependent yields, which carry the signature of the initial rotational excitation (alignment). However, the angular distribution of a particular ionic channel, especially at a fixed pump–probe delay, can help us to uniquely identify the pathway, which led to this final state.

**Hans Jakob Wörner** asked: Have you tried to measure electrons in coincidence with the ions?

**Artem Rudenko** responded: We did. However, the quality of the electron data was not very good, and we did not learn much there. In general, it is often pretty challenging to interpret electron spectra in strong-field molecular ionization at 800 nm.

**Hans Jakob Wörner** remarked: Could you use measurements at different relative polarizations to distinguish the electronic states of the cation that play a role in your measurements?

**Artem Rudenko** responded: This is a good point. We probably could, but we did not vary the polarization during the experiment.

**Hans Jakob Wörner** asked: What are the relative roles of impulsive stimulated Raman excitation and ionization depletion in creating rotational excitation in the ground state of CO<sub>2</sub>?

**Artem Rudenko** answered: I guess, the question addresses vibrational excitation in the ground state of CO<sub>2</sub>. We did not see any signatures of ionization depletion (“Lochfrass”) mechanisms in our CO<sub>2</sub> data. The phases of the vibrational wave packet we observe match those expected for impulsive stimulated Raman excitation.

**Markus Kowalewski** opened a general discussion of the paper by Ágnes Vibók: For the outcome of the control experiment, does it make a difference if the molecule is modeled with a LICI or could the dissociation probability also be steered through a light induced avoided crossing. Is it necessary to include the rotation to steer the dissociation probability?

**Ágnes Vibók** replied: Of course it is not necessary to include the rotation (as a dynamical variable) to steer the dissociation probability (that is what we do in the 1D calculations). But these results then often strongly differ from the realistic 2D calculations (where the LICI is properly taken into account) which includes the

rotational degree of freedom as a dynamical variable. Since the laser rotates the molecule the 2D model should provide more accurate results generally.

**Hans Jakob Wörner** said: Have you observed the expected signatures of geometric phase in your calculations concerning dynamics at light-induced conical intersections?

**Ágnes Vibók** responded: Yes, we could show the quantum interference effect of the LICI by numerical simulations.<sup>1</sup> This effect was also measured experimentally.<sup>2</sup> By analyzing the photodissociation process of the  $D_2^+$  molecule carefully, we found a robust effect in the angular distribution of the photofragments that serves as a direct signature of the LICI, providing undoubted evidence of its existence.<sup>3</sup>

1 G. J. Halász *et al.*, *Phys. Rev. A*, 2013, **88**, 043413.

2 I. Kruse, K. Lange, J. Peise, B. Lücke, L. Pezzè, J. Arlt, W. Ertmer, C. Lisdat, L. Santos, A. Smerzi and C. Klempt, *Phys. Rev. Lett.*, 2016, **116**, 143004.

3 G. J. Halász, Á. Vibók, and L. S. Cederbaum, *J. Phys. Chem. Lett.*, 2015, **6**, 348.

**Albert Stolow** remarked: For Hamiltonians with band structure (*e.g.* molecules, solids), the non-resonant, non-perturbative dynamic Stark effect introduces two source terms which drive the coupled equations of motion of the state coefficients.<sup>1,2</sup> One of these is a dipole-type coupling (analogous to a first order Stark effect) and the other is a polarizability-type coupling (analogous to a second order Stark effect). Which term dominates the equations of motion depends greatly on the Hamiltonian: specifically, it depends on whether or not the states of interest are directly dipole-coupled to each other. If the polarizability term dominates, as for neutral homonuclear diatomics, then the superposition in the field follows the envelope of the laser pulse, a method we have termed Dynamic Stark Control.<sup>3</sup> However, if the dipole term dominates, then the superposition in the field oscillates at the carrier frequency (*i.e.* every couple of femtoseconds). These two regimes will lead to very different quantum dynamics. Have you considered these two regimes in your simulations?

1 B. J. Sussman, J. G. Underwood, R. Lausten, M. Yu. Ivanov and A. Stolow, Quantum control *via* the dynamic Stark effect: Application to switched rotational wave packets and molecular axis alignment, *Phys. Rev. A*, 2006, **73**, 053403.

2 B. J. Sussman, M. Yu. Ivanov and A. Stolow, Non-perturbative quantum control *via* the non-resonant dynamic Stark effect, *Phys. Rev. A*, 2005, **71**, 051401R.

3 B. J. Sussman, D. Townsend, M. Yu. Ivanov and A. Stolow, Dynamic Stark control of molecular photodissociation, *Science*, 2006, **314**, 278.

**Ágnes Vibók** replied: The papers mentioned in the question are interesting, but the situation in our studies is different. The Stark effect is obtained non-resonantly by an infrared field which is then used to modify the curve-crossing barrier at a specific time for a pair of molecular states which exhibit an avoided crossing in the absence of the field. In our scenario we wish to have a resonant excitation which then leads to the appearance of one or more LICI. Let us briefly address the example studied in the references 1–3 addressed in the question. There, the diatomic molecule (IBr) possesses 3 electronic states 1(X), 2(B) and 3(Y). The latter two are dissociative and exhibit an avoided crossing.

The dissociation is initiated by absorption of a visible photon bringing population from 1(X) to 2(B). An applied infrared field modifies the crossing region by inducing a non-resonant Stark effect. Manipulation of this field can be used to control the relative output of the two dissociation channels. In our context, we would use a pulse to excite 1(X) to 2(B) and in this way create a LICI between these two adiabatic states. This LICI produces its own dynamics which can compete with that resulting from the avoided crossing between 2(B) and 3(Y). A totally different situation. Of course, one could combine such an exciting pulse with an infrared field which induces Stark effects.

**Hans Jakob Wörner** addressed **Ágnes Vibók** and **Albert Stolow**: This is also a comment on a previous question from Albert Stolow. It seems to me that the light-induced conical intersections emerge within a dressed-state formalism. Therefore the rapid oscillation of the carrier wave of the coupling laser pulse is already included in the nature of the dressed state and does not need to be considered further in describing the dynamics. Do you agree?

**Albert Stolow** responded: Formally, of course, the carrier wave is always there. In their quantum dynamics, all states are coupled to all (allowed) others by dipole matrix elements, which contain the carrier frequency. The dynamics of this set of coupled states is the formal solution: anything else is an approximation of one sort or another. This is true even for the well-known case of laser-induced molecular alignment, where the carrier field is typically (adiabatically) eliminated in the derivation of an effective Hamiltonian.<sup>1</sup> One starts by assuming a Hamiltonian having band structure (*e.g.* electronic states, each with vibrational structure) and a strong non-resonant laser field interaction, leading to nearby 'states of interest' and a set of 'far away' states. The question is: are the strongly coupled 'states of interest' (*e.g.* those forming the LICI) directly dipole-coupled together or are they rather indirectly coupled by the set of all 'far away' states. In either case, the laser electric field is always present and strongly interacting – this is not perturbation theory. It is in the limit where the strongly coupled 'states of interest' only interact through the set of 'far away' states that the carrier wave plays a minor role in their quantum dynamics (*e.g.* alignment of a homonuclear diatomic, dynamic Stark control of IBr photodissociation). If, in contrast, the strongly coupled 'states of interest' directly interact through dipole matrix elements, the carrier wave then plays a major role. Which situation is attained will depend, therefore, on the specific Hamiltonian under study. The quantum dynamics of the 'states of interest' will be very different for these two limiting cases. Of course, real molecular systems will generally be somewhere in between these limits, therefore having aspects of each.

1 Benjamin J. Sussman, Jonathan G. Underwood, R. Lausten, Misha Yu. Ivanov and Albert Stolow, *Phys. Rev. A*, 2006, 73, 053403.

**Ágnes Vibók** replied: The LICIs were first demonstrated by applying the Floquet representation for the nuclear Hamiltonian.<sup>1,2</sup> This presentation provides a very illustrative picture and is often used to explain various phenomena in the area of strong field physics. The appearance of the LICI in diatomics can also be demonstrated impressively in this picture. The question arises: what is the

performance of the  $2 \times 2$  Floquet approach? Namely to what extent the results produced by the static  $2 \times 2$  Floquet picture can be compared to those obtained from the experimental measurements using real laser pulses with switching times comparable or even longer than the period of the laser. It has been discussed in ref. 3, where the performance of the  $2 \times 2$  Floquet representation, the rotating wave approximation and the “exact” method based on the time-dependent exact Hamiltonian have been compared in the presence of a LICl. Avoiding the numerical inaccuracy that originates from the Floquet approximation, the time-dependent exact Hamiltonians are used in our dynamical simulations.

- 1 Nimrod Moiseyev, Milan Šindelka and Lorenz S. Cederbaum, *J. Phys. B.*, 2008, **41**, 221001.
- 2 Milan Šindelka, Nimrod Moiseyev and Lorenz S. Cederbaum, *J. Phys. B.*, 2011, **44**, 045603.
- 3 Gábor J. Halász, Ágnes Vibók, Nimrod Moiseyev and Lorenz S. Cederbaum, *J. Phys. B.*, 2012, **45**, 135101.

**Oleg Kornilov** said: The wavepacket dynamics are treated using the MCTDH method and the potential energy surfaces (PES) in the light-induced potential picture. However, for the chirped pulses these PES change as quickly as the wavepacket propagates. Do equations of motion of the MCTDH method still hold in this case (the PES changing with the speed of nuclear propagation)? Is the explicit time dependence of the Hamiltonian treated exactly in MCTDH?

**Ágnes Vibók** responded: We use  $2 \times 2$  Floquet representation only to demonstrate the concept of the LICl. The validity of this description is strongly dependent upon the intensity of the applied laser field. During the numerical simulations we did not use this picture. In our working Hamiltonian we use the true time dependent electric field and so the PES itself does not depend on the external electric field. On the other hand, in this case the coupling between the surfaces is changing even more rapidly. Using a proper propagation scheme MCTDH can handle correctly even these fast time dependent couplings in the Hamiltonian.

**Hans Jakob Wörner** asked: What would in your opinion be the ideal time-resolved measurement on the manifestation of light-induced conical intersections?

**Ágnes Vibók** answered: Probably the experimental investigation of the dissociation probability of the  $D_2^+$  would be appropriate. First to ionize the  $D_2$  molecule with a pump pulse and then applying a probe laser pulse with time delay of  $t_{\text{delay}}$  to measure the angular distribution of the total dissociation rate. For certain situations one should obtain enhanced dissociation yield approaching the  $\theta = 90^\circ$  position. However, this effect would be more prominent starting with the initial nuclear wave packet from one of the vibrational eigenstates, which of course experimentally is a more difficult task.

**Hans Jakob Wörner** asked: Could you comment on the importance of light-induced conical intersections in the dynamics of polyatomic molecules?

**Ágnes Vibók** responded: In polyatomics there are, of course, also laser-induced CIs, but the situation is more complicated than the one described for diatomics.

In polyatomics the interplay of LICIs with the CIs given by nature will lead to a wealth of new phenomena.

However, the investigation of polyatomic systems in intense laser fields is more involved than in the case of diatomics, the nuclear dynamics has more dimensions and is expected to be more complex and the consequences more diverse.

**Artem Rudenko** asked: You present the calculation for the  $D_2^+$  ionic target. Would experimental observation of the light-induced conical intersection become possible with angle-resolved and vibrational state-resolved measurement of the fragmentation of such an ionic target?

**Ágnes Vibók** responded: Yes. To our present knowledge one possible direct observation of the effect of the light induced conical intersection would be for measuring of an enhanced dissociation yield of the  $D_2^+$  photofragments approaching the  $\theta = 90$  position by applying a vibrational state-resolved experimental technique.

**Wolfgang Domcke** opened a general discussion of the paper by Christian Burger: You are starting the dynamics by double ionization of acetylene. There have been earlier experiments considering the dynamics triggered by the excited state of the mono-cation. Could you comment on the differences of these experiments and their results. What is the motivation to prepare the di-cation?

**Christian Burger** answered: While the timescale for isomerization in the cation was determined as  $(41 \pm 10)$  fs by Ibrahim *et al.* (reference 14 in the paper) and  $(52 \pm 15)$  fs by Jiang *et al.* (reference 21 in the paper), precise measurements of the isomerization time in the dication are scarce. So far, only upper limits, *e.g.* 100 fs (reference 12 in the paper) and 60 fs (see references 13 and 31 in the paper), were known, which motivated us to investigate the reactions in the dication. For a detailed discussion concerning the differences and similarities to previous experiments, please also refer to our response to Oliver Gessner.

**Wolfgang Domcke** asked: It could be that an H-atom isomerizes or a proton. In the first case, the system remains essentially nonpolar. In the second case, it would acquire a substantial dipole moment. Can your experiment distinguish between these two cases?

**Christian Burger** replied: Within this experiment we were not able to distinguish between both scenarios. According to the theory isomerization takes place *via* hydrogen migration rather than proton migration.

**Oliver Gessner** asked: While your experiment is slightly different from those described in Hishikawa *et al.*,<sup>1</sup> and Ibrahim *et al.*,<sup>2</sup> I wonder why you do not observe the reverse isomerization dynamics described in these articles. Can you discuss the differences in the experiments and possible reasons for the different observations in more detail?



