

## Electronic and non-adiabatic dynamics: general discussion

Andrew J. Orr-Ewing, Jan R. R. Verlet, Tom J. Penfold, Russell S. Minns, Michael P. Minitti, Theis I. Sølling, Oliver Schalk, Markus Kowalewski, Jon P. Marangos, Michael A. Robb, Allan S. Johnson, Hans Jakob Wörner, Dmitrii V. Shalashilin, R. J. Dwayne Miller, Wolfgang Domcke, Kiyoshi Ueda, Peter M. Weber, Raluca Cireasa, Morgane Vacher, Gareth M. Roberts, Piero Decleva, Filippo Bencivenga, Daniel M. Neumark, Oliver Gessner, Albert Stolow, Pankaj Kumar Mishra, Iakov Polyak, Kyoung Koo Baek, Adam Kirrander, Danielle Dowek, Álvaro Jiménez-Galán, Fernando Martín, Shaul Mukamel, Taro Sekikawa, Maxim F. Gelin, Dave Townsend, Dmitry V. Makhov and Simon P. Neville

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**Jon Marangos** opened a general discussion of the paper by Fernando Martín: The work was in part motivated by IR XUV probes and strong IR field experiments. Couplings to cation resonances are clearly very important in the IR/vis region – what do you anticipate to be the role of these strong field couplings and how can you unpick this effect in the experiment?

**Fernando Martín** responded: In the experiment, the molecule is ionized by using a single XUV attosecond pulse. This process is clean and it is not contaminated by the presence of an IR pulse. This second pulse is used to probe the dynamics induced by the attosecond pulse. Therefore it is at this stage where the IR field can induce additional couplings between the cationic states that might complicate the analysis of the dynamics induced by the attosecond pulse or even blur it. Our calculations were able to describe the dynamics induced by the pump pulse, but did not take into account the probing step. Surprisingly, the results of these calculations catch most of the features that are observed in the experiment after probing the system with the IR pulse. Why is this so? We do not know yet. Preliminary results shown during my talk suggest that, if the probe pulse is not very intense, the additional features introduced by this latter pulse do not destroy the original dynamics generated by the pump pulse, although of course the analysis is more cumbersome because the signature of this dynamics is superimposed to that induced by the probe pulse. If this is a general conclusion for all systems, I cannot say. We should develop more sophisticated theoretical tools that allow us to accurately describe the probing step in such complicated

systems. In parallel, additional experiments performed with weak IR probe pulses or, even better, XUV probe pulses that lead to further ionization of the system without introducing additional couplings between cationic states, should be carried out.

**Kiyoshi Ueda** asked: You pointed out that the electron migration is not affected by the nuclear motion in the first 8 fs but has a significant effect later. Could you explain what happens at about 8 fs? Is the nuclear motion that affects the charge migration related to the vibrational motion of the hydrogen atoms? Does the diabatic transition at the conical intersection occur at about 8 fs?

**Fernando Martín** answered: It is a combination of all the above. In 8 fs, light nuclei have enough time to move significantly, but also the corresponding nuclear wave packets have enough time to pass through a conical intersection. The precise number, 8 fs, is only meaningful for the particular example that was discussed during my presentation. We have other examples where the effect of nuclear dynamics occurs earlier or later. It depends very much on the characteristics of the conical intersection and of how far away they are from the initial position of the nuclear wavepacket that is created after ionization.

**Daniel Neumark** remarked: Can you offer an intuitive explanation as to why the temporal oscillations associated with charge migration appear specifically in the immonium dication signal?

**Fernando Martín** responded: We cannot say from the present simulations because they do not include the effect of the probe pulse, which is ultimately responsible for the observed fragmentation. Therefore, I will answer your question based on my intuition. Our calculations show that the observed oscillations in phenylalanine are mainly associated with charge migration from the amino and the carboxyl groups to the other end of the molecule, the phenyl ring. Hole states mainly localized in this ring actively participate in the migration process. So, all fragmentation channels associated with the break up of the ring are unlikely to exhibit any oscillations, since the complex dynamics associated with fragmentation of the ring will be superimposed to the charge migration dynamics initiated by the attosecond pulse and can obscure it. In contrast, the channel leading to immonium fragments respects the ring and is associated to the loss of the small carboxyl group. Intuitively, I would say that the dynamics associated with this fragmentation channel is much simpler than in the former case and less perturbed by the IR probe pulse, therefore, there is a larger chance to observe the original charge migration dynamics. Also, previous experimental work<sup>1</sup> suggests that the probe pulse preferentially removes electrons from the amino group, thus giving additional support to the preferential role played by this group in displaying the XUV-induced dynamics. In any case, these are only speculations. A definite conclusion can only be obtained by including the nuclear dynamics and the probe pulse in the theoretical simulations. We are still far from doing so accurately, but our work shows possible directions to take.

1 L. Belshaw, F. Calegari, M. J. Duffy, A. Trabattani, L. Poletto, M. Nisoli and J. B. Greenwood, *J. Phys. Chem. Lett.*, 2012, 3, 3751–3754.

**Albert Stelow** commented: Could you comment on the role of a selected observable (e.g., the photoelectron spectrum) in elucidating complex wavepacket dynamics? How does the choice of observable “filter” the wavepacket dynamics?

**Fernando Martín** answered: Indeed, the choice of a given observable filters the wavepacket dynamics. So, by just looking at a single observable one loses a lot of information. In the experiments with which we were comparing the results of our theoretical calculations, only charged molecular fragments were detected. In my opinion, this is not the best observable to choose when investigating electron dynamics induced by attosecond pulses because a lot of other things must happen before fragmentation occurs. Detection of the photoelectron and, in particular, of the corresponding energy and angularly resolved photoelectron yields, would be a much better option, because it would give direct access to dynamics induced by the pump pulse, *i.e.*, well before fragmentation occurs. I know that this is not so easy when working with attosecond pulses because of their low intensity and hence poor statistics in the measured yields. However, I encourage experimentalists to make efforts in this direction.

Even better would be to measure electrons and ions in coincidence, which would give access to a more complete description of the dynamics of the system, but this is even more challenging for the reasons mentioned above.

**Danielle Doweck** remarked: This question is related to the description of the first step in the studied ultrafast electron dynamics taking place in an attosecond pump–probe process, *i.e.*, ionization of the molecule by the attosecond pulse, including the influence of the emitted electron, while it still interacts with the remaining electrons of the cation long after the interaction of the system with the attosecond pulse. From the study of photoionization dynamics in small molecules, we know that this dynamical electronic correlation may induce electron emission anisotropies in the molecular frame (asymptotically), which *a priori* leave a residual footprint in the electronic state in which the cation is left. In the reported time resolved studies, one might then consider that the “initial state” of the cation mirrors the dynamics of the emitted electron and therefore may be influenced accordingly. The results of the calculations describing the effect of the ionized electron on the cation dynamics in terms of hole density, presented Fig.1 and 2 in the paper, show that after 1 femtosecond the effect of correlation induced by the ionized electron vanishes, in the sense that the  $N$ -electron system and  $(N-1)$ -electron system calculations lead to similar hole densities: so that the conclusion of this interesting section of the paper is that the description of the electronic wavepacket generated by the XUV pulse must account for ionization, however that it does not mean that it also accounts for this part of the ionization process. The question is why is it so? Is this expected to be general or could we imagine some situations where the effect could be durable?

**Fernando Martín** responded: I would tentatively say that this is a general conclusion when the only ionized electrons are the photoelectrons, *i.e.*, those that are ejected by directly absorbing the photon, and the energy of these photoelectrons is not too low. Under this circumstance, the electron escapes very rapidly from the molecule, so that 1 fs later is too far away to have any significant influence on the remaining electrons. The situation would be completely different

when Auger electrons are produced. In this case, the electrons will take much longer to be emitted and therefore one can expect that they will have a significant effect on the cation dynamics at much longer times. This is reinforced by the fact that Auger electrons may be slow, so that they will stay longer around the molecule. However, in this case, there will be an additional factor that will seriously affect the cation dynamics: by the time the Auger electron is produced, the nuclei may have moved significantly, so that the cation electron dynamics will no longer correspond to the original geometry of the molecule.

When Auger electrons are not produced, there is still a possibility to see a significant effect of the photoelectron on the cation electron dynamics. Imagine a large 3D molecule and an ionization process that selectively removes an electron from the central region of the molecule. Under this circumstance, the photoelectron will certainly have the chance to interact with the molecular periphery in its way towards the vacuum. Thus, any charge migration process involving this peripheral region will be affected by the photoelectron until the latter has completely escaped from the molecular environment.

**Hans Jakob Wörner** asked: What is the role of electronic decoherence of the ionic states, caused by the departing photoelectron (see Ref. 1)? How is this included in your calculations?

1 S. Pabst and R. Santra, *Phys. Rev. Lett.*, 2011, **106**, 053003.

**Fernando Martín** replied: The effect of the departing electron is included in our calculations. Our theoretical method allows us to calculate the actual continuum state that is generated by an attosecond pulse in a large molecule. This state represents both the electrons that remain bound to the cation and the electron that is ejected into the continuum. The details of the method can be found in the Faraday Discussion paper related to this meeting and in the references therein (DOI: 10.1039/C6FD00074F). To quantify the actual role of the departing electron, we have compared the electron wavepacket dynamics resulting from this full calculation with that resulting from a calculation in which the departing electron is supposed to reach the asymptotic region instantaneously. For the latter calculation, we use a density matrix formalism similar to that described in the reference you mention. From this comparison we conclude that the departing electron only plays a significant role during approximately the first 0.5 fs. After this, the ejected electron does not affect the cation dynamics any more.

**Adam Kirrander** asked: As far as I understand, the calculations in your paper account for direct ionisation into the flat continuum of the molecule. Have you considered investigating the effect of closed ionisation channels (*i.e.* the structured continuum) on the charge migration? Presumably the rescattering of the autoionising electron could lead to interesting dynamics, along the lines of what has been examined for Rydberg wave packets in simple molecules (see *e.g.*, Ref. 1).

1 A. Kirrander, Ch. Jungen and H. H. Fielding, *Phys. Chem. Chem. Phys.*, 2010, **12** 8948–8952.

**Fernando Martín** responded: Several years ago, we did this in detail for the hydrogen molecule (see Refs. 1–3 and references therein). We found that the dynamics associated with autoionization is indeed very interesting, but also more challenging to describe theoretically, mainly because autoionization is a “slow” process and the nuclei can move significantly in the meantime. As a result, the theoretical treatment must account for the coupling between electronic and nuclear degrees of freedom. A similar treatment is still possible for other diatoms, but not for large molecules, mainly because of the difficulty to describe electronic and nuclear dynamics in the molecular continuum on an equal footing. In our group, we are taking the first steps towards achieving this goal.

1 I. Sánchez and F. Martín, *Phys. Rev. Lett.*, 1997, **79**, 1654–1657.

2 F. Martín, *J. Phys. B*, 1999, **32**, R197–R231.

3 A. Palacios, J. L. Sanz-Vicario and F. Martín, *J. Phys. B: At., Mol. Opt. Phys.*, 2015, **48**, 242001.

**Morgane Vacher** remarked: The exact composition of the initial electronic wavepacket, *i.e.* the relative weights and phases of the electronic states, will depend on the experimental setup. By using the relative weights and phases of the electronic states as free parameters in our own simulations, we have learnt how important the initial composition of the electronic wavepacket is for the subsequent electron and nuclear dynamics.

One of the challenges of theory is to be able to predict the exact composition of the electronic wavepacket in a given experiment. My understanding is that the amplitude and phase of each frequency component within the pulse bandwidth are imprinted on the weight and phase of the electronic state excited by that frequency component. The electric field polarisation also plays an important role. Having access to all these experimental parameters is not always possible.

It seems like in the present work, you use only the temporal envelope of experimental pulses to determine the initial wavepacket; for instance, the optical phase  $F$  is fixed to zero (see section 2.1). Can you comment on the potential errors made in the predicted initial electronic wave packet by such assumptions?

**Fernando Martín** replied: You are right. In order to evaluate the actual electronic wavepacket that is created in a real experiment, one has to use the actual wavepacket used in that experiment. As you say, very often only the spectral shape of the pulse is known, and this is not so easy to measure! In the experiment with which we compare, the optical phase is not known. However, since the attosecond pulse used in that experiment contains many cycles, the effect of the phase is expected to be small. Indeed, we have explicitly checked that the results do not change significantly when we use a pulse with a phase different from zero. For shorter pulses, however, this conclusion is not valid and knowledge of the optical phase is essential.

**Theis Sølling** asked: You mentioned the need for a wide variety of parameters when modelling dynamics. How are the coupling between electronic surfaces obtained and how accurate are they?

**Fernando Martín** responded: For small systems, *e.g.*, diatomic molecules, the quality of the calculated couplings is similar to that provided by standard multi-

reference quantum chemistry packages. The latter can only provide such information for electronically bound states. When electronic continuum states are involved, as it is always the case when molecules are irradiated by attosecond pulses, we use codes that we have developed in our lab along the years, which provide a similar level of accuracy. For large molecules, like phenylalanine, the accuracy of these couplings is substantially reduced. However, it is still good enough to provide photoelectron spectra in good agreement with those obtained in synchrotron radiation experiments. Hence we can assume that they are also good enough to describe ionization by attosecond pulses, since the dipole couplings are essentially the same as those involved in synchrotron radiation experiments.

**Shaul Mukamel** said: Fragmentation patterns result from complex multi-step dynamics. A much clearer probe of elementary electron and hole migration may be provided by ultrafast non-linear spectroscopy that can observe electronic coherence and electron and nuclear correlation functions

**Fernando Martín** replied: I fully agree with this comment. If instead of ionic fragments, ejected electrons were detected in a similar pump-probe scheme, one would have direct access to the dynamics occurring at the probing step without the distortions introduced by nuclear motion and fragmentation, which occur at a much later step. Even better would be the use of XUV pulses for the probing step instead of IR pulses, as discussed in the manuscript.

**Raluca Cireasa** asked: Your calculations based on single-electron excitations show that the charge migration in glycine is influenced by the ejected electron for less than 1 fs and by the nuclear dynamics after 8 fs, but without destroying the coherences created by the attosecond pulse for several tens of fs. Electron correlations occur on similar timescales and can lead to the migration of a localised hole through the whole system. Could you comment on the possibility of including the electron correlations in the calculations and their effect on the coherences?

**Fernando Martín** responded: There is absolutely no problem in including electron correlations during the migration dynamics initiated by a coherent superposition of single-electron excitations. Although electron correlations were not taken into account during the charge migration dynamics in our original paper<sup>1</sup> because they did not play a significant role, the TDDFT results on glycine presented in the present manuscript do include the effect of electron correlations (at the DFT level, of course). A much better way to do it would be to use a fully *ab initio* description of the molecular states involved in the migration process, which is feasible by using multi-reference configuration interaction quantum chemistry methods if one neglects the effect of the ejected electron (which, as shown in the manuscript, is a very good approximation). Here, I want to emphasize once again that inclusion of the ejected electron is essential for an accurate description of the initial wavepacket created by the attosecond pulse, but that, once the electron is ejected, it does not play a significant role in the charge migration dynamics. Concerning the role of electron correlation in the evolution of the wavepacket that results from the coherent superposition of single-excitation states, I do not expect

significant changes during the first few femtoseconds of the evolution since the early stages of this dynamics is mainly controlled by the initial superposition of singly excited states of the cation. However, at longer times, it will have an important effect, certainly comparable to that due to the coupling with nuclear dynamics.

1 F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. B. Greenwood, F. Martin and M. Nisoli, *Science*, 2014, **346**, 336–339.

**R. J. Dwayne Miller** opened a general discussion of the paper by Wolfgang Domcke:† It is quite unusual to increase coherence times by increasing damping. Normally damping leads to faster decoherence. I gather you are referring to coherence of the excited nuclear wavepacket and are not considering the electronic decoherence of the excited state. Is the reason for the increased coherence time that this coupling mode has less chance to drive the crossing of the conical intersection, which opens up other relaxation pathways and faster decoherence?

**Maxim Gelin** answered: The reason for this counter-intuitive phenomenon is the fact that the isolated conical intersection intrinsically exhibits dissipative behavior in the sense that coarse-grained observables such as population probabilities of electronic states or coherences of vibrational modes exhibit irreversible dynamics, see Ref. 1. This is a consequence of the exceptionally strong non-adiabatic coupling of the electronic states and the very pronounced local anharmonicity of the adiabatic electronic potentials near the conical intersection. In the model considered here, the coupling mode becomes particularly highly excited during the ultrafast internal conversion process at the conical intersection and is therefore particularly susceptible to damping by the bath (the damping rate of a damped harmonic oscillator increases linearly with the vibrational quantum number). The damping of the coupling mode by the bath reduces the intrinsic damping of the tuning mode. In the example considered, this effect is stronger than the direct damping of the tuning mode by the bath, which results in the counter-intuitive “de-damping” of the tuning mode.

1 R. Schneider *et al.*, *J. Chem. Phys.*, 1990, **92**, 1045.

**R. J. Dwayne Miller** remarked: How did you damp the mode? Was the parameter based on physically reasonable damping, presumably to the bath (system–bath coupling). The reason I ask is that normally vibrational damping times for relatively high frequency coupling modes are on the order of ps relative to much faster motions to the CI region. This mechanism may not be operative.

**Maxim Gelin** responded: We considered a minimal model of a so-called dissipative conical intersection. Namely, two coupled electronic states and two vibrational modes are considered as the system, which is bilinearly coupled to an environment. The results of our studies demonstrate that the conical intersection induces highly non-linear dynamics which is very sensitive to even weak coupling

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† Wolfgang Domcke's paper was presented by Maxim Gelin, Technische Universität München, Garching, Germany.



to the bath. If the electronic coupling at the conical intersection were set to zero, the weakest system–bath couplings considered in the present work would virtually produce no effect on the wavepacket dynamics on a picosecond timescale. The dynamics at the conical intersection, on the contrary, is highly non-linear and chaotic and hence very sensitive to even weak system–bath couplings.

**Andrew Orr-Ewing** asked: Can your results for a conical intersection which is bound along both the tuning and coupling coordinates provide some insights about the role of a dissipative medium on the dynamics of passage through a conical intersection in which the tuning coordinate is dissociative? For example, can we learn something about how a solvent affects the non-adiabatic dissociation of heteroaromatic molecules excited to repulsive  $\pi\sigma^*$  states?

**Maxim Gelin** answered: The role of vibrational energy relaxation due to the coupling to a vibrational bath in photodissociation reactions driven by repulsive  $\pi\sigma^*$  states was explored for a model of the photodissociation of pyrrole by Lan and Domcke.<sup>1</sup> It was shown that sufficiently strong system–bath coupling reduces the dissociation probability and enhances the probability for internal conversion to the electronic ground state. This finding is in qualitative agreement with the experimental observation that H-atom photodetachment *via* dissociative  $\pi\sigma^*$  states is suppressed in larger chromophores with more vibrational degrees of freedom, see *e.g.*, M.-F. Lin *et al.*<sup>2</sup> While H-atom photodetachment is the dominant photochemical channel in pyrrole and indole, it is completely quenched in tryptophan and larger chromophores.

1 Z. Lan and W. Domcke, *Chem. Phys.*, 2008, **350**, 125.

2 M.-F. Lin *et al.*, *J. Chem. Phys.*, 2007, **126**, 241104.

**Dmitrii Shalashilin** commented: Is the computational approach you are using generic or can it only be used for specific types of Hamiltonian?

**Maxim Gelin** replied: The approach assumes that the bath is described by a collection of harmonic oscillators and the system bath coupling is linear in the bath coordinates. The system Hamiltonian may be quite general.

**Adam Kirrander** remarked: Could one adapt your model of a bath to describe a specific system, for instance, a particular solvent or an anisotropic environment such as a protein embedding a chromophore? Would it make sense to tackle such a problem with this type of formalism?

**Maxim Gelin** responded: The present model of the bath can be applied to specific systems. The procedure goes like this: the harmonic (Gaussian) bath is fully specified by its spectral density function (in the frequency domain) or, equivalently, by its memory function (in the time domain). For specific systems, the functional form of the memory function can be retrieved, *e.g.*, from molecular dynamics simulations or optical measurements. The next step is to fit the bath memory function by a linear combination of exponentials. The so-represented memory function can readily be incorporated into the hierarchy equation of motion scheme, see Tanimura *et al.*<sup>1</sup> In many applications, the system–bath



coupling can be considered as weak and the bath memory is short on the system dynamics timescale (Markovian bath). Then, simpler descriptions (*e.g.*, Redfield theory) are valid.

1 Y. Tanimura, *J. Phys. Soc. Jpn.*, 2006, 75, 082001.

**Pankaj Kumar Mishra** asked: The authors have very nicely discussed the effect of a dissipative environment on the ultrafast non-adiabatic dynamics at conical intersections in pyrazine (the system studied) coupled with infinitely many harmonic oscillators in thermal equilibrium. If one tries to mimic the effect of the solvent by harmonic oscillators, how can the interaction of the oscillators with themselves be included within this hierarchy of equations of motion? Can that authors also comment on achieving the thermal equilibrium at a particular (desired) temperature?

**Maxim Gelin** answered: The interaction of harmonic oscillators with themselves can readily be included up to the second order in vibrational displacements, but the so-obtained Hamiltonian can be diagonalized by the introduction of normal modes, resulting in a collection of independent harmonic oscillators. The dynamics of any system in a harmonic bath obeys the so-called fluctuation–dissipation theorem, which ensures the relaxation of the system to equilibrium at the bath temperature. The temperature of the bath is a given external parameter. In many applications, the consideration of the fine characteristics of the bath is not necessary; it is sufficient to consider the strength of the system–bath coupling and the bath relaxation time, see, *e.g.*, Ref. 1.

1 U. Weiss, *Quantum Dissipative Systems*, World Scientific, Singapore, 1993.

**Wolfgang Domcke** opened a general discussion of the paper by Dmitrii Shalashilin: In the paper, you mention that the second-derivative non-adiabatic coupling operator is neglected. This has two consequences: (i) the Hamiltonian including only the first-derivative operator is not Hermitian; (ii) the second-derivative term is singularly repulsive at the conical intersection and repels the wave packet from the intersection. The non-Hermiticity of the Hamiltonian and the lack of repulsion could have significant consequences for the dynamics at the conical intersection.

**Dmitrii Shalashilin** responded: Our interpolation for the matrix element is of course an approximation, which helps to decrease the computational cost. It fails when the trajectory hits the conical intersection. However, in a multidimensional case this never happens in practice. The interpolation can be improved at the expense of more calculations. Also I would like to add that no approximations are used when running individual Ehrenfest trajectories, which together with cloning, accounts for the majority of the dynamics. The approximation for the matrix elements is only needed for coupling the amplitudes of the Ehrenfest configurations, which provides only a small correction.

**Michael Robb** commented: Why do you need cloning? I would have thought that the set of Gaussian basis functions floated on Ehrenfest trajectories was

complete. Or is it more efficient to do cloning than to run more Ehrenfest trajectories? If so why?

**Dmitrii Shalashilin** replied: Although in principle cloning is not necessary, in practice it speeds up the convergence of the results putting the basis in the right place. Too many Ehrenfest trajectories would be required without it.

**Iakov Polyak** said: In your work you run Ehrenfest dynamics on the basis of 3 adiabatic electronic states. May it be that restriction to just 3 adiabatic states could lead to some of the numeric issues that you have to account for by using “cloning”? Would it be beneficial to use a diabatic basis (configuration state functions) spanning all adiabatic states instead?

**Dmitrii Shalashilin** responded: An adiabatic basis is used in our direct dynamics because most of electronic structure codes yield adiabatic states and non-adiabatic coupling matrix elements (NACME). Using a limited set of adiabatic states can represent a problem and one always need to check whether the number of states is sufficient. In principle, a diabatic basis can be an alternative, but defining efficient sampling techniques, such as cloning for example, in a diabatic basis is not trivial.

**Andrew Orr-Ewing** remarked: The simulated image in Fig. 5 of your paper shows a radial structure in the high TKER component. Is this structure associated with the production of the pyrrolyl radical in different vibrational modes? If so, can the outcomes be compared to the high-resolution TKER measurements of Ashfold and coworkers<sup>1</sup> in which such a vibrational structure is observed and assigned?

1 B. Cronin, M. G. D. Nix, R. H. Qadiri and M. N. R. Ashfold, *Phys. Chem. Chem. Phys.*, 2004, 6, 5031.

**Dmitrii Shalashilin** responded: No, the structure is not related with the vibrational levels. We believe that it is simply noise.

**Wolfgang Domcke** asked: While the minimum energy reaction path is linear for H-atom detachment in pyrrole, it is generally strongly curved in H-atom transfer reactions. The tunneling path will then not follow the reaction path and you will not know where the tunneling path emerges on the other side of the barrier. How are you going to deal with this problem?

**Dmitrii Shalashilin** responded: On the other side of the barrier we put a train of the basis functions, not just one Gaussian. Our hope is that if the train is long enough it will cover significant space in the tunnelling region, which will overlap with the end point of the curved path.

**Adam Kirrander** commented: Looking at Fig. 3 in your paper, the low-energy part of the TKER spectrum does not change very much with the inclusion of tunneling, despite the fact that one might naively expect that it should. Can you comment? Also, how sensitive are the calculated tunneling rates to the value of

the Gaussian width-parameter? We have seen in other calculations that these can influence results, at least until calculations are fully converged.<sup>1-2</sup>

1 A. Kirrander, K. Saita and D. Shalashilin, *J. Chem. Theory Comp.*, 2016, **12** 957–967.

2 A. Kirrander and D. Shalashilin, *Phys. Rev. A*, 2011, **84**, 033406.

**Dmitrii Shalashilin** responded: The inclusion of tunneling certainly increases the low energy contribution, but in this particular case the low energy contribution is small. We hope that for other molecules we are considering the influence of tunneling will be stronger. As we use train basis sets here, the influence of the width parameter should be smaller than in the previous works, where a simpler version of the approach has been used. However, admittedly we have not yet checked this here.

**Markus Kowalewski** addressed Dmitrii Shalashilin and Dmitry Makhov: Does the *ab initio* multiple cloning approach describe the time evolution of the electronic coherence created upon cloning correctly? Is the decay of the electronic coherence in the vicinity properly described by the method?

**Dmitrii Shalashilin** responded: In principle our approach is a fully quantum one. In practice, of course, full convergence is hard to achieve. We tested the approach on model systems and found that full convergence can be achieved for a multi-configurational Ehrenfest method. This will be reported elsewhere.

**Dmitry Makhov** answered: The electronic coherence is not created upon cloning: cloning does not change the wave function, it changes only the ensuing dynamics. The decay of the coherence is always present in the Ehrenfest configurations: the phases of all electronic states are propagated in the dynamics and, because of the energy difference, they become essentially independent after some time. Cloning does not change much here.

**Jon Marangos** opened a general discussion of the paper by Morgane Vacher: The importance of the zero point geometry distribution in the dephasing of the coherent distribution is clear. What I am curious about is the fact that when the Ehrenfest dynamics was also included, the dephasing time was somewhat increased in the data shown. Is there a simple/general explanation for that behaviour?

**Morgane Vacher** replied: The zero point energy alone (with fixed nuclear geometries) leads to the fast dephasing of electron dynamics: in BMA[5,5], studied in the present work, the predicted coherence half-life is about 7 fs. This coherence half-life is slightly increased to 8 fs when the nuclear motion is taken into account (with the Ehrenfest method). We were also surprised by this result, expecting the nuclear motion to further damp the electron dynamics oscillations. According to our model presented in a previous article,<sup>1</sup> the coherence half-life is determined by the width of the energy gap distribution across the ensemble of geometries used to represent the nuclear wavepacket. We checked the time evolution of the energy gap distribution width but the latter was not becoming narrower with time. Our current hypothesis to explain this somewhat surprising result is the

following. In section 3.3 of the present work and in previous work,<sup>2</sup> we have shown that the nuclear motion can decrease the amplitude of the oscillations in the electronic density. By decreasing the amplitude of the oscillations for some nuclear geometries of the ensemble, the dephasing caused by these geometries will be less important, leaving on average a higher amplitude oscillation.

1 M. Vacher, L. Steinberg, A. J. Jenkins, M. J. Bearpark and M. A. Robb, *Phys. Rev. A*, 2015, **92**, 040502.

2 M. Vacher, D. Mendive-Tapia, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2015, **142**, 094105.

**Jon Marangos** addressed Morgane Vacher and Fernando Martín: The dephasing timescales due to the zero point geometry spread is clearly a general phenomenon that will affect all “charge migration” experiments. Do you anticipate that it will be important for the situation considered in Fernando Martín’s work?