- 1 Akiyoshi Hishikawa, Akitaka Matsuda, Mizuho Fushitani and Eiji J. Takahashi, *Phys. Rev. Lett.*, 2007, **99**, 258302.
- 2 Heide Ibrahim, Benji Wales, Samuel Beaulieu, Bruno E. Schmidt, Nicolas Thiré, Emmanuel P. Fowe, Éric Bisson, Christoph T. Hebeisen, Vincent Wanie, Mathieu Giguère, Jean-Claude Kieffer, Michael Spanner, André D. Bandrauk, Joseph Sanderson, Michael S. Schuurman and François Légaré, *Nat. Commun.*, 2014, **5**, 4422.

**Christian Burger** replied: Thank you for this question, as this is likely the most debatable aspect in this experiment. An interpretation of the different experimental results is not straightforward as the parameters of earlier experiments and ours are very similar and our statistics are considerably higher. The main difference to Hishikawa *et al.*,<sup>1</sup> appears to be that we did not record sufficient quality single pulse data to allow for the background subtraction applied in their publication. We therefore might not have been as sensitive to the back-isomerization. When we, however, take the new analysis of the 4-fold coincidence channel into account and apply a high-energy filter, indications for such a back-isomerization are seen (see response to Oliver Schalk regarding the presence of 4-fold coincidences), resolving this discrepancy.

When compared to Ibrahim *et al.*,<sup>2</sup> we obtain similar results after the application of a high energy filter. In addition, however, we investigated another dissociation channel. We see that both channels yield different behavior indicating an alternative explanation for the observed maximum in the isomerization yield (Figure 7a). We cannot exclude, however, that we do not populate the state from which isomerization takes place as efficiently as done in previous experiments, which could be due to the broader and slightly shifted spectrum of the pulses used in our experiment. A low population probability would result in low signal strength and the high energy filter alone might not provide the same contrast as in earlier work for the visualization of the backwards isomerization.

- 1 Akiyoshi Hishikawa, Akitaka Matsuda, Mizuho Fushitani and Eiji J. Takahashi, *Phys. Rev. Lett.*, 2007, **99**, 258302.
- 2 Heide Ibrahim, Benji Wales, Samuel Beaulieu, Bruno E. Schmidt, Nicolas Thiré, Emmanuel P. Fowe, Éric Bisson, Christoph T. Hebeisen, Vincent Wanie, Mathieu Giguère, Jean-Claude Kieffer, Michael Spanner, André D. Bandrauk, Joseph Sanderson, Michael S. Schuurman and François Légaré, *Nat. Commun.*, 2014, **5**, 4422.

**Daniel Neumark** said: Your plot of the angle  $\theta$  vs. time in Fig. 4 shows strong evidence for isomerization. What do you learn from the time-dependent signal for the angle  $a$ ?

**Christian Burger** answered: From angle  $a$  we can learn that the major part of molecules stay in the acetylene configuration independent of the chosen energy filter. This is a very important difference of the H–C–CH channel to the H–H–CC channel which shows the isomerization very nicely. Additionally, the angle  $a$  indicates a small amount of isomerization at short time delays which disappears for larger delay times (compare Figure 4a). This could be similar to the isomerization and back-isomerization seen by Hishikawa *et al.*<sup>1</sup> but with smaller isomerization probability.

- 1 Akiyoshi Hishikawa, Akitaka Matsuda, Mizuho Fushitani and Eiji J. Takahashi, *Phys. Rev. Lett.*, 2007, **99**, 258302.



**Daniel Neumark** asked: In your experiment, you don't have control over the total energy deposited in the vinylidene dication since it is prepared by strong-field ionization. It would seem that the isomerization dynamics would depend sensitively on this. Do you have any means of estimating the total available energy?

**Christian Burger** replied: The maximal recollision electron energy is given by  $3.17 U_p$ . Considering the cycle-averaged laser intensity of  $5 \times 10^{14} \text{ W cm}^{-2}$  and a central wavelength of 690 nm we estimate the ponderomotive energy to be 22.2 eV and the maximal recollision energy to be 70.4 eV:

$$U_p = 9.33 \times 10^{-14} I [\text{W cm}^{-2}] \lambda [\mu\text{m}] \text{ eV} = 9.33 \times 10^{-14} \times 5 \times 10^{14} \times 0.69 \times 0.69 \text{ eV} \\ = 22.2 \text{ eV} \rightarrow 3.17 U_p = 70.4 \text{ eV}.$$

As the energy difference between the  $A^3\Pi_u$  state and the cation ground state is 25.6 eV a maximum excess energy of 44.8 eV is available. While most of this energy is carried away by the recolliding electron we can certainly efficiently populate the  $A^3\Pi_u$  state.

**Kiyoshi Ueda** said: In the case of Hishikawa *et al.*,<sup>1</sup> they employed a 9 fs, 800 nm pulse and observed that the hydrogen migration in deuterated acetylene dication proceeds in a recurrent manner. In case of Ibrahim *et al.*,<sup>2</sup> they employed a 266 nm pulse and observed that hydrogen migration in the acetylene cation proceeds in a recurrent manner. You employed a 4 fs, 690 nm pulse and observed hydrogen migration in the acetylene dication with no trace of recurrence. It seems the states you probed were different from the above two previous observations. Could you identify the states you probed? What is the reason for the no recurrence?

1 Akiyoshi Hishikawa, Akitaka Matsuda, Mizuho Fushitani and Eiji J. Takahashi, *Phys. Rev. Lett.*, 2007, **99**, 258302.

2 Heide Ibrahim, Benji Wales, Samuel Beaulieu, Bruno E. Schmidt, Nicolas Thiré, Emmanuel P. Fowe, Éric Bisson, Christoph T. Hebeisen, Vincent Wanie, Mathieu Giguère, Jean-Claude Kieffer, Michael Spanner, André D. Bandrauk, Joseph Sanderson, Michael S. Schuurman and François Légaré, *Nat. Commun.*, 2014, **5**, 4422.

**Christian Burger** responded: We were able to identify the dication as the intermediate state by studying the vibrational wave packets and therefore, we conclude that the isomerizing molecules are in the  $A^3\Pi_u$  state, which is the lowest energy state of the dication from which isomerization can take place.

For a detailed discussion concerning the differences and similarities to previous experiments, please also refer to our response to Oliver Gessner.

**Chelsea Liekhus-Schmaltz** commented: What electronic state do you believe is involved in the isomerization, and is there a barrier to isomerization on that state?

**Christian Burger** replied: As shown in Figure 6 of the paper, the theory suggests that the isomerization starts from the  $A^3\Pi_u$  state of the dication. Beginning from the Franck–Condon point the molecules can either relax into the local minima ( $t1'$

and  $t1''$ ) or surpass the energy barrier ( $t\text{-TS1}'$  and  $t\text{-TS1}''$ ) allowing the molecule to isomerize.

**Chelsea Liekhus-Schmaltz** commented: One issue that can arise in Coulomb explosion experiments is that the molecule is not stationary when it explodes. As a result, it is not necessarily easy to connect the momentum image that you have collected to the original geometry of the molecule at the time of Coulomb explosion. This problem could be exasperated because you additionally have a carbon-carbon ion fragment that would have its own angular momentum. Have you found any way to resolve these kinds of issues in your analysis of the data?

**Christian Burger** answered: This problem is indeed difficult to approach, but previous experiments on small molecules have also relied on using the assumption that the extracted momenta correspond to the configuration at the time of Coulomb-explosion. Not only the molecular configuration of acetylene (Hishikawa *et al.*<sup>1</sup> and Ibrahim *et al.*<sup>2</sup>) but also the chirality of molecules can be extracted utilizing this Coulomb-explosion imaging technique.<sup>3</sup>

Likely, the mentioned problem will broaden the retrieved angular distribution but still the average angle will stay similar enabling the reconstruction of the molecular configuration at the time of Coulomb-explosion. Furthermore, in our previous single pulse experiments under similar conditions we see a directional emission dependence of the fragments on the carrier envelope phase (CEP), see reference 8 of the paper. If the relation between retrieved momenta and original geometry is not valid we would not have been able to observe such CEP-effects as all directionalities would wash out. In summary, we agree that it is important to consider the validity of the recoil approximation for larger molecules in Coulomb-explosion imaging, but in our case it appears reasonable to rely on the approximation.

1 Akiyoshi Hishikawa, Akitaka Matsuda, Mizuho Fushitani and Eiji J. Takahashi, *Phys. Rev. Lett.*, 2007, **99**, 258302.

2 Heide Ibrahim, Benji Wales, Samuel Beaulieu, Bruno E. Schmidt, Nicolas Thiré, Emmanuel P. Fowe, Éric Bisson, Christoph T. Hebeisen, Vincent Wanie, Mathieu Giguère, Jean-Claude Kieffer, Michael Spanner, André D. Bandrauk, Joseph Sanderson, Michael S. Schuurman and François Légaré, *Nat. Commun.*, 2014, **5**, 4422.

3 M. Pitzer *et al.*, *Science*, 2013, **341**, 1096.

**Oliver Schalk** asked: In your paper, you mentioned the presence of 4-fold coincidences. Were you able to obtain relevant information from these coincidences? The data should not be prone to rotational momentum stored into, *e.g.* the C-C bond. In addition, they should provide a sanity check of the observed dynamics.

**Christian Burger** replied: Thank you for this nice question. You are right, that the 4-fold coincidence enables us to extract even further information compared to 3-fold coincidences. It is difficult, however, to directly compare this channel to the other channels presented in the paper as it is not completely known which intermediate channels we populate.

In the following, we show the evolution of the angle between the protons obtained from the 4-fold coincidence channel (see Fig. 2). The momentum sum of both carbon ions acts as center of gravity.

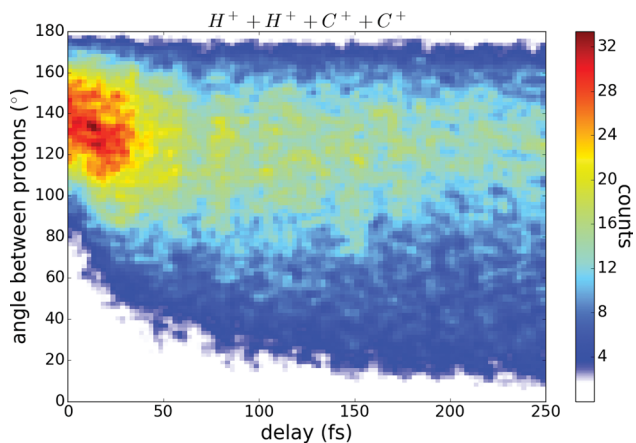


Fig. 2 Angle between the protons vs. the delay between the few-cycle pulses.

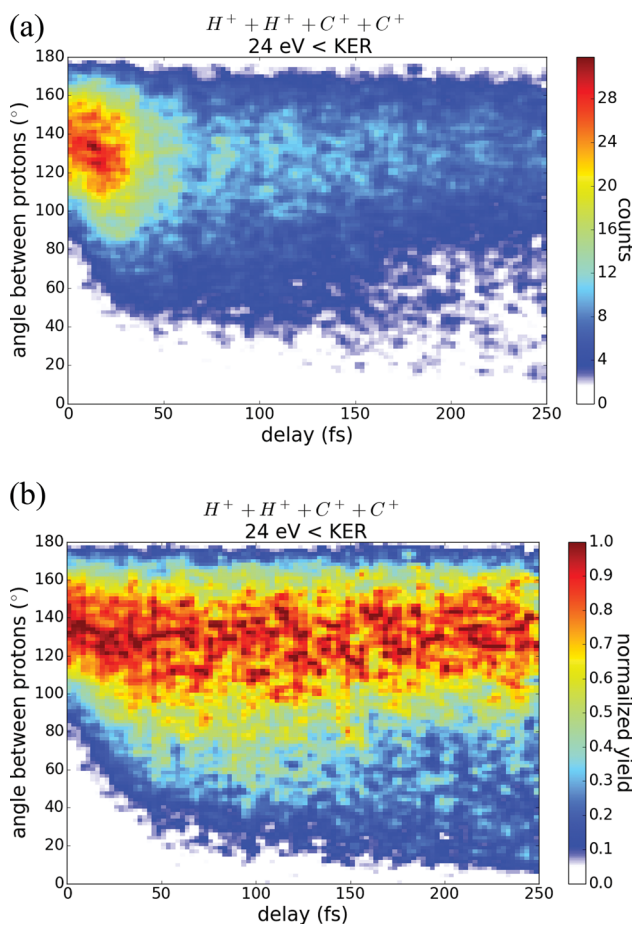


Fig. 3 (a) Same as Fig. 2, but with an applied filter of  $\text{KER} > 24 \text{ eV}$ . (b) Same as (a), but with the yield normalized to facilitate easier comparison at different pulse delays.

Similar to the presented H–H–CC channel, we observe an isomerization within the first tens of fs (see Fig. 2), whereas a back-isomerization is not directly visible. Applying an additional high energy filter (>24 eV, as performed in reference 15) results in a slightly different plot where a back-isomerization could be identified, similar to the findings in the respective paper (see Fig. 3).