**Morgane Vacher** replied: We have now looked at the effect of the zero point energy on the electron dynamics in several molecules, including some phenylalanine derivatives.<sup>1</sup> In each case, we observe the fast dephasing of oscillations in the electronic density: this result calls into question the commonly held picture of long-lived electronic oscillations at a well-defined frequency (obtained with the single-geometry approximation).<sup>2</sup> We believe that the dephasing of electron dynamics due to the natural width of the nuclear wavepacket is general and will be common to all molecular systems. We therefore anticipate it to be important for Fernando Martín’s work, for all electron dynamics simulations, and we also expect it to be particularly relevant for the interpretation of “charge migration” experiments.

The time scale of the oscillations dephasing is system-dependent. In the systems we have studied so far, the coherence half-lives range from 2 fs to 10 fs. The half-life obtained here for BMA[5,5] is therefore one of the longest times we predicted. We can rationalise the different coherence half-lives using our simple analytical model.<sup>3</sup> One of the challenges for theory may be to suggest molecular systems in which the oscillations in the electronic density survive for longer. But for this, one must go beyond the single-geometry approximation and describe realistically the nuclear wavepacket width.

1 A. J. Jenkins, M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2016, **144**, 104110.

2 F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. Greenwood, F. Martin, M. Nisoli, *Science*, 2014, **346**, 336–339.

3 M. Vacher, L. Steinberg, A. J. Jenkins, M. J. Bearpark and M. A. Robb, *Phys. Rev. A*, 2015, **92**, 040502.

**Fernando Martín** replied: It will certainly play a role, especially for molecules containing light nuclei, for which the geometrical spread is larger. Even more importantly, the intrinsic quantum nature of the nuclear dynamics, specially near conical intersections, further contributes to the dephasing of the electron wavepacket dynamics. Both effects will play a crucial role in determining the molecular fragments that are produced in XUV pump/IR probe experiments. Since it is precisely these fragments that are actually detected in a real experiment, accounting for the above dephasing effects is crucial for a direct comparison with experiment.

**Adam Kirrander** asked: In the paper you discuss different factors that influence the dispersion of the electronic wavepacket, including nuclear motion, the initial nuclear wavepacket, and the slopes of the potential energy surfaces. Given that Ehrenfest wavepackets may over-emphasize coherence, in particular when surfaces have different gradients, have you investigated this using a different method, such as DD-vMCG? Also, have you considered using an implementation of Ehrenfest that includes a *breaking force* such as proposed by D. Shalashilin and collaborators?<sup>1-2</sup> This would potentially make it possible to disentangle the influence of the spread of oscillators at different geometries *versus* the motion of the wavepacket on different electronic states.

D. V. Makhov *et al.*, *J. Chem. Phys.*, 2014, **141**, 054110.

D. V. Makhov *et al.*, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3316.

**Morgane Vacher** answered: For the Ehrenfest method, coming from a single-configuration ansatz for the molecular wave function, the nuclear motion is bound to be the same for all electronic states. It cannot describe the nuclear wavepackets on the different electronic states moving in different directions, which would add another origin for decoherence of electron dynamics. We are currently working on approaches going beyond the Ehrenfest method to check whether more elaborate methods are needed to describe these processes. The first step to go beyond an ensemble of independent Ehrenfest trajectories (without using an *ad hoc* procedure) would be to couple the amplitudes of the trajectories,<sup>1</sup> as proposed by Shalashilin and collaborators.<sup>2-3</sup> Then, if one uses quantum mechanics to guide the coupled trajectories (instead of classical mechanics), one arrives at the DD-vMCG method.<sup>1</sup> There, a multi-configurational ansatz for the molecular wave function is used and the nuclear wavepackets could move in different directions on the different electronic states, according to quantum mechanics.<sup>5</sup> Although such quantum dynamics calculations would include all effects at the same time, some post-analysis of the time-dependent molecular wave function might allow us to disentangle the importance of each factor in the decoherence of electron dynamics.

1 J. Shang, T. Yuan and H. Zhu, *Theo. Chem. Acc.*, 2016, **135**, 1.

2 D. V. Shalashilin and M. S. Child, *Chem. Phys.*, 2004, **304**, 103.

3 D. V. Shalashilin, *J. Chem. Phys.*, 2009, **130**, 244101.

4 G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt and B. L. Lasorne, *Int. Rev. Phys. Chem.*, 2015, **34**, 269.

**Peter M. Weber** said: In our experiments on tetramethyl diamine and other molecules, there is a high degree of structural flexibility that can affect the electron dynamics. We have interpreted the observed long timescales, about 1 ps, as due to the fact that the nuclear geometry must find the right place in its multi-dimensional space before charge transfer can take place. Listening to the talk I wonder if, in addition, the effect observed here – that the dephasing time becomes slower with the inclusion of nuclear motion – might play a role as well. In the flexible molecules there are several low frequency, large amplitude vibrations. Is it possible for large amplitude zero point motions to push the timescales significantly toward the picosecond regime? See, amongst others, Refs. 1-3.

- 1 X. X. Cheng, Y. Zhang, Y. Gao, H. Jónsson and P. M. Weber, *J. Phys. Chem. A*, 2015, **119**, 2813–2818.
- 2 X. X. Cheng, Y. Zhang, S. Deb, M. P. Minitti, Y. Gao, H. Jónsson and P. M. Weber, *Chem. Sci.*, 2014, **5**, 4394–4403.
- 3 X. X. Cheng, Y. Gao, F. Rudakov and P. M. Weber, *Chem. Sci.*, 2016, **7**, 619–627.

**Morgane Vacher** responded: It is helpful to distinguish between electron dynamics induced by nuclear motion, called *charge transfer* in the literature, and electron dynamics induced by an electronic wavepacket (coherent superposition of electronic states) that happens even with fixed nuclei, called *charge migration*. The two mechanisms are quite different and particularly the role of the nuclear degrees of freedom is different.

In the first case, upon electronic excitation, the electronic state is stationary (a single electronic eigenstate is populated); the nuclei will first respond to the change in electronic distribution upon excitation and then, as the nuclei explores new regions of the potential energy surfaces where the electronic character may change, we observe charge transfer, *i.e.* immediate rearrangement of the electronic distribution to the current position of the nuclei. In this context, low frequency modes sound consistent with a timescale of about 1 ps.

In the second case, a coherent superposition of electronic states is populated. This superposition is non-stationary, *i.e.* its probability density oscillates with time at a period inversely proportional to the energy gap between the populated electronic states. The nuclei are not “active” in this type of electron dynamics. In the present work and in earlier works,<sup>1–2</sup> we have shown that the distribution of geometries within the nuclear wavepacket width at the zero-point energy leads to a distribution of energy gaps, and therefore to a distribution of oscillation periods in the electronic density. The oscillations at individual geometries will dephase with time leading to, on average, a damped oscillation with a half-life of a few fs. In that context, low frequency modes mean larger amplitude motions, *i.e.* a larger nuclear wavepacket, and therefore a larger distribution of energy gaps and faster dephasing.<sup>1</sup> It looks therefore *a priori* difficult for large amplitude zero-point motions to push the dephasing timescale of charge migration toward the pico-second regime.

- 1 M. Vacher, L. Steinberg, A. J. Jenkins, M. J. Bearpark and M. A. Robb, *Phys. Rev. A*, 2015, **92**, 040502.
- 2 A. J. Jenkins, M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2016, **144**, 104110.

**Daniel Neumark** remarked: Why did you choose this particular molecule for your calculations, and what experiments have previously been performed on it?

**Morgane Vacher** replied: The real reason we chose to study the BMA cation is that, in order to understand the nuclear motion induced by an electronic wavepacket, we were searching for a molecular system where the induced changes in the nuclear geometry would be simple, localised and therefore straightforward to follow and analyse. Some of the other molecular systems we have looked at so far involve phenyl rings: there, the nuclear distortions become delocalised, complicated and it is harder to get some physical insights. Here, in BMA, removal of an electron from the bonding  $\pi$  orbitals simply results in the stretching of the methylene bonds. With such a system, we were able to demonstrate that the

population of a single adiabatic state results in a symmetric stretching while the population of a superposition of the ground and first excited state breaks the symmetry by localising the unpaired electron on one methylene group and leads to an asymmetric stretching. This is a demonstration of “charge-directed reactivity”. When taking into account an ensemble of trajectories, the asymmetry in stretching eventually disappears as the dephasing of electron dynamics leads to an equal delocalisation of the unpaired electron on the two methylene groups. The BMA cation had already been studied theoretically in the past.<sup>1-2</sup> There, the focus was not on the dynamics upon photoionisation though. Adamantane itself is a colourless, crystalline chemical compound; it is also the simplest diamondoid. Photoionization energies have been determined for adamantane (as well as for several bigger diamondoids).<sup>3</sup> Adamantane itself has few applications since it is merely an unfunctionalised hydrocarbon. The BMA cation is a model donor–linker–acceptor system where there is an intramolecular electron transfer between the two methylene groups connected by the adamantane framework. Such chemical structures may be used as basic units to make oligomers to produce new organic semiconductor materials or to make new molecular parts in the building of molecular computers.

1 L. Blancafort, F. Jolibois, M. Olivucci and M. A. Robb, *J. Am. Chem. Soc.*, 2001, **123**, 722–732.

2 L. Blancafort, P. Hunt and M. A. Robb, *J. Am. Chem. Soc.*, 2005, **127**, 3391–3399.

3 K. Lenzke, L. Landt, M. Hoener, H. Thomas, J. E. Dahl, S. G. Liu, R. M. K. Carlson, T. Möller and C. Bostedt, *J. Chem. Phys.*, 2007, **127**, 084320.

**Hans Jakob Wörner** asked: In this paper and in earlier work you showed that the relative phase of an electronic superposition state can influence nuclear dynamics. Do you expect this result to be general for sufficiently close-lying electronic states or are there additional conditions, *e.g.*, concerning the strength of non-adiabatic couplings *etc.*?

**Morgane Vacher** answered: First, we note that different electronic eigenstates, having different electronic characters, lead to different nuclear motions. This happens even in the Born–Oppenheimer approximation without involving any non-adiabatic coupling. Then, an equal superposition of delocalised eigenstates (typically “left+right” and “left–right”) leads to a localised hole density (“left” or “right” – or a more complicated density according to the relative phase). This is a general fact that does not rely on any interaction or coupling or condition on the energy gap. A nice illustration of this is the series of BMA[5,5], BMA[6,5] and BMA [6,7] cations, studied in the present work: these molecules exhibit the same charge migration but with different energy gaps between the two electronic eigenstates (and therefore different periods of oscillation). The same was observed in benzene, toluene and *para*-xylene cations, with the extreme situation where the period of oscillations is infinite in the benzene cation because of the zero energy gap.<sup>1</sup> Now, a given superposition of states leads to a nuclear motion determined by its own electronic character (different from those of the individual electronic eigenstates). The electronic character of the superposition is itself determined by the relative phase (and weight) of the states. In this case, the nuclear motion occurs on an *effective* potential energy surface, rather than on an *adiabatic* potential energy surface. We have shown in previous works,<sup>2-3</sup> the importance of the derivative coupling in such an effective potential energy



surface, to describe the nuclear motion induced by a superposition of states. In practice, such delocalised “left+right” and “left–right” electronic eigenstates often occur in the vicinity of avoided crossings where we expect the non-adiabatic coupling to be non-negligible.

- 1 M. Vacher, D. Mendive-Tapia, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2015, **142**, 094105.
- 2 J. Meisner, M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Theory Comput.*, 2015, **11**, 3115–3122.
- 3 M. Vacher, J. Meisner, D. Mendive-Tapia, M. J. Bearpark and M. A. Robb, *J. Phys. Chem. A*, 2015, **119**, 5165–5172.

**Shaul Mukamel** asked: Extensive work has been carried out on energy transfer (rather than electron transfer) in donor–bridge–acceptor systems. Could you comment on the comparison of your work to those studies?

**Morgane Vacher** replied: We believe that energy transfer can proceed by the same mechanism as charge migration (or electron dynamics). The same methods that we use to study coupled electron and nuclear dynamics can thus be used to investigate these energy transfer processes. We are actually looking at such chemical problems now.

**Adam Kirrander** said: When investigating the charge migration in your paper, you generally stop at 20 fs, with, for instance, Fig. 6 in the paper showing strong damping at that point. Have you explored the dynamics at longer times? Would you expect that any form of revivals could occur, for instance, related to vibrational beatings? Ultimately, I suspect that this would depend on whether the spectrum of states is a broad continuum or if it has some structure. Certainly in smaller molecules beatings related to rotational, vibrational, and electronic motion are common (see *e.g.*, Ref. 1 and 2). Also, have you investigated to what degree the preparation of the initial state, and in particular the initial phase relationship between the electronic states, can influence the observed charge dynamics? In much simpler molecules we have found that phase can influence the dynamics quite significantly (see *e.g.*, Ref. 3 and 4).

- 1 H. H. Fielding, *Annu. Rev. Phys. Chem.*, 2005, **56**, 91–117.
- 2 A. Kirrander, H. H. Fielding and Ch. Jungen, *J. Chem. Phys.*, 2007, **127**, 164301.
- 3 A. Kirrander, H. H. Fielding and Ch. Jungen, *J. Chem. Phys.*, 2010, **132**, 024313.
- 4 A. Kirrander, Ch. Jungen and H. H. Fielding, *J. Phys. B*, 2008, **41**, 074002.

**Morgane Vacher** replied: We have not explored the dynamics at longer times. For this, a multi-configurational approach would be recommended to give reliable results. Let me try to explain why we do not *a priori* expect the occurrence of revivals. In general, a coherent superposition of (non-degenerate) eigenstates evolves with time with each eigenstate acquiring a time-dependent phase proportional to its energy. With only two eigenstates, as time passes, the interference between the two states alternates between constructive and destructive. The oscillation period is inversely proportional to the energy difference between the two states. With more than two states in the coherent superposition, the time evolution is more complicated. The revival period is governed by the least common multiple of all the pairwise oscillation periods between its component

eigenstates. While this revival time is long, it always exists if a finite number of eigenstates are populated. The decoherence studied in the present and previous works,<sup>1-2</sup> is due to the dephasing of the continuous distribution of oscillation frequencies within the intrinsic width of the nuclear wavepacket; in other words, there are only two electronic states but an infinite number of oscillation frequencies (which can be totally in phase only at one moment in time) because of the geometry-dependence of the energies. For this reason, we believe revivals are not relevant in this context, unless one is able to select a few discrete nuclear geometries during the ionisation step. Besides, we have investigated the importance of the initial relative phase between the two electronic states on the subsequent coupled electron and nuclear dynamics in the current article (Fig. 9 and 10, section 4.2) and in previous works.<sup>3-4</sup> We found that indeed it significantly influences the dynamics: by determining the initial hole localisation, the initial relative phase controls the initial nuclear motion. This opens up the possibility to control chemical reactions *via* a coherent control technique.

- 1 M. Vacher, L. Steinberg, A. J. Jenkins, M. J. Bearpark and M. A. Robb, *Phys. Rev. A*, 2015, **92**, 040502.
- 2 A. J. Jenkins, M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2016, **144**, 104110.
- 3 J. Meisner, M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Theory Comput.*, 2015, **11**, 3115–3122.
- 4 M. Vacher, J. Meisner, D. Mendive-Tapia, M. J. Bearpark and M. A. Robb, *J. Phys. Chem. A*, 2015, **119**, 5165–5172.

**R. J. Dwayne Miller** commented: It is very difficult to optically direct momentum *via* optical excitation. Normally some form of coherent control is needed. The absorbed photon has no momentum or better cannot conserve momentum so that quantum interference in the superposition states with some phase relation picks out the specific momentum (see work by van Driel and Sipe on the control of electron motion in semiconductors).<sup>1</sup> The idea of a charge-directed reactivity using the preparation of an excited superposition state is interesting in this context. It seems, however, when you studied a distribution the effect vanished. I gather this was from the random motions in the ground state and FC projection to the excited state surface that washed out the idea of asymmetric excited state preparation to direct electron distributions through the coupling of nuclear motions to electron distribution. Did you extend your calculations in time to see if the same effect of averaging over an ensemble would occur if the process is averaged over time. This point is raised with respect to similar ideas for coherent control of electron motion.

- 1 J. Hübner, W. W. Rühle, M. Klude, D. Hommel, R. D. R. Bhat, J. E. Sipe and H. M. van Driel, *Phys. Rev. Lett.*, 2003, **90**, 216601.

**Morgane Vacher** answered: Our simulations are typically up to 20 fs, including all vibrational modes. Preparing an equal superposition of the two lowest energy electronic states in modified-BMA cationic species (studied in the present work) initially localises the hole on one methylene group. Considering a single fixed nuclear geometry, the hole oscillates back and forth between the two methylene groups with a constant period. Considering an ensemble of fixed nuclear geometries to describe the vibrational ground state of the neutral species and projecting it into the cation, the hole is still initially localised on one methylene group but the oscillations at each individual geometry dephase with time (because of

different periods), leading to a hole symmetrically delocalised onto the two methylene groups at about 15 fs. We have shown that considering a single nuclear trajectory (*i.e.* with the nuclei allowed to move along all vibrational modes), the oscillations in the electronic density are not perfect anymore: the period and the amplitude of the oscillations are affected after only a few fs (this time is of course system-dependent). As a consequence, already within the first 20 fs, the “symmetry” in the oscillations of the asymmetrically localised hole is lost. This effect could become larger with time as charge transfer comes into play. A good description of coupled electron and nuclear dynamics at longer times requires using a multi-configurational method for the nuclear motion (beyond the Ehrenfest method).

**Adam Kirrander** opened the discussion of the papers by Fernando Martín, Wolfgang Domcke, Dmitrii Shalashilin and Morgane Vacher: Given the number of theoreticians in the room, I would like to open the general discussion with a very broad question. In your view, how far away are we from a truly reliable theoretical description of photochemical reactions? What are the biggest obstacles and hurdles, as well as areas of opportunity, for theory and quantum molecular dynamics? Likewise, are there any particular (types of) experiments that you wish that experimentalists took upon themselves to perform, and which might be particularly useful from the perspective of advancing theory?

**Dmitrii Shalashilin** responded: The complexity of quantum dynamics is in my opinion the main challenge for theory. However, we are now at the stage that fully quantum simulations are becoming possible, albeit for very short times only. Luckily many photochemical processes are very fast and we should thank experimentalists for moving towards faster and faster processes providing a playground for theory.

**Fernando Martín** answered: Theoretical description of photochemical reactions, occurring either in the femtosecond and sub-femtosecond timescales, is accurate for small molecules, mainly diatomics and very simple polyatomics. There has been a lot of theoretical progress in the last few years to treat more and more complex molecules rather accurately, however, as we heard during the conference, experimentalists can always choose an even larger molecule for which accurate theoretical modeling is not possible. So, in my opinion, the key question is if theory can reach the necessary accuracy to treat systems with the minimum level of complexity that would allow us to obtain some general rules and patterns that can be extrapolated to those molecular systems that will remain forever inaccessible to theory. I think that we have not yet reached this point, mainly because of the difficulty to describe the coupling between electronic and nuclear motions in systems with a large number of degrees of freedom. Also, we are even further away when the dynamics implies ionization of the system, as *e.g.*, when irradiated with XUV pulses or when Auger processes play an important role. Theoreticians still need the support of detailed experiments performed in benchmark molecules (triatomics and small polyatomics), so that the different approaches can be rigorously tested. Theory also needs to be contrasted with other theories, even simplified theories, to check the validity of simplified models, the only alternative when dealing with very large systems.

**Michael Robb** responded: There is no doubt that quantum dynamics is becoming essential for the treatment of photochemistry. It is like the early days of electronic structure methods; quantum dynamics methods and computer programs are becoming “general” and “user friendly”. “On the fly” methods mean that one only computes those parts of the potential surface that are important. Quantum dynamics means that all the reaction pathways are explored simultaneously and the “importance” is thus ascertained from quantum mechanics. However, the accuracy and cost of the electronic structure part of the computation will continue to be an issue.

Concerning the experiments, it is clear that theory needs to be able to “simulate experiment”. This raises big theoretical challenges such as including the electric field and an outgoing electron in an ionisation experiment. The influence of the probe on the intrinsic dynamics of the system and the fact that there is very little knowledge and control over the initially populated electronic states (initial conditions of the dynamics) are outstanding questions. I am not sure resolving these would “advance” theory but it would help with testing it.

**Wolfgang Domcke** addressed Dmitrii Shalashilin and Fernando Martín: In my opinion, it is essential to test theory against theory, rather than theory against experiment. We need non-trivial and representative systems and models for which we can exactly solve the Schrödinger equation numerically. Against these solutions we can then benchmark approximate, but computationally less expensive, methods. In the comparison of theory with experiment for complex systems and/or dynamics, too many approximations and error cancellations are involved. It is also essential to explicitly include the photon field to compute the actually measured observables.

**Dmitrii Shalashilin** responded: I completely agree with this. Our multi-configurational Ehrenfest method has been extensively tested on a number of models, such as the spin–boson model for example, where good benchmark calculations are available. We currently are preparing a review article which describes the details of such tests. The conclusion there is that, in the case of models, the techniques we are using in our current direct dynamics “on the fly” calculations lead to good convergence with a similar number of the Ehrenfest trajectories.

**Fernando Martín** answered: I also fully agree with this point of view. However, this is not in contradiction with the fact that theory, even at an approximate level, is usually indispensable to shed some light on complicated experiments, either by identifying the dominant channels leading to a particular observation or by providing the basic mechanisms that operate under certain circumstances. Both aspects are extremely important to develop a know-how applicable to those cases where theoretical simulations are out of reach.

**Daniel Neumark** addressed Fernando Martín: In the time-resolved charge migration experiments that you have simulated, it seems that using near-infrared strong field ionization as the probe pulse is far from ideal, as its effect on the system under study is difficult to characterize. What in your view would be the ideal means of probing attosecond-induced charge migration dynamics?

**Fernando Martín** replied: In my opinion, the best way to probe the system is by using another XUV attosecond pulse. This pulse will further ionize the molecular cation created by the pump pulse, but it does so by absorption of just one photon. In this way, one would avoid introducing additional couplings between cationic states and, consequently, the original charge migration dynamics would be directly projected on the double ionization continuum. In other words, one would avoid all the possible resonant ionization transitions that take place in multi-photon ionization processes as those induced by an IR probe pulse (REMPI). Furthermore, due to their short wavelength (*i.e.*, a Keldysh parameter much larger than one), XUV pulses barely perturb the system, so that one can expect that the original dynamics induced by the pump pulse is barely affected by the probe pulse.

These expectations have been recently confirmed by XUV-pump/XUV-probe numerical experiments performed on the hydrogen molecule,<sup>1</sup> for which theory can provide nearly exact results. The results of that work show that the unperturbed molecular wavepacket created by the pump pulse can be reconstructed if the required energy and time resolutions are available. In our current Faraday Discussions paper, we also provide an example for the glycine molecule (although in this case, nuclear motion was ignored). For this molecule we show that the actual beating associated with the electron dynamics generated by the pump pulse remains intact after interaction with the probe pulse and are relatively easy to identify (notice that the beatings shown in the four central panels of Fig. 7 are the same as those appearing the bottom panel of Fig. 8).

1 A. Palacios, A. González-Castrillo and F. Martín, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 3973–3978.

**Albert Stolow** addressed Dmitrii Shalashilin and Fernando Martín: Could you offer any general comments as to the strengths and limitations of semi-classical methods in excited state molecular dynamics simulations?

**Dmitrii Shalashilin** answered: First of all, I would like to point out that our approach is not semi-classical. We use classical trajectories to speed up fully quantum simulations, but the *ab initio* multiple cloning technique is fully quantum. However, of course various semi-classical methods exist and in many cases they represent the most efficient way of simulating non-adiabatic dynamics. Their main strength of trajectory-based methods is that they explore only the most relevant regions of space, and can be implemented in the form of direct dynamics. The treatment of tunnelling and zero point energy effects is difficult though.

**Fernando Martín** responded: By using a classical description of the nuclear dynamics in combination with a quantum mechanical description of the electron dynamics, we are losing coherences that may show up in a real experiment, *e.g.*, around conical intersections. However, a full quantum mechanical description is out of reach for very large systems, so one should rely on semi-classical methods to get some qualitative understanding.

**Fernando Martín** remarked to Dmitrii Shalashilin: Semi-classical methods in which electronic motion is treated quantum mechanically and nuclear motion

classically are probably the only ones that are applicable to large molecules. However, in doing so, one is losing part of the coherence due to the coupling between electronic and nuclear degrees of freedom. Your method seems to overcome this limitation by associating quantum phases to the nuclear classical trajectories. Do you think that such an approach would be workable for very large systems?

**Dmitrii Shalashilin** replied: Yes, the techniques we are using are formally exact and they associate proper quantum phases with trajectory-guided functions. We are now pushing this techniques towards larger and larger systems. Our hope is that in large systems decoherence occurs very quickly and the required simulation time will be short. If there is a longer quantum coherence then typically a small quantum subsystem can be identified and a fully quantum approach may work also.

**R. J. Dwayne Miller** addressed Wolfgang Domcke, Michael Robb, Fernando Martín and Dmitrii Shalashilin: I am wondering if the level of theory needed to understand photochemical reactions could not be reduced by focusing on the structural changes, the actual chemistry, as opposed to calculating spectroscopic observables. The level of accuracy is really high if one wants to calculate electronic states and changes with structure as probes of the underlying dynamics. The energy differences are on the order of 10's of wavenumbers or better than 0.1 eV accuracy and this then requires very high-level treatment and convergence. However, I think we are missing a bit of physics that makes the problem much simpler if we focus on the structural dynamics to cast out the dominant reaction modes. Synthetic chemists have not been worried about such nuances in electronic states and detailed issues of vibrational non-adiabatic coupling. They typically use "arrow pushing" to conceptualize how the electrons will redistribute to give the lowest energy product or intermediates. If you reflect on this exercise, this approach involves a highly localized basis to rationalize the chemistry. Similar statements can be made for the concepts used to infer transition state structures to guide synthesis. It involves a very localized basis in which the most direct connection from reactant to product is typically invoked. They have not been held back by the details – and this strategy has worked. Over time, there are hundreds of named reactions that can be employed on nearly every molecular target to get the desired chemistry and make nearly any conceivable structure within near biological scales. These ideas are oversimplified but there is something in this view that transcends to different molecules independent of the significant differences in structure and many body potential/properties. There must be a reduction in dimensionality during barrier crossing. This process only has to be faster than all other competing processes to get drive the desired chemistry. We only need to get relative barrier heights and the most strongly coupled modes right to understand the observed chemistry.

With the latest advances in real time imaging of chemical reaction dynamics and inversion methods of femtosecond diffraction data, it is possible to obtain full atom resolved chemical reactions (see Ishakawa *et al.*).<sup>1</sup> Is there any computational saving or means to scale theoretical calculations to try to cast out the key modes that direct the chemistry and to compare to the structural dynamics? New approaches that could be formulated, such as coarse grain

sampling or imposed correlations? The level of accuracy needed should be far less than calculating electronic states to properly model shifts in X-ray absorption spectroscopy, electronic, or vibrational spectroscopy as indirect probes of the chemical dynamics. It is this detail that is needed to enable the development of simple rules/guidelines based on reaction modes by which one would be able to better approximate what the structure is at the critical point/barrier and better design means to control barrier heights. This would give a dynamic structural basis to understand chemistry and would be a major advance over “arrow pushing”. It would also scale to arbitrarily large systems as the synthetic chemists have admirably shown with synthetic-based approaches to solving chemical problems.

1 T. Ishikawa, S. A. Hayes, S. Keskin, G. Corthey, M. Hada, K. Pichugin, A. Marx, J. Hirscht, K. Shionuma, K. Onda, Y. Okimoto, S. Y. Koshihara, T. Yamamoto, H. Cui, M. Nomura, Y. Oshima, M. Abdel-Jawad, R. Kato and R. J. D. Miller, *Science*, 2015, **350**, 1501–1505.