In conclusion, applying a high-energy filter enables us to see indications of a back-isomerization in the H–C–CH channel as well as in the H–H–C–C channel. As elaborated during the discussion, it would be nice to excite a larger part of the isomerizing intermediate states to facilitate their separation from states where no isomerization takes place.

**Martin Centurion** asked: While the rotation of molecules is usually on picosecond time scales, after interacting with a femtosecond laser pulse, the rotation can be very fast. For example, in the case of impulsive alignment for small molecules, the angular distribution can change significantly on a time scale of 100 fs. How do you account for this in your experiments?

**Christian Burger** answered: You are right that the rotation of the isomerizing acetylene after interaction with the first laser pulse plays an important role. As you can see in Fig. 1(a) of reference 8 (of the paper), the averaged momentum distribution is indeed almost isotropic indicating that a rotation has taken place (assuming that the ionization probability is highest along the polarization direction and therefore a Coulomb explosion without prior rotation would yield momenta along the polarization direction). In our double pulse experiment, however, we are not only investigating fragmentation along the polarization direction but we measure the full 3D momenta of all coincident particles. Thereby, we are able to reconstruct the molecular configuration at the time of Coulomb explosion. Rotational changes occurring between the two laser pulses may influence the ionization probability by the second pulse but not the molecular arrangement (which we are interested in).

The only case where we cannot rule out that rotation of the molecule introduces problems is if we have dissociation prior to the second pulse and the remaining molecule (for example the  $\text{CCH}^+$  ion) rotates by *e.g.*  $180^\circ$ , at which point the second pulse ionizes this fragment further. Then, indeed, the rotation of the molecule would obscure our experimental results. However, knowing that Xie *et al.*,<sup>1</sup> applied impulsive alignment to  $\text{C}_2\text{H}_2$  and observed a quarter rotation within 400 fs, we think that this process is too slow to influence our measurements.

<sup>1</sup> Xie *et al.*, *Phys. Rev. Lett.*, 2014, **112**, 163003.

**Daniel Neumark** remarked: Following up on my previous question, how do your results compare to the synchrotron experiments in which the acetylene dication was prepared by absorption of a single high energy photon and the resulting isomerization dynamics monitored by coincidence detection of the ion fragments?

**Christian Burger** answered: Compared to the synchrotron measurements (see reference 31 of our paper and Osipov *et al.*<sup>1</sup>) we see that similar isomerization

times can be obtained indicating similar dynamics. In strong-field ionization the characterization of populated intermediate states is challenging, whereas in the case of synchrotron measurements this issue was solved by investigating the Auger electron energy in coincidence with ionic fragments (Osipov *et al.*<sup>1</sup>). In our study we utilize the observation of vibrational wave packets for an assignment of the intermediate state.

Another important difference between both experiments is the extraction of isomerization times. In synchrotron measurements only an upper limit of the isomerization times is obtained. We can directly measure the temporal evolution of the migration process.

1 T. Osipov, T. N. Rescigno, T. Weber, S. Miyabe, T. Jahnke, A. S. Alnaser, M. P. Hertlein, O. Jagutzki, L. Ph. H. Schmidt, M. Schöffler, L. Foucar, S. Schössler, T. Havermeier, M. Odenweller, S. Voss, B. Feinberg, A. L. Landers, M. H. Prior, R. Dörner, C. L. Cocke and A. Belkacem, *J. Phys. B: At. Mol. Opt. Phys.*, 2008, **41**, 091001.

**Hans Jakob Wörner** opened a general discussion of the paper by Oleg Kornilov: You extracted anisotropy parameters for the two states involved in the measured autoionization dynamics. What are the error bars on these parameters?

**Oleg Kornilov** replied: Fig. 3 of the paper shows fits to the angular distributions of the two contributions. The asymmetry parameters are  $\beta_2 = 1.3(2)$  and  $\beta_2 = 0.05(6)$ , where the number in the parentheses is the  $1\sigma$  uncertainty.

**Albert Stolow** commented: A time-evolving photoelectron angular distribution (PAD) can also be due to the nuclear coordinate dependence of the ionization transition dipole? In other words, the failure of the Franck–Condon approximation. For example, as was discussed for excited state dynamics in CS<sub>2</sub>, time-resolved Molecular Frame PADS can give a direct view of the evolution of excited state electron character upon nuclear motion.<sup>1</sup> Have you considered this as a possible contribution to the fitting of the PADS shown in your data?

1 P. Hockett, C. Z. Bisgaard, O. J. Clarkin and A. Stolow, Time-resolved imaging of purely valence-electron dynamics during a chemical reaction, *Nat. Phys.*, 2011, **7**, 612.

**Oleg Kornilov** replied: This is an absolutely valid point. We have carefully considered the possibility, that the time-dependence of PADs comes from nuclear dynamics and to the best of our knowledge this is not the case. High kinetic energy resolution of our photoelectron images allows us to establish with certainty, that the IR-induced feature (labeled Ry+IR) corresponds to the IR ionization of the  $3d\pi_g$  member of the Hopfield emission series. This series is attached to the  $B_2\Sigma_u(\nu = 0)$  ionic threshold, where  $\nu = 0$  labels the lowest vibrational state of the ion. According to the literature excitations of higher vibrational states are negligible. Therefore no nuclear (vibrational) dynamics could be observed in the intermediate state contrary to the experiment of Hockett *et al.* (see ref. in the question), where a group of vibrational (quasibound) states forms a nuclear wavepacket, which evolves on the electronic potential energy surface and leads to the time dependence of PADS.

**Hans Jakob Wörner** remarked: Can you attribute the two zero-order states of your model to Rydberg series converging to specific ionic states?

**Oleg Kornilov** replied: We assume in our model, that the two states are attributed to the members of the two Rydberg series predicted by the calculations of Raoult *et al.* (ref. 12 of the paper), namely the  $4^{\prime}s^{\prime}\sigma_g$  and the  $3d\pi_g$  states. These series both converge to the same ionic threshold, the  $B^2\Sigma_u$  state of the  $N_2^+$  molecular ion.

**Oliver Gessner** asked: The experiment is essentially designed such that the critical dynamics take place while the XUV-pump pulse and the IR-probe pulse overlap in time. Have you considered possible contributions to the observed dynamics from processes other than the continuum coupling of the two Rydberg states discussed in the manuscript, such as coupling between a greater manifold of Rydberg states?

**Oleg Kornilov** responded: We have considered a range of other possible explanations for the observed time dependence of the photoelectron angular distributions (PADs): (i) nuclear dynamics are excluded based on the considerations described in the answer to Albert Stolow; (ii) attribution of the signal to a  $n = -1$  sideband of one of the states is excluded, because the sideband signals peak at directions parallel to the IR light polarization and vanish perpendicular to it, whereas in our experiment at  $t = 0$  photoelectrons are emitted perpendicular to the laser polarization with high probability; (iii) two other possible explanations include an IR-enabled XUV excitation of other Rydberg states or a coupling of the excited Ry state to the continuum by the IR field. Both options require multiphoton interactions by the IR field. We exclude these possibilities considering the fact that the second order ( $n = 2$ ) sidebands are not observed in our experiments indicating that two-photon processes (IR) are too weak. Of course, contributions of such higher order process can only be fully excluded if the particular matrix elements are evaluated, which goes beyond the scope of the present paper; (iv) it is possible to reconstruct the observed signals by assuming saturation in the second ionization step by IR, but this is excluded based on the conditions of our experiment and the successful fits of the exponential decays to the transients extracted from the SVD analysis; (v) one more possible reason is discussed in the answer to the question posed by Kiyoshi Ueda regarding the change of  $\beta_2$  as a function of delay.

**Daniel Neumark** commented: If you look at other peaks of this Rydberg series, do you see similar dynamical effects attributable to interference between overlapped autoionizing features?

**Oleg Kornilov** replied: In this work we limited the XUV spectrum bandwidth such that it only excites one resonance of the Hopfield series. This is confirmed by photoelectron spectra showing only one peak corresponding to an autoionizing state. We expect a similar behavior for other members of the “emission” series up to some high  $n$  numbers, where rotations might completely decouple the resonances (see Huber *et al.*, ref. 13 of our paper). The absorption series, on the other hand, consists of isolated Rydberg resonances and should not show these dynamics effects.

**Hans Jakob Wörner** commented: The XUV pulses generated from your monochromator appear to be quite far from the Fourier limit. How much temporal broadening is caused by the monochromator?

**Oleg Kornilov** responded: A properly aligned monochromator induces 2–4 fs pulse stretch in the photon energy range of 10 to 50 eV caused by geometric aberrations of the toroidal optics. Bear in mind, that XUV pulses produced *via* HHG already carry a substantial chirp induced by the generation process (e.g. K. Varjull *et al.*<sup>1</sup>), which can actually be reduced for each photon energy by a slight realignment of the monochromator optics. More information can be found in M. Eckstein *et al.*,<sup>2</sup> and M. Eckstein, PhD thesis.<sup>3</sup>

1 K. Varjull *et al.*, *J. Mod. Optics*, 2005, **52**, 379.

2 M. Eckstein *et al.*, arXiv:1604.02650 [physics.ins-det]

3 M. Eckstein, PhD thesis, Berlin, 2015.

**Artem Rudenko** asked: What is the bandwidth used in your experiment?

**Oleg Kornilov** replied: The bandwidth of the monochromatized XUV pulse is about 0.5 eV (FWHM).

**Hans Jakob Wörner** commented: Does predissociation play a role for your experiments?

**Oleg Kornilov** responded: It is well established in the literature, that photo-dissociation plays a negligible role for these resonances. See, for example, ref. 13 in our paper and the references therein.

**Kiyoshi Ueda** said: Your observation of the change of  $\beta_2$  as a function of delay might be interpreted by additional phase accumulations *via* non-resonant contribution when the two pulses are overlapped (rather than autoionization dynamics). Please have a look at our theoretical<sup>1</sup> and experimental<sup>2</sup> investigations on this issue (on atomic non-autoionizing Rydberg states) and see if it is relevant to your observations. At least this effect should also be in your observations.

1 Kenichi L. Ishikawa, A. K. Kazansky, N. M. Kabachnik and Kiyoshi Ueda, *Phys. Rev. A*, **90**, 023408.

2 S. Mondal, H. Fukuzawa, K. Motomura, T. Tachibana, K. Nagaya, T. Sakai, K. Matsunami, S. Yase, M. Yao, S. Wada, H. Hayashita, N. Saito, C. Callegari, K. C. Prince, C. Miron, M. Nagasono, T. Togashi, M. Yabashi, K. L. Ishikawa, A. K. Kazansky, N. M. Kabachnik and K. Ueda, *Phys. Rev. A*, **89**, 013415.

**Oleg Kornilov** responded: We are very grateful to Kiyoshi Ueda for this point. It is indeed important to understand what role this effect may play in our experiments. In our work we neglected all non-resonant effects based on the argument, that two photon processes (XUV + IR) induced by pulses with parallel polarizations should lead to enhanced signals in the direction of the polarization and result in no enhancement or depletion in the perpendicular direction. Analyzing the theoretical results of Ishikawa *et al.*<sup>1</sup> we indeed see that for all cases of strong asymmetry variation (H atom, Ne and Ar) the intensity in the direction perpendicular to the polarization decreases at time zero. This is contrary to our experimental observation, where at time zero the perpendicular photoemission is large and decreases down to zero for longer delays between the pulses (see Fig. 2 of the paper). Also, no strong variation of the  $\beta_4$  is observed in the experiment, contrary to the calculations of Ishikawa *et al.*<sup>1</sup> We thus think that non-resonant



contributions cannot explain our observations, although the interpretation of the asymmetry parameter for the short-lived state (the one with the almost symmetric PAD) may indeed be influenced by this effect.

1 Kenichi L. Ishikawa, A. K. Kazansky, N. M. Kabachnik and Kiyoshi Ueda, *Phys. Rev. A*, **90**, 023408.

**Kyoung Koo Baeck** opened a general discussion of the papers by Artem Rudenko, Ágnes Vibók, Christian Burger: The noticeable non-adiabatic effect near ‘*natural*’ conical intersections (NCIs) corresponds to the mixing or coupling between nearby adiabatic electronic states by the ‘*natural*’ movement of nuclei. On the other hand, the light induced conical intersections (LICIs) may be thought as an artificial or intentional mixing between the adiabatic states due to the external fields. In either case of NCIs/LICIs, the mixing between different adiabatic electronic states could make a noticeable effect on the electron dynamics within the molecular system. It is probably too early to ask this question, but I wonder if you (Ágnes Vibók) or someone else has ever tried to investigate the noticeable change of the electron dynamics around LICIs theoretically or experimentally. Concerning this, as I already talked to Gabor J. Halász (one of the coworkers of Ágnes Vibók) in person, I wonder what will be the results if the current study of LICIs in the  $D_2^+$  system is extended to alkali-halide systems, like LiH and NaH, because the potential energy curves of their ground and first excited electronic states make the avoided-crossing, correspond to a ‘*natural*’ CI, very similar to that of LICIs in the  $D_2^+$  system. The alkali-halide systems correspond to the simplest prototype of the Harpoon reaction involving very fast temporal and wide spacial movement of electrons.