**Wolfgang Domeke** responded: These arguments are intriguing and challenging for chemical theory. Simple and generic guidelines for the prediction of photochemical dynamics would certainly be welcomed by both experimentalists and theoreticians. However, it may be worthwhile to point out that several empirical rules developed in the past and widely used for the interpretation of the spectroscopy of polyatomic molecules and photochemistry, such as the “energy gap law” or the “proximity effect” in aromatic molecules, were thrashed as soon as reasonably accurate first-principles calculations of excited-state potential energy surfaces and non-adiabatic chemical dynamics became available. These early empirically derived rules have been superseded by the concept of non-adiabatic chemical dynamics at conical intersections. As a counter-example, the Woodward–Hoffmann rules should be mentioned, which remain a useful concept for polyene photochemistry. There are fundamental differences between ground-state chemical dynamics and photoinduced chemical dynamics. Thermal reaction dynamics is determined by rare events, the crossing of relatively high energy barriers, which is the reason why transition-state theory works so well. Ultrafast (sub-picosecond) photochemical dynamics, on the other hand, is typically not dominated by barriers on excited-state potential-energy surfaces (otherwise, it would not be ultrafast). It is rather determined by usually just a few reaction coordinates leading to conical intersections and it is essential to identify and follow these excited-state reaction coordinates. Moreover, excited states are numerous, often densely spaced and difficult to calculate accurately from first principles. From this viewpoint, it appears unlikely that simple and generically applicable rules governing excited-state chemical dynamics can be found.

**Michael Robb** replied: Valence Bond theory may be a framework in which the problem posed by R. J. Dwayne Miller can be resolved. Excited states have a simple qualitative representation in this theory. For example, we have recently shown how one may rationalize the occurrence of conical intersections with the aid of a simple qualitative valence bond interpretation.<sup>1</sup> This type of qualitative theory is as accessible as “arrow pushing” for understanding excited state reactivity. Further, VB methods can be easily parameterized<sup>2–4</sup> for excited states. Here one is “fitting” an effective VB Hamiltonian rather than many potential energy surfaces.



The parameterization has a very simple form<sup>2</sup> and can be fitted to high accuracy computational data (and even with some experimental input). The crucial point is that the chemical nature of the excited states is clearly differentiated (*e.g.* zwitterionic states, the B state of polyenes have a completely different representation from the covalent states 2A/1A). Finally, the VB basis is inherently diabatic because its localized nature.

1 M. A. Robb, *Adv. Phys. Org. Chem.*, 2014, **48**, 190–239.

2 F. Bernardi, M. Olivucci, J. J. McDouall and M. A. Robb, *J. Chem. Phys.*, 1988, **89**, 6365–6375.

3 F. Bernardi, M. Olivucci and M. A. Robb, *J. Am. Chem. Soc.*, 1992, **114**, 1606–1616.

4 M. Garavelli, F. Ruggeri, F. Ogliaro, M. J. Bearpark, F. Bernardi, M. Olivucci and M. A. Robb, *J. Comput. Chem.*, 2003, **24**, 1357–1363.

**Fernando Martín** answered: I have little to add to what Michael Robb has explained, except that in the case of chemical phenomena occurring in the attosecond or few-fs timescales, as *e.g.*, charge migration, experimental investigation of the corresponding dynamics implies the use of light sources that always lead to ionization of the system, either at the pump step or at the probe step, or at both! Furthermore, ionization induced by these light sources can also occur from inner molecular orbitals that lead to Auger electron emission on a temporal scale similar to that of the nuclear motion. If, as we have seen, the concepts developed for chemistry in the ground state are difficult to extrapolate to photodynamics in excited states, any tentative approaches to do it for electronic continuum states, as those generated in attosecond experiments, are hopeless unless we first understand the electron dynamics that is generated at the ionization step. As we have heard during this Faraday Discussion, this is not a trivial task, even for simple molecules. Therefore, significant theoretical efforts are necessary in order to understand the chemistry resulting from ionization before trying to look for general rules similar to those used in chemistry performed at thermal energies.

**Dmitrii Shalashilin** responded: Of course modern theory is always about simplifications and the ideas of developing some key models of key processes is very natural, but the question is always whether these qualitative theories are right (at least qualitatively)

**Michael Minitti** said: looking at model systems, direct imaging wavepackets, and experiments with 300–400 eV X-ray pulses – is there a model system? What type of model systems should experimentalists focus on and run to best inform theory/computation efforts in calculating electron wavepacket dynamics? FEL sources such as LCLS and European XFEL are capable of producing very intense edge-specific soft X-rays having pulse widths on the order of 2–5 fs. Could these capabilities be used?

**Fernando Martín** answered: XFELs have a great advantage with respect to HHG sources: the pulse intensity is very large and, therefore, XUV-pump/XUV-probe or X-ray pump/X-ray probe experiments should be perfectly feasible. Earlier attempts performed at FLASH (Hamburg) several years ago worked nicely, but they did not have the necessary time resolution to observe electron dynamics. Definitely, the advent of shorter pulses will allow one to overcome this situation. A combination of pulses of let's say 2 fs duration should be good enough to observe such electron

dynamics if the time delay between the pump and the probe pulses can be controlled with sub-fs time resolution. This seems to be possible nowadays. My recommendation would be to start with a simple triatomic or tetraatomic molecule, so that theoretical calculations can be carried out with high precision and, therefore, provide the necessary input to understand what is going on in such experiments. In my opinion, this is necessary before moving to very large systems, because, as explained in my talk, the electron dynamics induced by the pump pulse reflects in the fragments that are detected experimentally after probing the system with the second pulse, and this is very difficult to model in large systems.

**Allan Johnson** opened a general discussion of the paper by Albert Stolow:<sup>‡</sup> In the plot of X-ray absorption, could you clarify what the color axis represents? What variable exactly is being plotted against time and energy here? Also, could you comment about the parameters of the pulses used in this simulation?

**Albert Stolow** and **Simon Neville** answered: The colour axis corresponds to normalised oscillator strengths. The initial wavepacket is taken to correspond to the instantaneous vertical excitation of the ground state to the  $S_2(\pi\pi^*)$  state. That is, the pump pulse in effect corresponds to a delta function. The probe pulse parameters enter into the TRXAS simulation phenomenologically *via* the convolution of the spectrum in the time domain with a Gaussian of full width at half maximum corresponding to the pump-probe cross correlation, which we take as 10 fs.

**Oliver Gessner** addressed Albert Stolow and Simon Neville: Have you compared your TRXAS results with estimates for time-resolved X-ray/inner-shell photoelectron spectroscopy (TRXPS) measurements? For example, the ~5 eV splitting of the C 1s-pre-edge features due to the onset of distinguishability of the two carbon atoms ~20 fs after excitation (Fig. 8a and d), should also affect the corresponding C 1s inner-shell photolines in XPS, provided the effect is at least in part caused by a difference in the C1s core levels. Comparing TRXAS and TRXPS predictions may highlight the strengths/weaknesses of both methods and their complementarity.

**Albert Stolow** and **Simon Neville** replied: We agree that it can be anticipated that the splitting of the two C 1s orbital energies that accompanies twisting and pyramidalisation should also manifest itself in the TRXPS. However, a key difference between the pre-edge TRXAS and the TRXPS is the number and energetic density of accessible final states. In the case of the pre-edge TRXAS, the dominant final states are very small in number and well energetically separated. In contrast, in the case of the TRXPS, it may be anticipated that there will be a much larger number of overlapping accessible core-ionized states. Indeed, recent calculations support this idea.<sup>1</sup>

1 S. Neville *et al.*, *J. Chem. Phys.*, 2016, **145**, 144307.

**Tom Penfold** addressed Albert Stolow and Simon Neville: During the simulations, did you observe any significant difference in the convergence of the

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<sup>‡</sup> Albert Stolow's paper was co-presented by Simon Neville, of University of Ottawa, Ottawa, Ontario, Canada.

spectroscopic observables with respect to the number of basis functions compared to that of the population dynamics?

**Albert Stolow** and **Simon Neville** responded: In the case of the time-resolved X-ray absorption spectrum (TRXAS) of photoexcited ethylene, we observe a rapid convergence of the qualitative features of the spectrum with respect to the number of initial Gaussian basis functions. This appears to be due to the vertically excited initial wavefunction being quite tightly localized about the Franck–Condon point, a consequence of the absence of low-frequency normal modes. As such, the preponderance of classically evolving basis functions are effectively funnelled towards the twisted-pyramidalised (Tw-Py) conical intersection along similar pathways.

**Daniel Neumark** asked: Looking at Fig. 6 in your paper, it appears that the total photoionization cross-section at early times (<10 fs) is much lower than at later times (around 100 fs). Is that correct and if so, can you explain why it is the case?

**Albert Stolow** responded: This is a consequence of the dominant  $\pi\pi^* \rightarrow 1s\pi^*$  transition in the initially excited  $\pi\pi^*$  state having a relatively small oscillator strength in the vicinity of the FC point. It should be noted that the dominant feature in the calculated TRXAS around  $t \sim 10$  fs is actually around 3 times weaker than the dominant transitions after 100 fs, at which point the  $S_0$  state is populated. This is in agreement with the ratios of the calculated oscillator strengths of the dominant pre-edge transitions for the  $\pi\pi^*$  and  $S_0$  states at the FC point, as shown in Fig. 7 of our paper (DOI: 10.1039/C6FD00117C).

**Daniel Neumark** asked: One of your primary conclusions is that time-resolved carbon-edge X-ray absorption spectroscopy (XAS) is a more incisive probe of dynamics in photoexcited ethylene than time-resolved valence photoelectron spectroscopy. It seems that a more relevant comparison would be between the XAS calculations and time-resolved core-level photoelectron spectroscopy at photon energies above the carbon K-edge. Can you comment on what such a comparison would reveal?

**Albert Stolow** responded: Our primary reason for comparing the calculated TRXAS and TRPES spectra was to contrast methods that probe the core *vs.* valence level electrons, and their respective sensitivities to non-adiabatic dynamics. Our calculations predict that the significant variation of the core-level electronic structure with nuclear geometry gives rise to much of the clear and distinguishable temporal evolution in the calculated TRXAS. As such, it may be anticipated that time-resolved X-ray photoelectron spectroscopy (TRXPS), which probes the core-level electrons, will also provide a good probe of the excited state dynamics. One potential caveat, however, is that the number of core-ionization channels predicted to be open within a few tens of eV above the carbon K-edge in the excited states of ethylene is rather large.<sup>1</sup> As such, the TRXPS may be anticipated to be somewhat more congested than the TRXAS.

1 S. Neville *et al.*, *J. Chem. Phys.*, 2016, **145**, 144307.

**Oliver Schalk** said: In Fig. 6, you are showing your calculated TRXAS traces which cover excited state as well as ground state dynamics. In the ground state, you see time-dependent changes. Are these changes subject to a limited number of sampled trajectories or do they reflect “real” dynamics induced in the sample (*i.e.* would you expect these features when converging towards an infinite amount of calculated trajectories)?

**Simon Neville** answered: In the short time limit, when statistical processes have not yet become dominant, we expect that our description of the re-populated ground state dynamics should be somewhat meaningful. As such, even with a moderate number of basis functions, we do expect that the calculated ground state TRXAS will capture the qualitative features of the “real” dynamics.

**Oliver Schalk** remarked: In your paper, you simulated the TRXAS spectrum of excited ethylene up to 150 fs (see Fig. 6). It has been shown previously that on that timescale, H<sub>2</sub> formation on the ground state surface is observed.<sup>1</sup> Do you observe dissociation of ethylene in trajectories and if not, how would this affect the spectrum? In general, is this technique sensitive for such a bond cleavage?

1 T. K. Allison *et al.*, *Opt. Lett.*, 2010, 35, 3664.

**Simon Neville** responded: We do not observe a significant amount of H<sub>2</sub> elimination within the timescale of our AIMS simulations. In general, the AIMS method should be amenable to the description of such dissociation processes provided that they are not statistical in nature. It should be noted, however, that the ADC(2) method, which we use for the X-ray cross-section calculations, is based on a correction to a single determinant reference and, as such, is not well suited to giving a good description of dissociation processes. It is also reasonable to question whether the paper cited<sup>1</sup> can definitively tell us whether the H<sub>2</sub> elimination channel is a significant reaction pathway at short times, as it does not yield information about quantum yields.

1 T. K. Allison *et al.*, *Opt. Lett.*, 2010, 35, 3664.

**Hans Jakob Wörner** addressed Albert Stolow and Simon Neville: Can you decompose the ~4.5 eV splitting of the two pre-edge absorption features at early delays into chemical shifts of the core levels and energy shifts of unoccupied orbitals? Which one dominates?

**Albert Stolow** and **Simon Neville** responded: Within the initially excited  $\pi\pi^*$  state, the ~4.5 eV splitting of the two dominant pre-edge peaks is almost entirely due to the splitting of the two C 1s orbitals. This splitting is found to arise due to the arrival of the wavepacket at the Tw-Py conical intersection seam, in the vicinity of which the C 1s orbitals are localized about the non-equivalent carbon atoms. In fact, the splitting of the pre-edge peaks maps directly onto the splitting of the energies of the C 1s canonical Hartree–Fock orbitals at the Tw-Py conical intersection geometry: 4.51 eV using the 6-311++G\*\* basis.

**Hans Jakob Wörner** asked: Have you included Auger-lifetime effects and the vibronic structures of the final state in your calculations?

**Simon Neville** replied: In effect, all sources of broadening are included phenomenologically *via* the convolution of the spectrum in the time domain with a Gaussian function, the FWHM of which is determined so as to reproduce the ground state FC point experimental spectrum.

**Hans Jakob Wörner** asked Albert Stolow and Simon Neville: This is also a comment on an earlier question by Daniel Neumark. Although carbon K-edge XANES and valence-shell TRPES will, in general, provide complementary information, they should both probe the dynamics of partially-occupied orbitals because, at least within the molecular-orbital approximation. Do your calculations validate this picture?

**Albert Stolow** and **Simon Neville** answered: It is true that the evolution of both the valence- and core-level electronic structure will contribute to the evolution of the X-ray absorption spectrum. However, we find that the temporal evolution of the calculated TRXAS is, in effect, dominated by the changes in the core-level orbitals. This is in particular exemplified by the large splitting of the C 1s orbital energies, by  $\sim 4.5$  eV, upon the approach to the Tw-Py conical intersection.

**Wolfgang Domcke** addressed Albert Stolow and Simon Neville: The excited electronic states of ethylene have been a nightmare in quantum chemistry for decades. Did you check whether the rather simple ADC(2) method is reliable for the excited states of ethylene? Did you check the ADC(2) results against more accurate multi-configuration multi-reference methods? Is ADC(2) applicable at the conical intersection of the excited states with the ground state?