**Ágnes Vibók** answered: Yes, the LICIs can be used intentionally to mix the adiabatic states. Without the external field such a mixing is not possible. However, as is the case in the presence of NCIs, the motion of the nuclei is dictating the mixing dynamics. For diatomics we need two nuclear degrees of freedom to have a LICIs, and these are the internuclear coordinate and the rotational angle. In polyatomics, all internal nuclear coordinates may participate as well as the rotations, but there is no need for the rotations to form LICIs as there are sufficiently many other nuclear degrees of freedom. Once the external field “dresses” the potential surfaces, the nuclei see these surfaces and move accordingly. This behavior can, indeed, be intentionally exploited to control a quantity of interest, *e.g.*, dissociation rate.

If I correctly understand the question about the mixing of the adiabatic electronic states, this is exactly what we study in our examples, namely, we compute fully the non-adiabatic dynamics for different field strengths and also by freezing the rotation. Comparing the results of the two different simulations we could show the impact of the LICIs on different measurable quantities.

The extension to alkali-halide systems is indeed an interesting issue. In principle, one can extend the theory and computations to different scenarios including that which is addressed in the question. Let’s assume that the system has three relevant adiabatic states in the energy range of interest, for example the ground state X and two excited states A and B, and that the states A and B exhibit a natural CI, or as is the case for diatomics, a natural avoided crossing. By the way,

from theory and calculations we know that a natural CI and a natural avoided crossing are not similar and behave qualitatively different,<sup>1</sup> but this is not of relevance to our reply. We can now have two scenarios. In the first, the pulse excites the state X to the manifold A+B. Then, according to the theory [polyatomics], there will be LICIs between X and this manifold and the natural CI will persist between A and B. We will have a  $3 \times 3$  time-dependent Hamiltonian which governs the dynamics. In the second scenario, the pulse is between A and B (may be after a weak pump pulse populating A and/or B initially). Then, the situation can be quite intricate and we will have competition between the LICI and the natural CI which is subject to a shift. The operative Hamiltonian will be  $2 \times 2$  in this case. Both situations are interesting and show that there is great potential for manipulating the non-adiabatic dynamics by LICIs.

1 H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.*, 1984, 57, 59–246.

**Daniel Neumark** addressed Christian Burger and Artem Rudenko: It seems that the strong-field pump–probe experiments on CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> that both of you are carrying out are poorly defined, since neither the number of pump nor probe photons is known. Now that intense high harmonic sources are becoming available, would it be more desirable to carry out experiments in which at least one of the pump–probe steps involved absorption of a single high energy photon? Or is there intrinsic value in experiments in which only strong-field ionization/excitation is used?

**Artem Rudenko** answered: The goal of our particular experiment on CO<sub>2</sub> was to characterize the wave packet produced by strong field excitation. Therefore, we have to use the intense IR (*e.g.*, 800 nm) as a pump pulse. It would be beneficial though to use a single photon probe, if the corresponding pulses of sub-10 fs duration and enough flux to efficiently probe the wave packet were available.

**Christian Burger** replied: We agree that it would be beneficial to have a light source providing high energy photons, where a defined state from which isomerization occurs can be populated by the pump pulse. Additionally, the probe step could be replaced by a high-energy photon, but it is less crucial in this case. Since high-flux high-photon energy, ultrashort light sources are not yet as stable as few-cycle near-infrared sources, it poses a challenge to carry out experiments over long acquisition times. In our experiments using strong-field ionization allowed for a combination of very good temporal resolution and stability over several days of data acquisition for the price of less control over the population step. Extreme ultraviolet sources with high repetition rate and stability over several days of operation may, however, now be within reach, making their application in pump–probe experiments indeed very desirable.

**Hans Jakob Wörner** addressed Artem Rudenko and Christian Burger: The three experimental papers in this session made use of some of the most advanced detection techniques or light sources. What would you consider the ideal combination of light sources and detectors to be for probing the dynamics of small molecules in the gas phase?

**Artem Rudenko** responded: For reactions, which do not require non-linear XUV/X-ray interactions, the ideal combination in my opinion would be a high repetition rate lab-based HHG source (with photon energies from  $\sim 10$  eV up to the water window) and a coincident ion/electron momentum imaging setup (COLTRIMS/“reaction microscope” or double-sided VMI with delay line detectors). For the reactions involving non-linear XUV/X-ray interactions we currently need FELs. With their current repetition rates VMI with phosphor screen detectors (ideally, double-sided) seems to be an optimal detection system. At the future high rep. rate FEL (European XFEL, LCLS-2), the coincident fragment detection would become a routine tool.

**Oleg Kornilov** responded: The papers of Rudenko *et al.* and Burger *et al.* use a reaction microscope combined with multiphoton ionization using ultrashort (sub 10fs) infrared pulses. In our experiment the pulse duration is more conventional (20–25 fs), but we employ an XUV pump pulse with tunable wavelength using the recently constructed time delay compensating monochromator coupled to an HHG source. For an ideal experiment one would certainly envision a combination of these techniques, *i.e.* a pump–probe experiment with the wavelength-tunable XUV sub-10fs or even attosecond pulse, an IR or visible pulse and a momentum-resolved coincident detection of both ions and electrons. However one should be careful in choosing the experimental arrangement. In one class of experiments the XUV pulse can be used in the excitation step (usually *via* ionization and shake-up), which is then probed by a single or few-photon ionization with IR. Here the combination of the well-defined XUV photon energy and the coincident electron-ion detection will allow us to single out the electronic states of interest. Even more interesting could be an experiment, in which the molecules are pumped by a tunable (but still short) IR/vis/UV pulse and probed by XUV ionization. The molecular frame angular distributions and multiply-charged states could be fully characterized. In either ideal case the detection of the photoelectrons in coincidence with the photoions is the key to accessing the full information on the molecular dynamics.

**Christian Burger** replied: Depending on the experiment, a combination of the following parameters would be ideal:

- (1) A light source providing a specific wavelength to excite only a limited amount of states – this would simplify the data analysis/data interpretation.
- (2) Short pulse durations for pump and probe pulses to allow for good temporal resolution.
- (3) A high repetition rate (50–100 kHz) to achieve sufficient statistics and meanwhile being able to separate events from shot to shot.
- (4) A reaction microscope as detection apparatus as it delivers an almost complete picture of the processes involved (including coincidence measurements).
- (5) Velocity-map imaging (VMI) measurements to allow for good single-shot signal, *e.g.* for recording CEP-dependencies in background-free channels or processes with very low cross sections.

**Hans Jakob Wörner** addressed Oleg Kornilov and Artem Rudenko: What would you consider to be the ideal experimental technique if you had simultaneous access to all experimental tools discussed in this session?

**Artem Rudenko and Oleg Kornilov** responded: We think the answer to this question depends on the type of experiment. Two broad categories of experiments can be suggested in our field: the experiments aiming at understanding the photoinduced (*e.g.*, molecular) dynamics and the experiments focused on the light–matter interaction itself. In the first category the light–matter interaction should be as simple as possible to allow one to extract the intrinsic properties of the reaction of interest, while in the second category optical setup and detection scheme should be optimized to reveal the mechanisms of the interaction. Consequently, for an ideal experiment of the first type we would imagine XUV/IR/vis/UV one photon pump, specifically triggering the process under consideration, one photon probe at high rep. rate, (most likely, from HHG sources) combined with the 3D momentum-resolved coincident detection of the fragments (generalized “reaction microscope” type of experiment). All this can be nowadays realized in a lab-based, table-top setup. For studying mechanisms of light–matter interactions, which are often non-linear, we might need a very particular, often intense light source. For example, if we want to study non-linear interactions in the XUV or X-ray regime, we need free-electron lasers. There, a simpler detection scheme, (*e.g.* VMI or TOF) is often a benefit, because of a limited rep. rate and large number of fragments produced. However, with the development of high rep. rate FELs like European XFEL or LCLS2, we expect a multi-coincident fragment detection and 3D momentum imaging, possibly combined with simultaneous detection of X-ray fluorescent photons, to become a standard and most efficient technique there as well.

**Hans Jakob Wörner** addressed Oliver Gessner: What is the state-of-the-art time resolution from timing tools at free-electron lasers?

**Oliver Gessner** responded: Few-femtosecond (Harmand *et al.*<sup>1</sup>) and even sub-femtosecond (Hartmann *et al.*<sup>2</sup>) resolution have been demonstrated with timing tools at the LCLS. Note, however, that the performance of such tools may vary depending on the particular experimental parameters.

- 1 M. Harmand, R. Coffee, M. R. Bionta, M. Chollet, D. French, D. Zhu, D. M. Fritz, H. T. Lemke, N. Medvedev, B. Ziaja, S. Toleikis and M. Cammarata, *Nat. Photon.*, 2013, 7, 215.
- 2 N. Hartmann, W. Helml, A. Galler, M. R. Bionta, J. Grünert, S. L. Molodtsov, K. R. Ferguson, S. Schorb, M. L. Swiggers, S. Carron, C. Bostedt, J.-C. Castagna, J. Bozek, J. M. Glowia, D. J. Kane, A. R. Fry, W. E. White, C. P. Hauri, T. Feurerand and R. N. Coffee, *Nat. Photon.*, 2014, 8, 706.

**Jon Marangos** opened a general discussion of the paper by Michael Minitti: Comment: molecules aren't aligned so it is like powder diffraction.

This is in the “diffract and destroy” regime – in these small molecules is the lack of inertia an issue *i.e.* does the molecule significantly distort through Coulomb explosion during the diffraction process? Could it distort the structural information?

Note: This point was discussed later in questions by several other participants.

**Michael Minitti** responded: On the comment of non-aligned molecules: The absorption of the optical pump laser gives the molecule a mildly aligned character, but this is far from being properly “aligned”. Techniques such as impulsive or adiabatic alignment with ps to ns laser pulses is the way to go. Attempts will be

made to employ these methods in future XFEL experiments if we are so fortunate to receive beamtime. The diffraction images obtained from the mildly aligned gas-phase targets are rotationally averaged, resulting in diffuse patterns.

Considering the experimental X-ray parameters we used (8.2 keV, 30 fs, 30  $\mu\text{m}$  FWHM focal spot), the dilute gas-phase targets would not absorb a tremendous amount of energy from the X-ray probe in order to Coulomb explode. Moreover if it did, we'd never observe it as we'd remove it as part of our data analysis.

During the experiment, we take a series of optical laser (pump) off as well as X-ray (probe) off frames to help us in handling X-ray only background as well as reference X-ray dark shots for the optical/X-ray cross-correlator (the time-tool). In the end, we take all background data and subtract them from each pumped and unpumped X-ray frame. Then we take the difference between those images and report them as a percentage change. If damage from the probe happens, one would argue that the damage is always happening, no matter whether the molecule is excited with the pump or not. Therefore since we subtract this out through the procedure described above, we'd never see it. Lastly, the diffraction is instantaneous in this single scattering event, multiple scattering or rescattering are tremendously low probability events.

**Wolfgang Domcke** addressed Michael Minitti and Brian Stankus: You are showing the potential energy curves of singlet and triplet states. However, the SO coupling in iodine is of the order of one electron volt and singlets and triplets are strongly mixed. What are the "high-level" *ab initio* calculations mentioned in the paper. Are these fully relativistic calculations?

**Michael Minitti** answered: Great point. We did not include the SO coupling in these CASSCF calculations. We are aware that by excluding this, the relative energies and oscillator strengths of the excited states could be effected. Since publication, higher level calculations at the CASPT2 level of theory have been done, which give significantly more accurate relative energies, but still don't account for SO coupling. We are working to incorporate it, but those calculations are expensive and are not yet complete.

**Brian Stankus** replied: The CAS(18,14) calculated potential energy surfaces do not account for spin-orbit coupling, so the oscillator strengths for triplet absorptions are strictly zero. We are currently working on two strategies for incorporating the spin-orbit coupling. The first is an approximate scheme that uses the empirical atomic spin-orbit coupling constant for iodine, which is the dominant contribution of spin-orbit coupling in this molecule. Second, we pursue relativistic calculations of spin-adiabatic states, using the same effective core potential as the current spin-orbit free calculations but a smaller basis set. It is worth noting that these calculations are computationally very expensive. As shown in iodobenzene by Sage *et al.*<sup>1</sup>, the spin-orbit coupling will have some effect on the oscillator strengths and vertical excitation energies, and thus could impact our present discussion, but arguably the most important effect of spin-orbit coupling is in terms of the asymptotic limits for dissociation.

<sup>1</sup> Alan G. Sage, Thomas A. A. Oliver, Daniel Murdock, Martin B. Crow, Grant A. D. Ritchie, Jeremy N. Harvey and Michael N. R. Ashfold, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8075–8093.

**Andrew Orr-Ewing** asked: The spin-orbit coupling will contribute oscillator strength to the states nominally assigned as triplets in your Table 1 of excited states. These states therefore need to be considered as candidates for the photon excitation step. A velocity map imaging study of the photofragment recoil anisotropy (*i.e.* a determination of the anisotropy parameter,  $\beta$ ), ideally as a function of excitation wavelength, might help to unravel the contributions to the absorption from the various accessible excited states.

**Michael Minitti** responded: Agreed. This would be a great addition to the experiment. Now we just need to get our hands on a time-resolved VMI setup! Thankfully, while at the Discussion, we kickstarted this idea with Theis Sølling and his group in Denmark to make such a measurement.

**Dave Townsend** addressed Michael Minitti and Brian Stankus: Your time-resolved photoelectron spectroscopy measurements on 1,4-diodobenzene were done with a 267 nm pump and a 300 nm probe. This gives a total photon energy of approximately 8.8 eV. The ionization potential of 1,4-diodobenzene is approximately 8.5 eV. As such, your experiments don't project very deeply into the ionization continuum and so potentially have a very restricted view of the reaction coordinate(s) along which the dynamics evolve. Is there a chance that you may be missing additional information that could be picked up by using a shorter wavelength probe?

**Michael Minitti** replied: This is a fantastic point, speaking to an experimental parameter we did not choose well. While we are confident of the dynamics and lifetimes we observe and report in our manuscript, revisiting this measurement whilst employing a shorter wavelength probe is definitely worth while.

**Brian Stankus** answered: The choice of probe wavelength was a delicate balance – the wavelength had to be short enough to allow for single-photon ionization out of the initially excited valence state, but long enough to avoid exciting the same absorption band that is pumped with 267 nm. Of course, more probe energy would allow access to a larger energy range, but we were limited by this valence absorption band. Our current assignment of the observed band as a bound state is based on the fact that the energy of the band does not change as a function of time. Even though, as pointed out, the probe wavelength does not project very deeply into the ionization continuum, the available energy range should suffice to reveal a direct dissociation if that were taking place. A larger range of valence band energies were probed *via* resonant two-photon ionization with 405 nm, but this data is still being interpreted.

**Artem Rudenko** remarked: You did not specify how tight you focus the LCLS beam. Does the (possibly non-linear) photoabsorption disturb the structure obtained from your scattering data?

**Michael Minitti** answered: Like in our 1,3-cyclohexadiene studies, the X-ray focus we used in the 1,4-diodobenzene was a modest 30 microns FWHM. Typically, the X-ray parameters were at 8.2 keV, 30 micron FWHM focus and about 2.5 mJ per pulse. We have no reason to believe that there is sufficient enough photon density in this regime to induce any non-linear effects in these single scattering events.

**Daniel Rolles** addressed R. J. Dwayne Miller and Michael Minitti: Regarding the radiation damage in X-ray scattering: Based on the cross section ratio between elastic and inelastic X-ray scattering, one will always get more ionization (=damage) than elastic scattering. This is why photoelectron diffraction seems like a good technique because there, we use the ionization for imaging.

**R. J. Dwayne Miller** replied: I agree with this statement. I would only add that one could use HHG sources as 100 eV photons which would give short enough de Broglie wavelengths to give atomic structure information, which I guess was one of your previous points. Surface studies have a major advantage as the photo-emission process can avoid multiple scattering with a large number of emission centres – all from a single plane in space. This approach is used for surface studies at synchrotrons as shown by Adam Hitchcock and colleagues.

**Michael Minitti** answered: This may be true, and photoelectron diffractive imaging has potential to be a strong alternative technique to traditional gas-phase X-ray scattering, but one concern I have about X-ray induced, photoelectron diffraction at current XFELs are the very low signal count rates obtained. These extremely low signal levels force the requirement of having extremely low beamline noise, *e.g.*, fractions of background X-ray counts per second. This is experimentally very demanding to get right. While worth developing, techniques like X-ray induced photoelectron diffraction will truly benefit from high-repetition rate XFELs like the European XFEL and LCLS-II when they come online in the near future.

**Daniel Rolles** addressed R. J. Dwayne Miller and Michael Minitti: This is a comment regarding the question of how much radiation damage affects the X-ray scattering. If more than one photon interacts with the molecule during the duration of the X-ray pulse, radiation damage may play a role since absorption of one X-ray photon results in ejection of 5 or more electrons. Given the pulse parameters given in the paper, this effect is not negligible for iodine at 8 keV.

**Michael Minitti** responded: This question is very similar in nature to Jon Marangos' question regarding the “diffract and destroy” regime, so I'll respond with the same answer. Considering the experimental X-ray parameters we used (8.2 keV, 30 fs, 30  $\mu\text{m}$  FWHM focal spot), the dilute gas-phase targets would not absorb a tremendous amount of energy from the X-ray probe in order to Coulomb explode. Moreover if it did, we'd never observe it as we'd remove it as part of our data analysis. During the experiment, we take a series of optical laser (pump) off as well as X-ray (probe) off frames to help us in handling X-ray only background as well as reference X-ray dark shots for the optical/X-ray cross-correlator (the time-tool). In the end, we take all background data and subtract them from each pumped and un-pumped X-ray frame. Then we take the difference between those images and report them as a percentage change. If damage from the probe happens, one would argue that the damage is always happening, no matter whether the molecule is excited with the pump or not. Therefore since we subtract this out through the procedure described above, we'd never see it.

Lastly, the diffraction is instantaneous in this single scattering event, multiple scattering or rescattering are tremendously low probability events.



**R. J. Dwayne Miller** answered: This mechanism requires there to be multiple X-ray scattering events from the same molecule in which case I agree. The ionization from the first X-ray photon will modify the molecular structure on timescales within the X-ray pulse width and/or induce a time dependent structure factor. It is relatively straightforward to expand the focusing to avoid this problem in diffraction. It is only for imaging single molecules (without crystals) that 100 nm focusing conditions are used to ensure one elastically scattered X-ray photon per atom for which there are 10 inelastic. In this observable, it is impossible to avoid this problem plus the issue of dramatically changing the electron distribution (per previous discussion). In our XFEL studies, we typically have  $10^{14}$  molecules within the sampled volume with  $10^{11}$  X-ray photon incident such that the probability for multiple X-ray scattering from the same atom is exceedingly low ( $10^{-6}$  without consideration of elemental differences in scattering cross section). The scattering efficiency for these conditions is typically on the order of a few percent as another condition. The gas phase numbers should be similar. Your point is well taken when one is using very tight focusing conditions.

**Pankaj Kumar Mishra** commented: Using pump-probe methodologies, the authors have presented the ultrafast photodissociation of 1,4-diiodobenzene (DIB). The authors have also used an efficient computational technique to compare the experimental results, which are fascinating. My question is related to the polarisation direction of the X-ray used during the experiment. Why was the X-ray probe horizontally polarized in all cases for the X-ray scattering probe in the experiment? What do you expect if X-rays are polarised along the vertical direction?

**Michael Minitti** replied: Knowing how the polarization of the optical laser is oriented with respect to the location of the iodine atoms in 1,4-diiodobenzene is important. By varying the polarization of the optical pump laser, we can change the observed  $I(f)$ . This helps us verify the relationship between the iodine atoms and the dipole moment of the molecule. When the large I atoms are in plane with the horizontally polarized XFEL pulse, the observed  $I(f)$  signal will have intensities at the poles of the X-ray CCD camera. Conversely, when rotated  $90^\circ$  by flipping the optical laser polarization, the I atoms will be aligned normal to the X-ray polarization, and thus preferentially scatter along the equator of the detector. As for the X-ray polarization, we had no choice but horizontal. This is simply what the LCLS produces.

**Sebastian Mai** said: As the paper explains, all quantum-chemical calculations were performed within  $C_{2v}$  symmetry. Did you consider that there might be bound-state, non-symmetric minima in diiodobenzene? If they existed, such minima could be located at energies too low to be detected by the experimental setup, where the pump and probe lasers provide just enough energy to reach the ionization potential at the Franck-Condon point.

In this case, might it be possible that the observed 35fs time constant does not relate to dissociation, but simply to relaxation to a bound-state minimum?

**Michael Minitti** replied: Yes, this could be a possibility. Since we did not employ a sufficiently short ionization pulse to probe the state, we could be

missing dynamics to a lower bound minimum. Although we are confident in our state assignment and observed lifetime, it is possible we are missing some lower state dynamics after the initial 35 fs decay time. Revisiting the experiment with a shorter probe pulse would be good, and plans are in the works to remeasure these dynamics.

**Hans Jakob Wörner** addressed Michael Minitti and Kiyoshi Ueda: Could you compare X-ray diffraction and angle-resolved X-ray photoelectron measurements for imaging molecular dynamics, such as the dissociation of diiodobutane, with respect to feasibility, signal levels and information content?

**Kiyoshi Ueda** responded: Angle-resolved X-ray photoelectron measurements for randomly oriented molecules result in a single parameter  $\beta_2$ , which has indeed the information about the electronic structure. But I assume here the comparison should be between molecular-frame core-level photoelectron angular distributions or photoelectron diffractions (PED) and X-ray diffractions (XRD). Historically the structural information of gaseous molecules have been determined by electron diffraction (ED) with the external electron source, not XRD, due to low X-ray scattering cross sections. Knowing it, and knowing the experimental difficulty of fs time-resolved ED, originally I myself as well as some of our colleagues in the AMO community thought that PED would be the way to capture the fs structural change of isolated molecules in photoreactions. However, only proof of principle experiments of PED for the stable molecules with known structures have been reported so far, using synchrotron radiations and FELs. The difficulties may stem from how to record the 3D diffraction pattern with high energy photoelectrons, ideally of keV, from the molecules fixed in space, ideally in field free conditions. On the other hand, as we learned today, other colleagues started to see photoreaction of isolated molecules using XRD and even fs time-resolved ED with the external pulsed electron source (instead of internally produced photoelectrons). I cannot say PED is better in terms of feasibility any more. I would say that all techniques have some difficulties and some advantages and so we should try all. Also, as we saw on other days, and as seen in our work, for relatively small molecules, Coulomb explosion momentum imaging will also catch the structural change.

**Michael Minitti** responded: I agree with your comments. Combining these techniques to fully resolve PEDs, electronic energy level structure and molecular structural dynamics would be a fascinating *tour de force*.

**R. J. Dwayne Miller** remarked: I was extremely impressed when your first work came out showing X-ray diffraction from gas phase molecules (CHD in this case). Given the extremely small X-ray scattering cross section, this work is a real testimony to the value of ultrabright sources. How does the X-ray case compare to electron diffraction, which has been the standard for structure determination of gas phase molecules, in terms of structural resolution? The X-ray wavelength being 1.5 Å and the weak scattering of X-rays limit the number of resolvable diffraction orders. I understand the inversion process using theory for refinement is more straightforward than electron diffraction. However, both sources can use the same level of theory for refinement. What do you see as the limit in spatial

resolution? The clear advantage of X-rays at present is the much higher time resolution.

**Michael Minitti** answered: I agree with all you say here. Ultimately we need harder and harder X-ray sources to remotely approach the spatial resolution of electron diffraction. Unfortunately, the limit now at most XFELs is about 12.8 keV, translating into roughly just over  $6 \text{ \AA}^{-1}$  spatial resolution. Until harder, ultra-bright, ultrafast XFELs come online, UED will win this battle. Sources like LCLS-II will be capable of generating hard X-rays up to 25 keV. Impressive upgrades will make it possible to extend to nearly  $10 \text{ \AA}^{-1}$  spatial resolution. This advancement will really assist theory in generating better and better structural refinement calculations from XRD results. So who will the real winner be in the spatio-temporal resolved race? It boils down to two things. Can UED make sufficiently short electron bunches, overcoming space charge? Or, will future XFEL technology outpace and produce 100s of keV X-rays, extending their overall resolution? Only time will tell. It should be a good show.

**Kiyoshi Ueda** communicated after the meeting as a clarification of the paper: In our paper, we mentioned that for the SCC-DFTB approach to simulate XFEL-induced Coulomb explosion, “various modification can be made” on the way of injecting kinetic energies into atoms. We have extensively explored different energy injection models and found that the best way is to treat the molecule as a sum of diatomic molecules upon kinetic energy injection, which is a version slightly modified from the one described in the paper. In the present sequential ionization model, the momentum vector of atom  $i$  is instantaneously changed from  $\vec{p}_i$  to  $\vec{p}'_i$  when the charge of the molecule switches to the higher one:

$$\vec{p}'_i = \vec{p}_i + \Delta\vec{p}_i \quad (1)$$

where  $\Delta\vec{p}_i$  is a momentum added according to the acquired vibrational energy upon each ionization. We assumed that the momentum  $\Delta\vec{p}_A$  that the atom A receives is constructed from the momenta  $\Delta\vec{p}_A$  (A–B) generated parallel to the bond axes between atom A and its surrounding atoms B. We prepared random values for the momenta along bond axes following a one-dimensional Maxwell–Boltzmann distribution. In the new model, we treat two atoms connected by a chemical bond like a diatomic molecule; *i.e.*, the momenta  $\Delta\vec{p}_A$  (A–B) and  $\Delta\vec{p}_B$  (A–B) of atoms A and B are generated under the additional constraint of momentum conservation,  $\Delta\vec{p}_A$  (A–B) +  $\Delta\vec{p}_B$  (A–B) = 0.