**Albert Stolow** and **Simon Neville** replied: We did check the ability of the ADC(2) method, used to calculate the X-ray absorption cross-sections, to give a satisfactory description of the MR-FOCI states, used in the AIMS dynamics calculations. As a suitable metric, we considered the overlap of the ADC(2) and MR-FOCI states at all geometries used in the calculation of the TRXAS. Those geometries for which the maximum overlap between the MR-FOCI state of the AIMS calculation and the ADC(2) states was not greater than 0.6 were excluded from the TRXAS calculation. For both the bound and continuum spectrum calculation, which employed different basis sets, around 90% of the geometries were retained. This indicates that, in general, the ADC(2) method is capable of giving a reasonable description of the excited states. Moreover, we did not observe a bias in the discarded geometries towards any particular region of nuclear configuration space.

**Wolfgang Domcke** commented to Albert Stolow and Simon Neville: My compliments on the results shown in Fig. 4(a). Your time-dependent electronic populations show recurrences driven by vibrational motion. These must generally occur in non-adiabatic electronic decay at such short timescales, when the vibrational motion is inertially driven. While many non-adiabatic classical dynamics simulations have been published recently for similar or other systems, the all exhibit just structureless decays. Your calculation is much better.

**Oliver Gessner** addressed Albert Stolow and Simon Neville: Is the splitting of the C1s pre-edge feature at ~20 fs delay (Fig. 8a and d) dominated by core or valence level shifts? In case of a strong core level shift contribution, the shifts should be related to a difference in core-hole screening on the different carbon atoms as a result of the pyramidalization. The relative positions of the split TRXAS features compared to the ground state pre-edge feature would then suggest that the pyramidalization leads to a charge transfer between the two carbon sites of the molecule. Is that the physics behind the predicted splitting?

**Albert Stolow** and **Simon Neville** answered: From the calculated CVS-ADC(2)x permanent dipole moments for the final core-excited states involved in these transitions, it is predicted that in both cases the final core-excited state exhibits a strong polarization, resulting in the pyramidalized CH<sub>2</sub> group acquiring a partial negative charge. As such, it seems reasonable that the predicted splitting of the pre-edge  $\pi\pi^*$  state signal is intimately linked to the polarization of the molecule at geometries close to the Tw-Py seam. This could conceivably be due to differential core-hole screening between the two types of carbon atoms associated with the differential charge of the two carbon atoms. However, the relaxation of the valence orbitals induced by the core-hole should also be taken into account here. Again, the differential charge of the two carbon atoms may reasonably be expected to result in a difference in orbital relaxation effects induced by the creation of a core-hole on each of the two carbon atoms. In short, it seems likely that the polarization across the C-C bond will induce differential core-hole screening and relaxation effects. However, it is not straightforward to predict the relative magnitudes of these two interrelated effects.

**Piero Decleva** asked: The adequacy of the CVS-ADC(2) approach for the calculation of core-excited spectra may be questionable in the case of excited initial states, as the approach uses the ground state as a reference, and core singly excited configurations which dominate the spectrum are in general doubly excited with respect to the ground state, apart from the valence-hole filling ( $1s \rightarrow \pi$ ) which is prominent in this case. I suggest benchmarking with convergent MRCI calculations which should be affordable on ethylene.

**Albert Stolow** answered: We acknowledge that benchmarking the calculated excited-state X-ray absorption spectra against a higher-level multi-reference approach would be desirable, and we are in fact working on such an approach. However, it should be noted that, at the CVS-ADC(2)x level of theory, doubly-excited configurations are in fact included in the description of the excited state wavefunctions.

**Adam Kirrander** said: In your calculations you assigned the lines a fixed Lorentzian width, presumably based on information from other sources such as experiments. Do you have any feeling for how sensitive the lifetimes are to molecular geometry? Could the shifts in line position and width be sufficiently large to complicate the interpretation of the experiment? Also, how computationally expensive are these calculations, for instance, compared to (valence) photoionization cross-sections?

**Simon Neville** answered: For a C 1s core-hole, which is relatively deep, it is not anticipated that the line width will vary significantly with the nuclear geometry. One caveat is that for dissociation processes that remove some valence electron density from the vicinity of the core-hole, it can be expected that the width may decrease significantly. However, dissociation processes negligibly contribute to our calculated AIMS dynamics of ethylene. As for the computational expense of our method, the pre-edge cross-section calculations are relatively simple, involving only the calculation of the initial valence-excited states, the final core-excited states and the transition dipole moments between the two. The calculation of the continuum part of the spectrum is somewhat more involved, requiring the generation of the Lanczos pseudospectrum of the CVS-ADC(2) Hamiltonian of sufficiently large dimension (typically of the order of  $10^3$ ) to converge the spectral moments. The main bottleneck in either case, however, is the  $O(N^6)$  scaling of the CVS-ADC(2)x method.

**Adam Kirrander** opened a general discussion of the paper by Taro Sekikawa: The timescales for the ring-opening reaction of 1,3-cyclohexadiene reported in your paper are significantly slower than the timescales reported in several recent experiments and theoretical simulations.<sup>1–3</sup> Can you comment?

1 O. Schalk *et al.*, *J. Phys. Chem. A*, 2016, **120**, 2320–2329.

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

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

**Taro Sekikawa** replied: I would like to point out that not all the previous works reported fast ring-opening reaction. Electron diffraction showed that hexatriene (HT) is formed with a time constant of 32 ps (Ref. 1) and it takes about 500 fs to complete the formation of HT according to photoelectron spectroscopy by VUV light.<sup>2</sup> In the latter case, the HT formation time is faster, but the difference seems to be acceptable, taking account of the different initial excited states.

In comparison with the raised references, I would like to describe two points: i) The dynamics might be changed due to the difference in the initial states, as described in later replies. ii) In photoelectron spectroscopy using ultraviolet light, the lifetimes of the excited states are short. However, HT formation was not observed because of the small photon energy of the probe light. The smaller probe photon energy might miss some excited states or transition states on the way to the conical intersection. If so, the observed lifetime of the excited state does not necessarily correspond to the ring-opening time.

1 C.-Y. Ruan *et al.*, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 7117.

2 S. Adachi *et al.*, *J. Phys. Chem. Lett.*, 2015, **6**, 343.

**Peter M. Weber** asked: In our 2011 paper,<sup>1</sup> we saw little evidence for crossing to 1B or 2A after excitation to the 3p Rydberg states. Do you have any evidence that such a curve crossing happens?

1 C. C. Bühler, M. P. Minitti, S. Deb, J. Bao and P. M. Weber, *J. At., Mol., Opt. Phys.*, 2011, 637593, DOI: 10.1155/2011/637593.

**Taro Sekikawa** answered: No, we do not. According to my collaborators, it is not easy to calculate the potential energy surfaces from the 3p Rydberg states



down to 1B states, because many states have to be included. The reference shows that the efficiency of the ring-opening is not zero but low. Therefore, we do not think that the relaxation pathway from the 3p Rydberg states to 1B or 2A is completely closed.

**Michael Minitti** commented: In your experiment with 1,3-CHD, you used 400 nm to excite *via* two-photon absorption. What was your percentage of excitation in order to guarantee only two photons were absorbed? In the manuscript, you mentioned your team used on the order of 40–50  $\mu\text{J}$  of pulse energy. This pulse energy, coupled with a presumably small focus, would be nearly impossible to control just two photons being absorbed. What focal spot size did you use?

**Taro Sekikawa** answered: In the middle of the same paragraph, it is described that the excitation energy was 19  $\mu\text{J}$ . We did not estimate the peak intensity, because the beam profile was far from the Gaussian or the uniform circular profiles. We tried to excite the molecules at the minimum energy so that we could observe some signals. In addition, as described in the subsection “Excited states” in the Results and discussion, the three-photon absorption ionizes the molecules. The ionization energy of the cation is usually larger than that of the neutral species due to the Coulomb interaction. Therefore, the spectrum of the cation did not overlap with that of the neutral species. The ionization did not deteriorate the observed spectra.

**Peter M. Weber** commented: A two-photon excitation with significant population transfer, as is the case here, requires a significant laser pulse intensity. Have you explored whether there are further absorption steps? The absorption of multiple further photons could result in fragmentation of the molecule. Have you looked for fragments in the mass spectrum?

**Taro Sekikawa** responded: Yes, we observed the photoelectrons only by the pump pulses. However, their kinetic energies were low and were energetically well separated from those by high harmonic pulses. We have never measured the mass spectra, but are worrying about the photofragments. We would like to investigate the dynamics under one-photon excitation for comparison.

**Oliver Schalk** commented: In 2015, Adachi *et al.* submitted data on a 267 nm pump, a HHG probe experiment on 1,3-cyclohexadiene (Fig. 2 in Ref. 1). In this paper, the authors showed formation of hexatriene which was strongly indicated by a peak appearing in the region between 10 and 10.5 eV binding energy, a region where 1,3-cyclohexadiene does not show ionization but hexatriene does. In the present contribution, the authors claim formation of hexatriene upon excitation with two photons of 400 nm (predominantly to the  $\pi 3\text{p}$ -Rydberg manifold); however, no changes of the spectrum in the region between 10 and 10.5 eV can be observed. Is there an explanation for such a behavior or does that mean that hexatriene is not formed under the present experimental conditions?

1 S. Adachi *et al.*, *J. Phys. Chem. Lett.*, 2015, **6**, 343–346.

**Taro Sekikawa** responded: We think HT was observed. For simplicity, we call the photoelectron band between 10.5 and 12 eV the C=C band, although it

consists of several molecular orbitals (MOs). After excitation, the C=C band increased at 607 and 1000 fs, as shown in Fig. 5. However, please note that the whole band was not increased: the photoelectron band with a lower ionization energy than 11 eV was enhanced faster than the energetically higher region. This indicates that a new MO is formed around 11 eV, shown in Fig. 5b. This should correspond to cZc-HT. In addition, our calculation predicts that the HOMO of cZc-HT is shifted to higher ionization energy than that of 1,3-CHD, it was also observed experimentally at 1000 fs as shown in Fig. 5b. These are described in the subsection of “Ring-opening dynamics” in the manuscript.

**Oliver Schalk** commented: As a reference to this comment, please see Fig. 1, taken from Schalk *et al.*,<sup>1</sup> where the distance between the two C atoms that break during the photodynamics of 1,3-cyclohexadiene is plotted against the propagation time.

In their paper, the authors claim the following mechanism:

a) The molecule is excited by two photons of 400 nm from the ground state to a  $\pi 3p$ -Rydberg state.

b) From there, the dynamics flows to the valence state within 37 fs from where it accesses the ground state after 500 fs.

c) In the ground state, the cZc conformation is formed, which rearranges to cZt after 800 fs before it finally ends up in the tZt conformation after 1.4 ps.

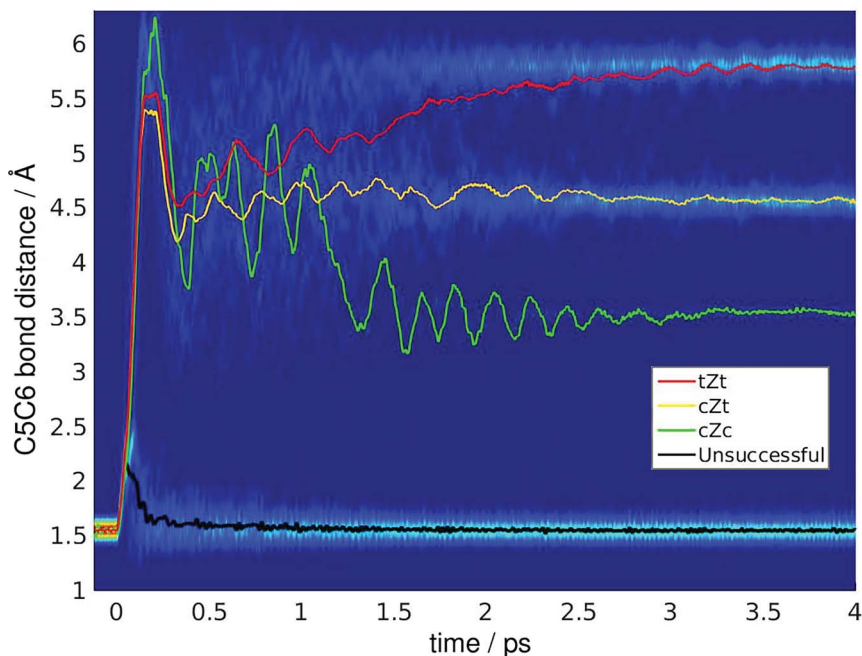


Fig. 1 Time evolution of the bond distance between C5 and C6 for all trajectories. The average values of the trajectories that lead to a certain rotational isomer are indicated by the colored lines. Adopted from Fig. 5 from Schalk *et al.*<sup>1</sup>, Fig. 5. Reprinted with permission from Schalk *et al.*, *J. Phys. Chem. A*, 2016, **120**, 2320. Copyright 2016 American Chemical Society.

Regarding this mechanism, could the authors explain the following: in the region below the IP, the signal must originate from excited state dynamics and is always a positive differential signal (*i.e.* no counts before time zero). If the molecule stays in the excited state for more than 500 fs, why don't you see a signal in this region?

1 O. Schalk *et al.*, *J. Phys. Chem. A*, 2016, **120**, 2320.

**Taro Sekikawa** replied: First of all, b) and c) are slightly different from what we described. The ring opens when relaxing to the ground state of HT. The ring begins to open to form cZc at about 500 fs and ends at about 800 fs. This experimentally observed timescale is determined by the temporal durations of the pump and probe pulses. We did not observe excited states explicitly between 200 and 500 fs. Experimentally, the collection efficiency of the magnetic bottle spectrometer for the faster photoelectrons is lower, because the faster electrons are not well guided to the detector due to the larger Larmor radius of an electron in the magnetic field. This makes it difficult to observe the fast electrons with lower ionization energies. As described in the manuscript, we had difficulty observing even the Franck–Condon 31A state just after excitation, shown in Fig. 4b, with a good S/N ratio in comparison with relatively larger spectral changes above 10 eV. Please make sure that the transient band observed in photoelectron spectra corresponds to the transition not to the ground state of the cation but to the excited states. The transition to the ground state of the cation should appear in the region of the lower ionization energy. Another reason for the low photoelectron yields of the excited states is that the Franck–Condon factors to the cationic states might be smaller under the distorted molecular structure.

**Oliver Schalk** asked: In previous time resolved studies (see *e.g.* the above cited paper of Schalk *et al.*<sup>1</sup> and papers cited therein, especially the review of Aruda and Sension<sup>2</sup> – there are 10+ studies agreeing on the rough timescale of the dynamics), excited state dynamics of sub 150 fs were observed. How does this agree with the 500 fs lifetime in this paper? One possible reason might be that another state is accessed initially, but passage to the valence state(s) is claimed to be fast and the gradients are supposed to be steep such that the conical intersection should be readily accessed once you are on the valence manifold.

1 O. Schalk *et al.*, *J. Phys. Chem. A*, 2016, **120**, 2320.

2 B. C. Aruda and R. J. Sension, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4439–4455.

**Taro Sekikawa** responded: In the present work, we excited to 3p Rydberg states in a two-photon absorption scheme, which is not the case with the previous works, except for that by Peter Weber's group. Since the initial excited state is different, the relaxation processes could be different. Certainly, the lifetimes of the observed excited states are short. However, HT formation was not directly observed. I am interested in the formation of HT.

**Oliver Schalk** remarked: The authors claim that the transformation between cZc, cZt and tZt conformers occurs between 300–500 fs. This significantly contradicts recent theoretical results (see Fig. 1 but also Ref. 1 and 2) which show that the tZt conformer is formed directly after ring opening and that

interconversion between these conformers occurs on a sub 100 fs timescale. I would like the authors to also comment on the following mechanism that might be consistent with the data presented in the paper: in accordance with previous results, return to the ground state is fast and occurs on a sub 100 fs timescale which is observed in the region below the IP (sub 8eV in Fig. 4b). There, you observe an extended bleach of the photoelectron bands which might be caused by a weak Franck–Condon overlap between the ring-opened hexatriene and the ionic manifold as emphasized by the “floppiness” suggested by the calculations shown in Fig. 1. This floppiness comes from the momentum stored in the motions along the ring-opening variable which enforces a fast interconversion between the three conformers. After 1 to 1.5 ps, IVR redistributes energy to other modes and the conformers show little interchange (see Fig. 1). This might increase the Franck–Condon overlap which leads to an increase in the ionization yields. The time-scales of the dynamics of theory and experiment match nicely.

1 Y. Lei *et al.*, *J. Photochem. Photobiol., A*, 2016, **317**, 39–49.

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

**Taro Sekikawa** answered: This could also be attributed to the initial excited states. In the references, the initial excited states are not 3p Rydberg states. Therefore, the dynamics is not necessarily the same. We agree that a molecule might rotate to form tZt after the ring breaks. It is difficult to distinguish among cZc, cZt and tZt experimentally from the photoelectron spectra as described in the paper. However, the HT isomers have lower MO energies of around 10 eV than CHD and the photoelectron band being less than 10 eV appears at 607 fs in Fig. 5b. This indicates the formation of HT. We also think that the formed HT transforms among the isomers coherently because of the impulsive excitation. We suspect that the intensity enhancement of around 10 ps in Fig. 7 might reflect the coherent motion. In our case, the molecules are excited by the pump pulses with a pulse duration of ~100 fs. Although the 100 fs oscillation is predicted by the theoretical calculation in Ref. 1, the oscillation would be washed out because the starting point of the oscillation has an ambiguity of ~100 fs. Therefore, we are not sure that the observed intensity revival is due to the predicted oscillation.

1 O. Schalk *et al.*, *J. Phys. Chem. A*, 2016, **120**, 2320.

**Michael Robb** said: Fig. 1 is a bit misleading. In reference 25 of your paper it is shown that the 2A/1A conical intersection seam lies parallel to the ring-opening co-ordinate (*i.e.* the reaction path). It follows that the 3s Rydberg state and the 1B state may intersect this conical intersection in different places resulting in different observed dynamics.

**Taro Sekikawa** responded: We appreciate your comments. We expect that the relation pathway from the 3s Rydberg state is different. The schematic diagram will be improved.

**Daniel Neumark** remarked: It seems that one source of your disagreement with the previous results of Prof. Weber is that he performed one-photon excitation of CHD at 200 nm, whereas you do two-photon excitation at 400 nm. Can you repeat

your measurements at 200 nm to investigate whether these discrepancies in interpretation disappear?

**Taro Sekikawa** replied: Yes. We are planning the experiment in which 200 nm light is used for the pump. I have one comment on the disagreement with the previous result. In the discussion with Peter Weber, we agreed that their data do not necessarily indicate non-ring opening because the photoelectron spectra in their paper showed some features of the bond cleavage. However, the efficiency of the ring-opening reaction was low. I would like to investigate CHD using 200 nm light.

**Hans Jakob Wörner** asked: I think that 1,3-cyclohexadiene does not have inversion symmetry, therefore there is no electronic parity (*g* vs. *u*). Consequently, one- and two-photon transitions may access the same electronic states. How can you reconcile your results with the results obtained following one-photon excitation at 200 nm by Peter Weber's group?

**Taro Sekikawa** replied: The comment on the symmetry is correct. So both one-photon and two-photon transitions are allowed. In Bühler *et al.*,<sup>1</sup> the final conclusion the authors described in the abstract is that "excitation to 3p does not induce ring opening". Experimentally, they observed the resonant ionization *via* the Rydberg states of CHD, occurring after the relaxation to the 2A state. The disappearance of the Rydberg states was attributed to the ring-opening reaction. In Bühler *et al.*,<sup>1</sup> upon excitation at 207 nm, the intensities of these Rydberg states were weaker than those upon excitation at 268 nm, indicating that the relaxation to the 2A state happens less upon excitation at 207 nm. Consequently, it was concluded that the ring-opening reaction does not happen.

I would like to raise two points. 1) The experimental results indicate that the Rydberg states appeared clearly, even by the excitation at 207 nm. The ring-opening process can take place. Therefore, I think that their final conclusion is too simplified. In fact, the authors described in the text that the ring-opening is not vanishingly small. During the Faraday Discussion, Peter Weber and I reached a consensus on this issue. 2) In Fig. 1 of Bühler *et al.*,<sup>1</sup> the intensities of the Rydberg states by 207 nm light look much weaker at a glance. However, the color scales indicate that the intensities of the Rydberg states less than 2 eV, both in Fig. 1a (207 nm excitation) and 1b (268 nm excitation), are on the order of 16~17. I wonder if they are comparable or not. Since the excitation peak intensity was not identical, it is difficult to estimate the absolute intensity of the Rydberg states only from the presented data. However, if comparable, the efficiency by 207 nm excitation might not be so low. Totally, since the one-photon excitation also opens the ring, I do not think there is a serious discrepancy. I will investigate the relaxation processes under the irradiation of 200 nm photons.

1 C. C. Bühler, M. P. Minitti, S. Deb, J. Bao and P. M. Weber, *J. At., Mol., Opt. Phys.*, 2011, 637593, DOI: 10.1155/2011/637593.

**Russell Minns** commented: For the signal going to negative times in Fig. 4, there appears to be an initial increase to 10 arb. units before it falls again to 8.5 arb. units giving a total change of 1.5 arb. units. The signal at this point still seems to be falling such that we do not know how far the signal would continue to fall,

what a true baseline at negative times is, or if these changes are due to probe–pump or pump–probe processes that are currently unaccounted for. The change in signal after time zero does seem to fall further, down to a minimum of about 7 arb. units, but it is unclear how significant this is without a true baseline to compare the changes with, or a measure of the uncertainty in the measurement itself. I wonder if you can therefore expand on the origin of the changes in the signal occurring at and before time zero seen in Fig. 4 and 7 of the manuscript. I believe you are using the dashed line in Fig. 7 to try to convey this baseline level, my understanding from the manuscript is that this is the average signal for negative times. I am therefore left wondering, depending on your answer to my initial point above, how good a comparison this is? If the changes in signal at negative times are affected by a probe–pump (or even pump–probe) contribution, then the dashed line seems inappropriate as a measure of the changes in signal and the plot needs to extend to much more negative times to obtain a reasonable measure. This would also mean the assignment of the spectrum at these early times would not be particularly accurate. If no such contributions are present, and the changes are due to uncertainties in the experiment then this is currently not captured in the error bars on the plots. Could you please expand on these points.

**Taro Sekikawa** responded: I suspect that the definition of “true baseline” is different for each of us. The true baseline to us is the average of the negative temporal time. We understand you are worrying about the pump effects by XUV pulses. In the beginning of this research, we compared the spectra without the pump with those at negative delay times longer than 1 ps and made sure that the spectra were almost identical except for the intensity fluctuation. So, at the present stage, we do not think that the pump effects in the negative delay times should be taken into account. In the research presented here, we decided not to measure the spectra in the negative temporal region longer than 200 fs. Although you worry that “this would also mean the assignment of the spectrum at these early times would not be particularly accurate”, we think there are no problems in the assignment because the spectral features between with the pump and without the pump were the same. On the other hand, at around 800 fs, the intensity ratio between the C–C and C=C bands changed. This is the evidence of the structural change of the molecule upon photoexcitation. Because high harmonic generation is the highly nonlinear process, we sometimes suffer from the stability of the light source. If the temporal behavior of only one particular band is focused, it is difficult to discuss the dynamics under the worse stability of the light source as you claim. However, we observe spectra covering multiple molecular orbitals and can see the appearance and disappearance of the energy levels simultaneously. Even using the unstable light source, it is not difficult to find new energy levels in comparison with other peaks. The different temporal behaviors among MOs are less distorted by the stability of the light source because the photoelectrons are ejected by the one-photon process and the spectral shape itself does not depend on the high harmonic intensity. This is one of the advantages of the broadband measurement of photoelectron spectra using high harmonics. Please note that the temporal behaviors of the C–C and C=C bands in the negative temporal range were almost identical, although they are different in the positive range with larger amplitude. The dynamics in the negative temporal range might be induced by the

XUV pump as you claim. However, we are not confident about that, which might come from the intensity fluctuation of high harmonics. So, in this paper, we focused on the dynamics after the pump with a larger amplitude. We can see the moment of the structural change without ambiguity, when the spectral shape was altered. We think that the application of high harmonics to spectroscopy has just started. We are neutral about the dynamics in the negative temporal range. We will be able to improve the experimental methods and conditions to investigate the dynamics in the negative temporal range in the near future.

**Kyoung Koo Baeck** said: Though the major emphasis of this paper was focused on the ring-opening mechanism between 150 fs and 800 fs after the initial photo-excitation, the observation of the lifetime of the initially excited transient 3p Rydberg state ( $R_{3p}$ ),  $\sim 37$  fs, seems a new exploration of the early-time dynamics not studied before. Moreover, I think, the longer time for the ring-opening reaction by the initial excitation to the  $R_{3p}$  than to the  $1^1B$  state was resulted in *not simply because* the internal energy of the initially excited  $R_{3p}$  is larger than that of the initially excited  $1^1B$  *but mainly because* there is a significant difference between the geometries of the  $R_{3p}/1^1B$  and the  $1^1B/2^1A$  conical intersections (CIs). Therefore, we need more information about the geometrical difference between the two CIs in order to get better understanding of the ring-opening mechanism. The  $1^1B/2^1A$  CI was studied before theoretically, but it seems the  $R_{3p}/1^1B$  CI has not been studied yet. Unfortunately, the theoretical study of CIs involving such high-lying Rydberg states is more difficult than CIs between valence excited states. Regarding this, I suggest to the authors to try the pre-excitation of vibration levels of the ground electronic state of CHD by IR laser just before the action of the two-photon excitation at 400 nm. The pre-excitation of some vibrational levels could make a noticeable change to the lifetime of the transient band reported in the present work. Then the characteristics of the vibrational mode could be very helpful for a future theoretical study of the  $R_{3p}/1^1B$  CI.

**Taro Sekikawa** replied: The idea to excite some vibrational modes is interesting. We wonder what the necessary amplitude of the vibrational modes is to observe the difference. Still, we appreciate the suggestion of the new experimental scheme. We will consider the scheme further.

**Fernando Martín** opened a general discussion of the paper by Danielle Doweck: The harmonics that are produced in the lab have a bandwidth. Do you know how much the polarization state of those harmonics varies within the bandwidth and from harmonic to harmonic? Experiments show a significant variation when resonances are involved. But what about those cases where only the smooth non-resonant continuum is playing a role? Since the determination of the polarization of emitted harmonics ignores this fact, it would be nice to have an estimation of the error that is made in making this assumption.

**Danielle Doweck** responded: To most generally answer your question about the possible influence of resonances in the determination of the polarization state of harmonics in an attosecond pulse train (APT), I think one may distinguish two aspects in the polarization analysis presented in this work.



Firstly, considering the high harmonic generation process, in particular the recombination step, the existence in the HH medium of narrow resonances relative to the bandwidth of the harmonics may induce a spectral dependence of the polarization state of the emitted radiation within the bandwidth of the harmonic (as well as from harmonic to harmonic). Such a variation of the polarization state within the harmonic bandwidth is not resolved by the molecular polarimetry method in the present conditions, due to the low statistics at 1 kHz repetition rate, therefore the polarization state is determined for each harmonic from the analysis of the MFPAD induced by the integrated peak attached to the selected harmonic. This situation is even invoked as a possible origin of the production of a measured “depolarization”, *i.e.* a non-zero  $s_4$  parameter. Note that the evolution of the polarization state from harmonic to harmonic is well resolved, as reported in the paper.

The second aspect lies in the way the complete polarization state of a given harmonic is measured: here the method relies on the analysis of the MFPAD resulting from photoionization of the NO molecule by the harmonics and, in particular for the determination of the  $s_3$  Stokes parameter, it requires the pre-determination of a reference  $F_{11}$  function. Although each harmonic has a given bandwidth (of a few hundreds of meV in the reported experiments) the reference  $F_{11}$  functions used in the work were measured using synchrotron radiation at the well-defined central energies of the relevant harmonics. Then an uncertainty could result from the use of this single calibration, for example if the  $F_{11}$  function would vary for photon energies sampling the harmonic bandwidth: such a situation might occur if the chosen NO inner-valence shell photoionization reaction would be affected by narrow resonances. This is not the case for the photon energy region addressed in this work: the direct photoionization continuum between 25 eV and 40 eV is affected by the shape resonance of the  $\text{NO}^+(\text{c})$  state, as shown in the paper, however the related variation of the MFPAD, including that of the  $F_{11}$  function, is smooth at the scale of the harmonic bandwidth. This is illustrated *e.g.* by the fact that the MFPADs measured for the overall harmonics are very similar to those measured at the central energies using synchrotron radiation. Finally this issue can also be checked experimentally by tuning the photon excitation energy around the central value of the synchrotron radiation. For the reported results, the estimated error on the determination of the polarization state of the harmonic due to the use of the central energies for  $F_{11}$  calibration can be neglected.