The kinetic energy distributions (KEDs) for 5-IU obtained by following the above momentum constraint are shown in Fig. 4. All the parameters such as the electronic temperature  $T_e$  are the same as those in Fig. 5 in the paper. Comparing the new figure (Fig. 4) with Fig. 5 in the paper, we notice that the SCC-DFTB results based on the new model agree better with experiments and are indeed more satisfactory. The discrepancies in the KED of  $\text{H}^+$  in the previous models were significantly reduced. The KED of  $\text{H}^+$  is well reproduced by the new model as shown in Fig. 4, though the peak energy of  $\text{H}^+$  was much lower in the SCC-DFTB approach without the momentum constraint than in the experiment. The KED of  $\text{H}^+$  is shifted to the higher energy side and that of  $\text{I}^{q+}$  is shifted to the lower energy side by consequences of the imposed momentum constraint introduced in the SCC-DFTB approach.

**Daniel Rolles** asked: In order to achieve sub-Ångström resolution with photoelectron diffraction, a few hundred eV photoelectron kinetic energy is sufficient. The question is at what kinetic energy do multiple scattering effects become small enough that we can interpret the scattering images in a single-scattering picture. My feeling is that this will be the case above 300 eV, but this is something we are currently investigating.

**Kiyoshi Ueda** responded: I agree. A well established Muffin-Tin potential approach (including multiple scattering) will work down to the range 100–200 eV.<sup>1</sup> It is also possible to employ DFT in the least square fitting in a similar energy range.<sup>2</sup> Using a more elaborated approach (*e.g.* multichannel Schwinger configuration interaction MCSCI method), we can handle ~ 50 eV photoelectrons and extract the bond length from PED, at least for diatomic molecules and CO<sub>2</sub>. All these studies have so far been based on SR. High rep rate FELs will be a big advantage to extend such studies to time-resolved structural changes of photoexcited molecules.

1 Vladislav V. Serov, Vladimir L. Derbov and Tatyana A. Sergeeva, *Phys. Rev. A*, 2013, **87**, 063414.

2 E. Kukkk, D. Ayuso, T. D. Thomas, P. Decleva, M. Patanen, L. Argenti, E. Plésiat, A. Palacios, K. Kooser, O. Travnikova, S. Mondal, M. Kimura, K. Sakai, C. Miron, F. Martin, and K. Ueda, *Phys. Rev. A*, **88**, 033412.

**Allan Johnson** remarked: We've done some work on using CEI to determine the structure of chiral molecules in Frankfurt and found a similar problem with hydrogen motion when using strong laser fields. We've found better results since using synchrotron radiation to trigger ultrafast Auger processes. For larger molecules it would be necessary to trigger Auger at multiple sites simultaneously, and an FEL is an obvious choice for the light source. How badly would the hydrogen motion you've observed affect a CEI experiment at SACLA? Are there any parameters for an XFEL you could use to suppress the hydrogen motion, making it more appropriate for CEI?

**Kiyoshi Ueda** replied: In the case of our SACLA experiments, the X-ray photon is absorbed by a single I atom in a molecule. *Via* Auger cascades the charges are built up and redistributed to the entire molecule. If the X-ray pulse is 10fs or below, the time scale of charge build up and redistribution is determined *via* the nature of the Auger cascades. Our empirical model confirmed that the charge buildup and redistribution time is about 10 fs for similar experiments at both SACLA (10 fs pulse width) and LCLS (5 fs pulse width). Hydrogen atoms significantly move within such time scales. However, what we found is that the direction of the H<sup>+</sup> ejections still reflects the original conformation of the molecules (see Fig. 6 and 7 of the paper, though the distributions were broadened) while the bond lengths are significantly elongated (see Fig. 8 of the paper). To use FEL as a source of Coulomb explosion momentum imaging, it is not absolutely necessary to use hard X-ray FELs; if one uses hard X-rays the time scale of charge buildup is determined by the Auger cascade and it is about 10 fs, it cannot be shorter. Use of ultra-intense (>10<sup>16</sup> W cm<sup>-2</sup>), ultra-brief (<5 fs), EUV or soft X-ray pulse may be better to simultaneously remove electrons as much as possible, within the pulse width <5 fs.

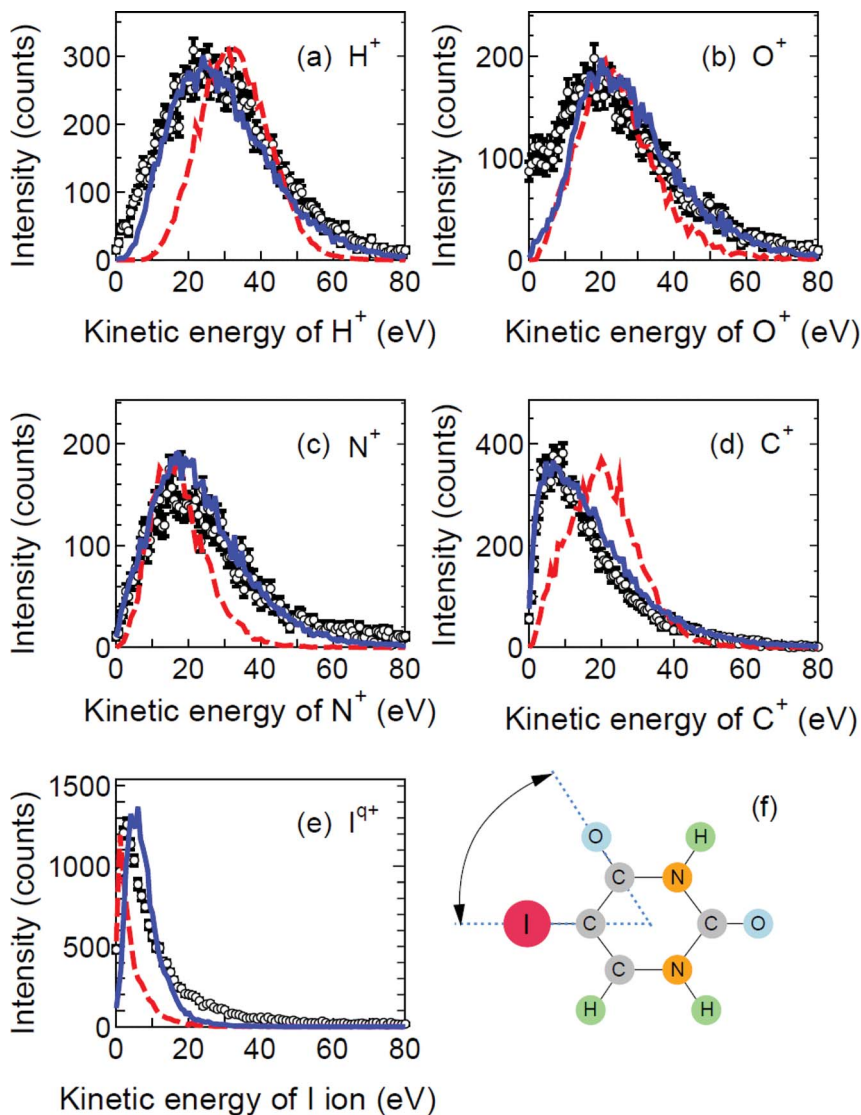


Fig. 4 Kinetic energy distributions (KED) of fragment ions emitted from XFEL-irradiated 5-iodouracil for (a)  $\text{H}^+$ , (b)  $\text{O}^+$ , (c)  $\text{N}^+$ , (d)  $\text{C}^+$ . KED data are summed up over  $\text{I}^{q+}$  of  $q = 1$  to 4. The open circles, red dashed lines and blue lines are the experimental data, CCE-CE results and SCC-DFTB results, respectively. (f) Molecular structure of neutral 5-IU molecule. In the SCC-DFTB approach.

**Fernando Martín** commented: To understand the results of your experiments, in particular, how the charge distributes in the molecule, you showed the results of molecular dynamics simulations. Molecular dynamics simulations are based on DFT approaches, but it is known that these methods can lead to unphysical fractional charges in the fragments – how do you deal with this?

**Kiyoshi Ueda** replied: Fernando Martín asked a question about fractional integers of charges for the fragment ions obtained from the SCC-DFTB approach.

They are indeed fractional integers. Based on further discussion with H. Kono and his group members, I would like to add the following comment as a reply. The charge distribution obtained by the SCC-DFTB approach is nearly unique after the fragmentation processes for a fixed maximum charge  $Q^{\max}$  of the parent cations and the charges of the fragment ions increase almost linearly as  $Q^{\max}$  increases. The charge of a fragment ion is thus nearly a certain fractional value for a given  $Q^{\max}$ . In the present paper, we left the fractional charge as it was to calculate the kinetic energy distributions and angular distributions of fragment ions; we virtually regarded the fractional charge just as an averaged one over fragmentation pathways through different excited states. Since  $Q^{\max}$  has a distribution, the charge of the fragment ion has also a distribution even in the present SCC-DFTB approach. The overall charge distributions of fragment ions obtained by the present SCC-DFTB approach are as follows:  $q = 0.3\text{--}0.8$  for  $\text{H}^{q+}$ ;  $0.5\text{--}1.5$  for  $\text{C}^{q+}$ ;  $0.5\text{--}1.5$  for  $\text{N}^{q+}$ ;  $0.5\text{--}1.5$  for  $\text{O}^{q+}$ ;  $0.5\text{--}2.0$  for  $\text{I}^{q+}$ . The round-off values of these fractional charges except  $\text{H}^{q+}$ , *i.e.*,  $q = 1$  and  $2$  for  $\text{C}^{q+}$ ,  $\text{N}^{q+}$ ,  $\text{O}^{q+}$ , and  $\text{I}^{q+}$ , correspond to the charges of dominant fragment ions shown in the experimental results of Fig. 1 (b) of the paper. The lowest value of  $q = 0.3$  for  $\text{H}^{q+}$  suggesting the possibility that neutral H exist as fragments as well as  $\text{H}^+$ . These fragmentation channels of different integer charges cannot be distinguished from one another in the present SCC-DFTB approach. One way to simulate the fragmentation channels of different integer charges or the integer charge distributions, *i.e.*, histograms in Fig. 1(b) (in the paper) is to use a constrained DFTB method where the charges on the departing fragments are fixed as integers, though this would make the on-the-fly DFTB/MD more expensive.

**Oliver Gessner** asked: The typical timescales for charge buildup and redistribution seem to be shorter than or comparable to the duration of the XFEL pulse. To what extent does the temporal shape of the XFEL pulse play a role then for the reconstruction of the electronic dynamics from the experimental observables?

**Kiyoshi Ueda** replied: The typical timescales of charge buildup and redistribution are about 10 fs and a few fs, respectively. Our X-ray pulse duration at SACLA is about 10 fs (FWHM) and so roughly the same order. We applied our model calculation (the classical Coulomb explosion model with charge evolution) to the experimental data at LCLS with the pulse duration of  $5\text{ fs}^{-1}$  and found that charge buildup time is about the same as the SACLA experiments. In this case Auger cascades seem to dominate the charge build up time scale. If the pulse duration is much larger than 10 fs, then the charge build up time is expected to be determined by the pulse duration. For example, for the  $\text{N}_2$  Coulomb explosion experiment of FLASH with the pulse duration of 100 fs, the FEL power density and the pulse duration determined the full Coulomb explosion dynamics.<sup>2</sup> From such studies (fitting the classical model calculations to the experimental data) we cannot learn much about the influence of the temporal shape of the XFEL pulse beyond the temporal duration of the pulse. However, according to the latest *ab initio* molecular dynamics calculations by Robin Santra's group, it seems the temporal shape also plays a role to fully reproduce the experimental observables.

1 B. Erk *et al.*, *Phys. Rev. Lett.*, 2013, **110**, 053003.

2 O. Kornilov *et al.*, *J. Phys. B*, 2013, **46**, 164028.



**Artem Rudenko** addressed Oliver Gessner: We have recently performed similar experiments with longer pulses and much higher intensities at LCLS. There, the comparison between the experiment and theory (by R. Santra's group) indicates that the exact pulse shape (pulse envelope) is important.

**Oliver Gessner** answered: It would be interesting to learn more about these experiments.

**Hans Jakob Wörner** remarked: From your experiments and calculations, is it possible to extract a general picture about the sequence in which chemical bonds are breaking, *e.g.* according to bond energies or the distribution of positive charges?

**Kiyoshi Ueda** responded: In principle yes. Comparing SCC-DFTB calculations that take account of the chemical bonds and CCE-CE calculations that neglect the chemical bonds with the experimental results, we can extract such information, but only to some extent. To fully answer the question, I discussed it with Hirohiko Kono (the second to last author on the paper). Let me now explain further details. Let us focus on the experimental and theoretical KEDs in Fig. 5 of the paper to discuss the role of chemical bonds in the sequence of bond breaking. In the case the CCE-CE results where chemical bonds are not taken into account, the kinetic energies of fragment ions are more or less governed by the mass ratio; the heavier the mass of a fragment under consideration is, the lower the kinetic energy. For the fragments of moderate weight, namely, for  $C^+$ ,  $N^+$ , and  $O^+$ , the CCE-CE results show that the peak energies in KEDs are around 20 eV, which is significantly lower than that of a light fragment  $H^+$  and higher than that of a heavy fragment  $I^{q+}$ . Without chemical bonding, the lighter fragment simply takes away more Coulomb repulsion energy.

This picture of Coulomb explosion is not always applicable to interpreting experimental results. In the experimental or SCC-DFTB results, the peak energy in the KED of  $C^+$  is smaller than that of  $O^+$  by 10–15 eV, though  $C^+$  is even lighter than  $O^+$ . According to our SCC-DFTB simulation, among  $C^+$ ,  $N^+$ , and  $O^+$ , the  $O^+$  fragments leave the gathering of atoms early (after  $H^+$  ejection), and then the  $C^+$  and  $N^+$  that are capped by a H atom follow. The remaining three  $C^+$  capped by the heavier atoms O or I are finally ejected. The fragments that are ejected earlier take away more Coulomb repulsion energy than those ejected later if the difference in mass is small. This “rule” is in accord with the experimental fact that the peak energy decreases in the order of  $O^+$ ,  $N^+$ , and  $C^+$ , not in the order of mass,  $C^+$ ,  $N^+$ , and  $O^+$ . Appropriate theoretical treatment of chemical bonds is inevitable to reproduce the accurate temporal order of fragment ejections. In the SCC-DFTB simulation, the bond distances between adjacent atoms in the uracil ring stretch almost at the same speed on statistical average. The mode of bond stretching between ring atoms is insensitive to the chemical nature of the bond, *i.e.*, whether the bond is a single or double bond in the neutral equilibrium structure. The energy that a fragment ion gains is rather sensitive to when it is ejected from the gathering of atoms.

**Oksana Travnikova** said: In your simulations the nuclear dynamics only in the final valence ionised states, which are formed after the charge buildup step, are



considered. However, during the charge buildup step core-hole states are generated in the course of Auger cascades with potential energy surfaces, which can be rather different from that of valence ionised states. Can nuclear dynamics during Auger cascades have an effect on charge redistribution and fragmentation?

**Kiyoshi Ueda** answered: In both the classical Coulomb explosion model with charge evolution (CCE-CE) and the self-consistent charge density-functional based tight-binding (SCC-DFTB) method, we took account of Auger cascades by introducing one parameter, a charge build-up time, which describes the exponentially increasing charge in the molecule. We took account of the nuclear dynamics during this charge build up time of about 10 fs. To be more precise, we employed this charge build up time as a fitting parameter to reproduce our multiple ion momentum correlation data. So we know that nuclear dynamics during Auger cascades certainly has an effect on fragmentation. As you pointed out, however, the potential surfaces of the inner shell hole states produced in the early stage of Auger cascades may be rather different from valence ionized states, even with the same total charge. Such differences were not explicitly taken into account in the current models but implicitly partly taken into account by another fitting parameter, *i.e.*, the charge redistribution rate in the CCE-CE model, which introduces a slight delay of the charge build up of other atoms than iodine (X-ray absorber). In the CCE-CE model, we empirically introduced the charge redistribution rate and used it as a fitting parameter. The resulting time scale is only a few fs. We consider the main mechanism of the charge redistribution is the later stages of Auger cascades where the electrons in the delocalized molecular orbitals participate in the decay. We checked the influence of the nuclear motion to the charge redistribution using the non-adiabatic quantum molecular dynamics (NAQMD) approach, where we assumed a 6+ charge state of the parent 5-UI and saw how the charge was redistributed (transferred) *via* nuclear motion. It turned out that the charge of iodine changes by one, following the H vibrational motion, in 5 fs and the charges of most of the atoms stabilize in 10–20 fs (*via* crossing conical intersections). This just gives us the idea of the time scale when the nuclear dynamics sets in and influences the charge dynamics. As you noted, however, the assumption here was that we have six valence holes as the initial state. From our current study, we cannot say much about competition between the nuclear dynamics and the charge redistribution during the Auger cascades.

**Tom Penfold** opened a general discussion of the paper by Martin Centurion: You stated that you have been able to extract not only the atomic positions but also the wavepacket itself from the experimental data. Have you compared this to quantum dynamics calculations? Also how far, in terms of number of nuclear degrees of freedom, do you think it will be possible to extend this in future experiments?

**Martin Centurion** responded: We have been able to extract the amplitude of the wavepacket of iodine molecules that were excited into a bound vibrational wavepacket. We did compare with simulations, with good agreement, and the results are published.<sup>1</sup> We don't yet have a general method to expand this to many degrees of freedom, but we expect that it should be possible to do it for a few

degrees of freedom. Many photochemical reactions can be described by a few degrees of freedom, so we expect that even with a few degrees of freedom the method will provide valuable information. How far this method can be pushed in terms of large molecules is still unknown.

1 J. Yang *et al.*, Diffraction Imaging of Coherent Nuclear Motion in Isolated Molecules, *Phys. Rev. Lett.*, 2016, **117**, 153002.

**Piero Decleva** asked: I would like to clarify the possibility of observing the vibrational wavepacket. I imagine that it is the probability distribution of nuclear positions, *i.e.* the modulus squared of the nuclear wavepacket that is imaged. Still I feel confused in the case of a split wavepacket moving onto two different electronic surfaces, what would be observed?

**Martin Centurion** replied: Yes, that is correct. What can be measured with this method is the absolute value squared of the nuclear wavepacket. In the case that the wavepacket splits onto two parts, what will be measured is still the absolute value squared of the wavepacket, so both parts will be detected. This is not too different from detecting the spreading of the wavepacket. As the wavepacket spreads, a broader wavepacket is observed. If it were to spread and split in two parts, two parts would be observed, assuming they are far enough apart to be resolved. This method is directly sensitive to the spatial distribution of charge, so it does not matter on which electronic surface a wavepacket is moving.

**R. J. Dwayne Miller** said: It is interesting to note that Ischenko *et al.*<sup>1,2</sup> were able to retrieve information on nuclear distributions, which you refer to as probability distributions. They treated theoretically dissociation of IBr, a reaction in this case, as well as CS product channels in the photodissociation of CS<sub>2</sub>. Similarly, it was suggested that with sufficient SNR one could even use their quantum tomography approach to determine electron distributions. In your case you are looking at the bound state vibration of I<sub>2</sub>. There is only 1 mode possible. Do you think you can disentangle this information from more complicated systems such as cyclohexadiene where there are multiple near resonant modes (C=C, C-C stretch)? If so, then it might be possible to observe the specific details of the mode coupling leading to photodissociation in this system as a prototypical example.

1 A. A. Ischenko, L. Schäfer, J. Y. Luo and J. D. Ewbank, *J. Phys. Chem.*, 1994, **98**, 8673.

2 A. A. Ischenko, J. D. Ewbank and L. Schäfer, *J. Phys. Chem.*, 1995, **99**, 15790.

**Martin Centurion** answered: In Ischenko *et al.*<sup>1,2</sup> they retrieved the nuclear probability density from simulated diffraction patterns of linear diatomic and triatomic molecules. In our case, because we looked at a diatomic molecule, iodine, we were able to use an algorithm similar to the standard algorithms used in gas electron diffraction to retrieve not only the interatomic distance but also the shape of the moving wavepacket.<sup>3</sup> Our method can in principle be extended to more complex molecules if there is sufficient alignment to retrieve the structure. In some cases, the alignment due to photoselection may be sufficient for this. What we would reconstruct is nuclear positions that are more spread out in space, where the spreading is due to the spread of the nuclear wavepacket. In practice, the limited spatial and temporal resolution also contribute to broadening of the

moving wavepacket so these will have to be accounted for to retrieve wavepackets accurately. Extending the method to molecules such as cyclohexadiene is in principle possible, but still a work in progress.

- 1 A. A. Ischenko, L. Schäfer, J. Y. Luo and J. D. Ewbank, *J. Phys. Chem.*, 1994, **98**, 8673.
- 2 A. A. Ischenko, J. D. Ewbank and L. Schäfer, *J. Phys. Chem.*, 1995, **99**, 15790.
- 3 J. Yang *et al.*, Diffractive Imaging of Coherent Nuclear Motion in Isolated Molecules, *Phys. Rev. Lett.*, 2016, **117**, 153002.

**Peter M. Weber** asked: In your paper you write that the electron beam has a diameter of 200  $\mu\text{m}$ . In the  $\text{N}_2$  plasma experiments, the laser has a diameter of 50  $\mu\text{m}$ , and in the alignment experiment it is 200  $\mu\text{m}$ . This implies that the plasma experiment only captures 1/16th of the molecules. Is this a problem? And, in the alignment experiment, one would expect a distribution of laser intensities across the nitrogen molecules. How does this distribution affect the interpretation of the experimental data?

**Martin Centurion** responded: For the plasma experiments, the only goal is to determine the temporal overlap of the laser and electron pulses. The plasma is used to deflect some of the electrons in the beam, and the deflected electrons are used to find the temporal overlap. While a larger laser spot size would increase the overlap with the electron, a higher intensity is more advantageous because the ionization rate depends nonlinearly on the intensity. Therefore, given a limited pulse energy, the number of deflected electrons was maximized with a smaller spot size. For the alignment experiments, the diameter of the laser and electron beams on the sample was the same. Ideally, the laser spot would be larger so that all of the molecules probed by the electron would experience the same laser intensity. We could not operate under these conditions because with the current setup it was not possible to reduce the electron beam size on the sample further without increasing the beam divergence, which would reduce the quality of the diffraction patterns. At the same time, making the laser spot size larger would have decreased the intensity. The way we accounted for this in the data analysis was that we used a scaling factor and considered an average intensity experienced by the molecules. This gave very good agreement between the simulations and the data. Effectively, the molecules under the more intense part of the field would be more aligned, but what we measure is the overall distribution, so the alignment is slightly lower than would be expected for uniform illumination.

**João Pedro Figueira Nunes** said: In diffraction patterns obtained from laser aligned molecules, do you observe any contribution from unaligned species? and if so, do you account for their isotropic contribution to the diffraction data?

**Martin Centurion** responded: When we analyze the diffraction patterns, we look at differences between patterns with and without the laser alignment. By taking a difference, we are removing the contribution of the molecules that are not excited by the laser, because their diffraction pattern does not change.

**Ruaridh Forbes** remarked: In experiments related to alignment or strong field processes a concern is intensity averaging over the laser focus. Intensity averaging typically results in a series of different radial intensities within the laser focus.

How did you deal with this in the data processing as well as minimise these effects during the data collection?

**Martin Centurion** replied: In order to minimize this effect, we made the laser spot size as large as possible, given the constraints of the experimental setup. This resulted in laser and electron spots of approximately the same diameter. This was taken into account in the data analysis by considering the average intensity experienced by the molecules. The molecules within the more intense part of the laser beam will be more strongly aligned, while the others will be less aligned. The angular distribution probed by the electrons will be the average over all the molecules, which can be well approximated by considering alignment with an “average” or effective intensity.

**R. J. Dwayne Miller** commented: Relativistic electrons have advantages over nonrelativistic sources in terms of being able to go to higher bunch densities before the onset of space charge effects. The problem is not so much in the longitudinal direction due the relativistic nature of the source but rather in the transverse direction. The difference in charge densities before the onset of undesirable emittance growth is however not too dissimilar to the same situation for nonrelativistic and leads very rapidly to a loss in spatial resolution (loss of transverse coherence). The most unique feature for gas phase studies is the near elimination of velocity mismatch between the laser excitation and electron pulses with respect to time resolution. However, you may be limited in the size of the system you can study because of transverse coherence issues. How far do you feel you can push the size of molecular systems you can study, assuming conventional laser excitation conditions (mJ laser systems)? What is the transverse coherence of your source at the sample position?

**Martin Centurion** replied: With the current setup, the transverse coherence length is 1.7 nm. The transverse coherence can be increased at the expense of beam charge. In order to do this effectively, one would need to increase the repetition rate of the system to increase the average beam current. Currently, the electron gun operates at 120 Hz, which is significantly less than what lasers can currently do. The technology to run electron guns at high repetition rates already exists,<sup>1</sup> and could be implemented in gas phase UED. Using a radio-frequency cavity to compress the electron pulses can also increase the beam current by two orders of magnitude [see for example ref. 2 and 3]. If a high repetition rate gun operating at around 100 kHz could be combined with pulse compression, the beam current could be increased by five or six orders of magnitude, which would allow to tune the beam to a transverse coherence of 100 nm or more, while maintaining a sufficient beam current for diffraction. Ultimately, photocathodes that are capable of generating brighter electron beams would be needed to investigate more complex systems and increase both the beam current and transverse coherence.

1 D. Filippetto and H. Qian, *J. Phys B.*, 2015, **49**(10), 104003.

2 X. H. Lu, CX Tang, RK Li, H To, G Andonian and P Musumeci, *Phys. Rev. ST Accel. Beams*, 2015, **18**, 032802.

3 T. van Oudheusden, P. L. E. M. Pasmans, S. B. van der Geer, M. J. de Loos, M. J. van der Wiel and O. J. Luiten, *Phys. Rev. Lett.*, 2010, **105**, 264801.

**Peter M. Weber** said: In our X-ray scattering we found that after accounting for an overall scale factor for the intensity of the X-ray beam, the X-ray scattering signal is in quantitative agreement with the computed signal. As your paper describes very carefully, the analysis of the electron scattering signals is much more convoluted, requiring multiple steps and analysis. This can probably be traced to the rapid  $1/s^4$  dependence in electron diffraction, which gives rise to the underlying shape of the scattering signal. Could you comment on how you see the advantages and limitations of electron scattering in this light? Does the convoluted nature of the analysis complicate the extraction of pump-probe data?

**Martin Centurion** replied: So far, in the pump-probe experiments, the structure as a function of time was retrieved from the diffraction pattern for each time step. For this, we used well established data analysis methods of gas phase electron diffraction. While there are several steps in the process, this method has been tried and tested many times over the last few decades in static patterns, and so far this has not been a limitation. For pump-probe data with more complex molecules, one could take advantage that the ground state structure is known, and use it as a starting point. In addition, one could add additional constraints, for example that the structure changes are continuous in time. I think what will be most interesting, and challenging, is to capture the dynamics when the position of the nuclei becomes delocalized, for example when there are multiple moving nuclear wavepackets spread in space such that they become very broad. This will present a challenge and an opportunity for both X-ray and electron diffraction.

**Adam Kirrander** said: In light of your previous work on reconstruction of molecular structure from diffraction data<sup>1</sup> and your recent measurements of vibrational wave packets in the iodine molecule,<sup>2</sup> how do you see the future of reconstructing structural dynamics from ultrafast scattering experiments? How feasible will it be to reconstruct the time-evolving molecular wave packet in molecules larger than diatomics? Laser-alignment and possibly holographic techniques would help, but imaging a wave packet that spreads across many degrees of freedom is hard. How do you see the state-of-the-art evolving, and what are the main limitations in your view?

I should perhaps add that our own take on this problem has been to calculate the scattering signal from a molecular wave packet,<sup>3</sup> and then bias this wave packet to reproduce the experimental scattering data as best possible, as a way of including pre-existing knowledge about molecular geometry, electronic structure, and dynamics. This was essentially the procedure followed in our ultrafast X-ray scattering study of the ring-opening reaction of 1,3-cyclohexadiene,<sup>4</sup> an analysis which was supported by time-resolved photoelectron spectroscopy.<sup>5</sup>

1 J. Yang *et al.*, *Struct. Dyn.*, 2014, **1**, 044101.

2 J. Yang *et al.*, *Phys. Rev. Lett.*, 2016, **117**, 153002.

3 A. Kirrander, K. Saita and D. Shalashilin, *J. Chem. Theor. Comput.*, 2016, **12**, 957–967.

4 M. Minitti *et al.*, *Phys. Rev. Lett.*, 2015, **114**, 255501.

5 C. Pemberton *et al.*, *J. Phys. Chem. A*, 2015, **119**, 8832–8845.

**Martin Centurion** replied: In the ideal case, the dynamics of the molecule would be completely measured by experiment, simulated using state-of-the-art theory (without interaction between the two), and then theory and experiment can

be compared. We are, of course, far from reaching that state with diffraction measurements, except for the simplest molecules. It is clear that for more complex dynamics an interaction between theory and experiment is needed to retrieve the dynamics. However, it is important to move towards minimizing the theoretical input in the interpretation of the experimental data. This will allow for more stringent tests on the theory, and more confidence in the dynamics retrieved from the experiment. As mentioned in the question, there are several approaches to extracting structures from experimental data. Currently, the main limitations in the experiment are the lack of a general algorithm for structure retrieval, and the limited spatial and temporal resolution that tend to blur out the details of the dynamics. Lastly, most diffraction experiments still suffer from low signal-to-noise ratios, so brighter sources will be important for the continued development of this research area.

**Oliver Gessner** opened a general discussion of the papers by Michael Minetti, Kiyoshi Ueda and Martin Centurion: As you have demonstrated, both ultrafast X-ray scattering and ultrafast electron diffraction provide access to structural dynamics in small molecules. However, there are important differences between the two methods. X-rays scatter predominantly off bound electrons, electrons off the Coulomb potential. Have you considered studying an example for unimolecular dynamics, such as the photoinduced ring-opening in CHD, with both methods and to compare the results? What differences would you expect and where do you see the particular strengths/weaknesses of each method?

**Michael Minetti** replied: Boy have we ever. These two techniques are extremely complimentary and need to be combined in some way. Now that MeV electron sources are becoming more and more prevalent, the task is to perform side by side measurements of each technique on a common target. 1,3-cyclohexadiene would be an ideal candidate.

A collaboration between Martin Centurion, SLAC, and LCLS will begin an ultrafast electron diffraction (UED) campaign at the ASTA electron source at SLAC, studying various gas phase targets, and 1,3-CHD will be one of them. It will be interesting.

As for strengths and weaknesses of the techniques, clearly UED offers exquisite spatial resolution when compared to X-ray diffraction. However, in the current state of the art, UED suffers from a lack of temporal resolution when compared to currently offered capabilities at XFELs. The trade-off with UED pulses in order to make them short enough, is to reduce the number of total electrons per pulse, due to the space-charge effect. This in turn will make the *s/n* ratio lower, thus needing longer and longer acquisitions times. Additionally, a challenge with UED is the ability to precisely time stamp the electron arrival time with that of any optical laser pump. Like the X-ray time-tools (cross-correlators, arrival time monitors... *etc.*), UED will greatly benefit from shot-to-shot time correction.

**Martin Centurion** responded: In most cases, X-rays and electrons will provide equivalent structural information because most of the charge is indeed concentrated near the nucleus. One interesting example where they will provide different information is in proton transfer reactions. If only a proton is moving during the reaction, the change will be captured by electron diffraction but not by X-ray

diffraction. One can envision a combination of X-ray and electron diffraction to determine whether a proton or a hydrogen atom is moving during the reaction, and to determine the path of proton and electron. In comparing the current state of X-ray and electron diffraction, X-ray diffraction provides higher temporal resolution because photons do not experience the repulsive Coulomb force that broadens electron pulses, while electron diffraction provides higher spatial resolution because of the smaller de Broglie wavelength and higher scattering cross section. The spatial resolution of X-ray diffraction is expected to increase as the repetition rate and photon energy of the FELs increases, while for the case of MeV UED there is a lot of room for improvement in both spatial and temporal resolution. For example, with RF compression, the pulse duration can be compressed to 20 fs, while also significantly increasing the charge per pulse, and thus improving the spatial resolution [see for example ref. 1]. The joint X-ray and electron experiments will be most interesting once both sources can reach temporal and spatial resolutions on the order of 50 fs and 0.1 Å. In the meantime, the main advantage of combining X-ray and electron diffraction data will be to take advantage of the high temporal resolution of X-rays and high spatial resolution of electrons.

1 X. H. Lu, C. X. Tang, R. K. Li, H. To, G. Andonian and P. Musumeci, *Phys. Rev. ST Accel. Beams*, **18**(3), 032802.

**Adam Kirrander** commented in response to an informal remark by Dwayne Miller (not recorded): Indirect observations of electronic state *via* changes in molecular geometry have been around for a while (see *e.g.*, ref. 1) but I agree with Dwayne that it would be incredibly interesting to directly observe excited electronic states using electron or X-ray scattering. In fact, we recently developed a code to predict elastic scattering from molecules in their ground and excited states based on their *ab initio* electronic structure wavefunctions<sup>2,3</sup> in anticipation of such experiments. However, in fairness one should remember that powerful techniques already exist to selectively study valence electronic structure, *e.g.* photoelectron spectroscopy and photoelectron imaging (including MF-PAD). In contrast, the scattering will contain contributions from all electrons, including core electrons.

1 M. R. Pressprich, M. A. White and P. Coppens, *J. Am. Chem. Soc.*, 1993, **115**, 6444–6445.

2 T. Northey, N. Zotev and A. Kirrander, *J. Chem. Theor. Comput.*, 2014, **10**, 4911–4920.

3 Thomas Northey, Andrés Moreno Carrascosa, Steffen Schäfer and Adam Kirrander, *J. Chem. Phys.*, 2016, **145**, 154304.

**R. J. Dwayne Miller** answered: I share your enthusiasm. Given the success of electron diffraction to enable quantum tomography on ns timescales to follow nuclear distribution of reaction products,<sup>1,2</sup> it is clear it should be possible to do the same on shorter timescales and with the theoretical advances you describe to be able to follow changes in electron distribution. The prospect of directly imaging electronic distributions is exciting as fs electron diffraction methods would enable a complete mapping of the forces at play in reaction dynamics and defining excited state potentials. As you point out, the problem will be the required signal-to-noise ratio to pull out these small changes. The changes at any atomic site relative will be relatively small compared to the total electron density



and Coulomb potential to give excitation dependent structure factors. From an experimental standpoint, the explicit use of differential detection and known initial structures should provide the needed contrast. Other improvements in source technology (stability), sample delivery methods, and new analysis methods should give us the tools to attain the required SNR to pull out these details.

1 A. A. Ischenko, J. D. Ewbank and L. J. Schäfer, *Phys. Chem.*, 1995, **99**, 15790.

2 A. A. Ischenko, L. Schäfer and J. D. Ewbank, *Proc. SPIE*, 1998, **3516**, 580.

**R. J. Dwayne Miller** addressed Michael Minitti and Martin Centurion: It is not clear to me that alignment is needed for enhancing structural resolution for the time resolved differential changes in structure involving known initial and final structures in the gas phase. This approach does provide additional information that would improve spatial resolution of unknown structures, however, one is always dealing with known structures in time resolved studies of structural dynamics. It is imperative that the excited state dynamics for the system are known as well as the electronic states excited in the preparation of the excited state. Therefore, only systems with known structures (and ideally excited state dynamics) are used in this class of experiments. There is also the additional complication of ionization and perturbation of the initial state preparation under the high field conditions needed for alignment. If there are high field effects for systems such as CS<sub>2</sub> with one of the largest Raman/differential polarizations for alignment, it seems relatively unlikely this approach will help in resolving structural dynamics. In the case of the use of alignment for unknown structures, even with adiabatic fields, the field ionization limits the utility of alignment. There are other ways to achieve alignment in this case without high laser fields.

**Michael Minitti** answered: I agree with you on some level, but an experiment to test the validity of alignment and whether or not it enhances the observation of time-resolved structural changes is to try it in a weak field case, such as adiabatically aligned targets. This should be done. These alignment techniques employ longer IR pulses, 100s of ps to ns at 1064 nm, to weak field align rotationally cold targets. The longer pulse widths tend to avoid imparting significant ionization effects or perturbation to the system. However, in order to achieve any decent alignment, these pulses require the target to be rotationally cold (a few K at best). This means lower target density, which in the case of gas phase X-ray scattering, is a bad thing given X-ray cross-sections. It is a definite trade off scenario, one that I don't have a good grasp of which parameter would win out and improve the overall resolution of the experiment. Only one way to find out, and that is to attempt it!

**Martin Centurion** answered: If the initial structure is known, this will indeed provide an advantage in determining the structure of the excited states, in particular if the structural changes are small, and it may be possible to determine the structure without alignment. In most experiments, a one-photon excitation is used, which results in selective alignment (even without active alignment) because of the angular dependence of the excitation. This already produces a significant alignment that can be used for structure retrieval. What we have seen in our experiments and simulations, is that in order to determine structures

directly from the data it is very beneficial to have alignment, in particular if two or more patterns are recorded where the angular distribution is different (and known). Regarding the complication of ionization and initial state perturbation, with impulsive alignment the alignment pulse can be applied before the excitation pulse, so that when the molecules are excited the alignment pulse is no longer present. Typically the alignment peaks at one or a few picoseconds after the interaction with the alignment pulse. Our previous experiments with CS<sub>2</sub> have shown that there is an intensity regime where significant alignment can be achieved without ionization and without multiphoton excitation.<sup>1</sup> If the laser intensity is increased beyond a certain threshold, the alignment no longer improves, and additional effects such as multiphoton excitation and ionization become significant. We are confident that impulsive alignment can be used [see also ref. 2] at least for the small molecules tested so far. For large molecules this will become more challenging, as the alignment pulse may also excite vibrations in the molecule. The regime of impulsive alignment of large molecules still needs to be explored.

1 J. Yang, J. Beck, C. J. Uiterwaal and M. Centurion, *Nat. Commun.*, 2015, **6**, 8172.

2 C. J. Hensley, J. Yang and M. Centurion, *Phys. Rev. Lett.*, 2012, **109**, 133202.

**Kiyoshi Ueda** commented: I am familiar only with the fluence of SACLA. At SACLA, a typical “peak” fluence of so called 1 μm focus at 5.5 keV is  $\sim 6 \times 10^{10}$  photons μm<sup>-2</sup>. The photoionization cross section of neutral xenon atoms at 5.5 keV is  $\sim 0.166$  Mb. So the “peak” fluence nearly saturates the single photon absorption. Due to volume focusing effects, however, still single photon absorption events dominate in the ion yield mass spectra. In the mild focusing conditions at LCLS, the single photon absorption of iodine atoms might not fully saturate. This might be a reason that the significant electronic damage in the hard X-ray scattering experiments at LCLS for the I-contained gaseous molecules was not observed in the X-ray diffraction.