**Albert Stolor** remarked: In your polarimetry analysis, did you need to make use of the  $s_4$  Stokes parameter and, if so, how may this be interpreted?

**Danielle Dowek** replied: For partially polarized light, the  $s_4$  “fourth” Stokes parameter measures the degree of unpolarized light of the analyzed radiation. The reported molecular polarimetry method enables us to determine its value, since the  $s_1$ ,  $s_2$  and  $s_3$  three Stokes parameters, which determine the polarization ellipse of the polarized component of the light, are measured and  $s_4 = 1 - \sqrt{s_1^2 + s_2^2 + s_3^2}$ . The precision in the determination of  $s_4$  is derived from that of the measured  $s_1$ ,  $s_2$  and  $s_3$ .

For the study reported in this paper, where high order harmonics are generated by the interaction of elliptically polarized IR driving laser with  $\text{SF}_6$  molecules,

the obtained polarization degree presented ( $P = 1 - s_4$ ) shows some deviation from the maximum value of 1, which corresponds to non-zero values of  $s_4$ , in particular for the H15 and H17 harmonics, although with rather large error bars. If non-zero values of  $s_4$  for such harmonics would be confirmed in future measurements with higher statistics and precision, these could be attributed *e.g.*, to the role of narrow resonances which are thought to influence the HHG process in SF<sub>6</sub> for such harmonics<sup>1</sup> and might therefore induce a spectral dependence of the polarization state of the light within the harmonic bandwidth analyzed as a whole. Other possible causes of depolarization may occur, in particular depending on the way symmetry breaking is performed in the generation process to produce elliptically polarized harmonics. We have investigated two other cases where HHG is driven by two color counter rotating circularly polarized fields in Ar atoms, and HHG is driven by linearly polarized light in aligned N<sub>2</sub> molecules. We found indications of depolarization for the generated HHs that will be discussed in forthcoming work. The detailed polarization state of harmonic radiation is a rich observable in high harmonic spectroscopy, and its description, including the degree of depolarization, raises interesting questions to be addressed in the future.

- 1 A. Ferré, A. E. Boguslavskiy, M. Dagan, V. Blanchet, B. D. Bruner, F. Burgy, A. Camper, D. Descamps, B. Fabre, N. Fedorov, J. Gaudin, G. Geoffroy, J. Mikosch, S. Patchkovskii, S. Petit, T. Ruchon, H. Soifer, D. Staedter, I. Wilkinson, A. Stolow, N. Dudovich and Y. Mairesse, *Nat. Commun.*, 2015, **6**, 5952.

**Álvaro Jiménez-Galán** asked: Your method can characterize beautifully the ellipticity and polarization state of a harmonic in the train. However, would it work for broadband pulses, *i.e.*, attosecond pulses? As far as I understand, the problems that may arise are due to the use of mirrors that have different reflectivities for different frequencies. Also, your method relies on comparison with synchrotron measurements at specific photon energies. Could you clarify where are the limitations of this technique when dealing with attosecond pulses?

**Danielle Doweck** responded: For broadband pulses such as single attosecond pulses (SAP), there are different issues in the analysis of the polarization state of elliptically polarized light due to the quasi-continuum of photon energies involved on a several eV bandwidth.

The first one, as pointed to in your question, is the need to characterize the transmission function of optical elements which transport the XUV pulses from the HHG source to the center of the end-station, such as the focusing toroidal mirror, in terms of complex reflectivities for numerous photon energies. This requires some effort, although the smooth evolution of their amplitudes and phases also opens the possibility for some extrapolation between discrete energies to be studied.

The second aspect is the photoionization analysis required to determine MFPADs, using reference  $F_{11}$  functions that must be recorded in a rather extended energy range corresponding to the bandwidth of the SAP. In the NO inner-valence photoionization region, after selection based on the ion fragment energy in the overall kinetic energy correlation diagram (KECD), the quasi-continuous photoelectron spectrum will be reflecting photoionization through the NO<sup>+</sup>(c) state at different photon energies. The method presented can *a priori* be extended by

selecting successive  $\Delta E$  slices centred at different photoelectron energies in the spectrum and extracting the corresponding MFPADs. This extension of the method should provide the polarization state as a function of the photon energy in the SAP.

**Filippo Bencivenga** asked: I'm wondering if another pair of insertable gold-coated mirrors at a  $45^\circ$  angle of incidence (as the two ones shown in Fig. 3) could be placed downstream the toroidal mirror to route the XUV light into the spectrometer. This is in order to get information on the effects of the optics on the polarization of the XUV radiation at the sample.

**Danielle Doweck** replied: The pair of insertable gold-coated mirrors you refer to in Fig. 3, combined with a rotatable halfwave plate, constitutes an optical polarimeter based on Malus' law: as described in the paper it provides the  $s_1$  and  $s_2$  Stokes parameters, however it does not contain a dephazer element so it does not give access to the ellipticity of the light. So such a couple of mirrors might be used for the analysis of the light transmitted by the mirror, however only for the orientation of the polarization ellipse, characterized by  $s_1$  and  $s_2$ . Here instead, we are using the molecular polarimetry technique itself in order to characterize the transmission function of the mirror (amplitudes and phases), for each harmonic, using incoming linearly polarized light at different orientations (this is required for the further analysis of HHG elliptically polarized light).

**Russell Minns** asked: You mentioned in your presentation that the requirements of coincidence imaging mean that it requires a large number of laser shots to obtain good signal levels and reasonable statistics. I wonder if you could expand on this and outline how long each measurement took and what would be necessary to perform time-resolved experiments with this technique?

**Danielle Doweck** answered: It is indeed challenging to measure doubly differential observables such as molecular frame photoelectron angular distributions (MFPADs) induced by an attosecond pulse train (APT), relying on coincidence electron-ion 3D momentum spectroscopy, by employing a 1 kHz laser source. In the reported experiments, providing MFPADs for each harmonic in an APT composed of 4 to 5 relevant harmonics, an acquisition lasting about three hours was required. As illustrated in our paper, this achievement benefited from the efficient data analysis that we developed earlier, taking advantage of the general analytical form of the MFPAD. For future pump-probe experiments aimed at measuring time-resolved MFPADs, the potential applicability of this method will critically rely on the development of HHG sources at a higher repetition rate: this is in progress since HHG sources running at 10 to 100 kHz are being developed by different groups. In Saclay, we will use the FAB10 HHG source of the ATTOLAB facility which will be operational soon. Nevertheless, these experiments will remain quite demanding, in particular in terms of the stability of the XUV light source for each studied delay.

**Raluca Cireasa** asked: The method proposed for determining the polarisation of the harmonics through measurements of MFPAD is very powerful, but it is an experiment in itself that implies long acquisition time and complex data analysis.

Could it then be envisaged to set it up and use it just as an *in situ* molecular polarimeter? In this context, please, comment on the importance of the choice of the molecular systems to be photo-ionised by the harmonics.

**Danielle Dowek** responded: Using the molecular polarimetry method, as demonstrated in our paper, as a standard diagnostic of the complete polarization state (three Stokes parameters) of an XUV light source requires one to measure MFPADs: so it intrinsically calls for a coincidence experiment and related data analysis, even if a dedicated more compact instrument and standard analysis routines may be optimized. The choice of a prototype molecular system as a target for that purpose is influenced by some criteria, such as a large dissociative photoionization (DPI) cross-section, the identification of one DPI reaction characterized by (i) a significant asymmetry parameter in the ion fragment angular distribution (which also ensures validity of the axial recoil approximation), and (ii) a significant circular dichroism in the molecular frame, which acts as the dephasing element in the polarization analyzer. When the XUV light is composed of harmonics, it is interesting to favor molecular systems which minimize the overlap of DPI processes induced by different harmonics. The inner-valence shell of the NO molecule considered in the paper is quite favorable with respect to most of the criteria listed above.

**Raluca Cireasa** asked: The energy of the harmonics used for the experiments presented in the paper is 20–40 eV. Is it possible to extend this method to accurately determine the Stokes parameters, defining the polarisation of harmonics of much higher energy?

**Danielle Dowek** replied: At much higher photon energies, now becoming available in HHG XUV sources, the molecular polarimetry method can be applied relying on MFPADs measured for other photoionization (PI) reactions, such as inner-shell PI of simple molecules, *e.g.*, PI of the CO molecule at photon excitation energies above the C (1s) threshold ( $\sim 293$  eV). MFPADs for O (1s) PI of CO ( $I_p \approx 542.5$  eV) induced by elliptically polarized synchrotron radiation was reported as an example in Refs 1–2. The fact that the inner-shell PI of such molecular targets is followed by subsequent Auger decay results in dominant dissociative photoionization (DPI) processes. This is quite favorable for molecular polarimetry coincidence experiments based on MFPADs, since a single PI reaction dominates above each inner-shell ionization threshold, and most of the PI events are dissociative.

- 1 D. Dowek and R. R. Lucchese, in *Dynamical Processes in Atomic and Molecular Physics*, Bentham, Bussum, Netherlands, 2012, pp. 57–95.
2. K. Veyrinas, PhD Thesis, Université Paris-Sud 11, U. F. R. Scientifique d'Orsay, 2015.

**Oliver Schalk** opened a general discussion of the paper by Dave Townsend: In section 5.2, you write: “The lack of negative amplitude in any region of the  $\tau_1$  DAS also appears to suggest that the decay of the  $2\pi\pi^*$  state in both *N,N*-DMA and 3,5-DMA does not involve population transfer to either the  $S_1(\pi\pi^*)$  or  $S_2(3s/\pi\sigma^*)$  states ...”. In Fig. 4, you show that  $\tau_1$  is within the time resolution of the experiment and that you essentially fit a Gaussian to account for the amplitude of the

$2\pi\pi^*$  state. In this case, there is no way that you would see a delayed rise (or a negative amplitude) that would indicate passage from  $2\pi\pi^*$  to a lower lying state, even if you had 100% population transfer. Therefore, I do not see how your argument leads to the claim that you do not see any population transfer from  $2\pi\pi^*$  to a lower lying state and, hence, why the photoinduced dynamics in *N,N*-DMA and 3,5-DMA would be different to aniline in this respect.

**Dave Townsend** answered: If internal conversion between the  $2\pi\pi^*$  state and the lower-lying states were taking place, we believe this should be resolvable in the DAS analysis we have undertaken. This is illustrated, for example, in related TRPEI work on aniline using 238 nm excitation with a similar time resolution to our present measurements – as published recently by the Fielding group.<sup>1</sup> In this work, the aniline DAS analysis does indeed reveal signatures of ultrafast internal conversion between the  $2\pi\pi^*$  state and the singlet states that sit energetically below it. The absence of such features in our *N,N*-DMA and 3,5-DMA data therefore appears to suggest that in these cases, the  $2\pi\pi^*$  state decays (extremely rapidly) *via* another pathway. More critically, this assertion is also supported by the temporal evolution of the anisotropy parameters that we report (see Fig. 5), which indicates that the timescale to access the correct geometry for internal conversion from the  $2\pi\pi^*$  state to either the  $S_1(\pi\pi^*)$  state or the  $S_2(3s/\pi\sigma^*)$  state is too slow (> 250 fs) to effectively compete with this much faster alternative pathway.

1 O. M. Kirkby, M. Sala, G. Balerdi, R. de Nalda, L. Bañares, S. Guérin and H. H. Fielding, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16270.

**Michael Robb** asked: What is the chemical nature of the two  $\pi\pi^*$  states? One should be locally excited (LE), one should be CT (from the lone pair to the benzene), and one a LE benzene (lowest). In addition there is the role on the  $\text{NH}_2$  twist (for a theoretical discussion see Gómez *et al.*).<sup>1</sup>

1 I. Gómez, M. Reguero, M. Boggio-Pasqua and M. A. Robb, *J. Am. Chem. Soc.*, 2005, **127**, 7119-7129.

**Gareth Roberts** responded: Regarding the nature of the second  $^1\pi\pi^*$  state ( $2^1\pi\pi^*$ ) in aniline and whether it shares any electronic characteristics with the  $2^1\pi\pi^*$  state of 4-(dimethylamino)benzoinitrile (DMABN), I can confirm that this indeed appears to be the case. Prior excited state valence bonding analysis using the CASSCF method by Paterson, Stavros and co-workers<sup>1</sup> has indicated that in the vertical Franck–Condon (vFC) region, aniline's  $2^1\pi\pi^*$  state exhibits partial intramolecular charge-transfer (ICT) character, with ~0.2 of an electron transferred from the lone pair in the *n*-orbital of the  $\text{NH}_2$  group to the 4-position of the phenyl ring (see the valence bond structure in Fig. 1). This is akin to DMABN, but in the absence of any electron accepting/withdrawing group in the 4-position, it means that aniline's  $2^1\pi\pi^*$  surface possesses no stable adiabatic minimum, leading to its ultrafast ballistic decay from the vFC region, the latter of which is discussed in Dave Townsend's paper. However, there is no obvious evidence to date that any so-called twisted intramolecular charge-transfer (TICT) process plays a role in aniline. As previously reported by Michael Robb,<sup>2</sup> this may not be the case for DMABN and the addition of the electron withdrawing CN group *para*

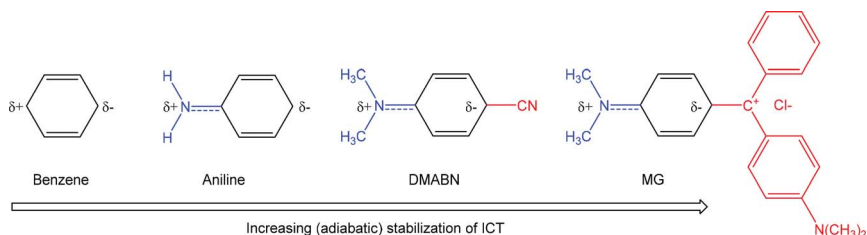


Fig. 2 Scheme showing the zwitterionic ICT valence bonding structure of benzene's  $2^1\pi\pi^*$  ( $1^1B_{1u}$ ) state in the vertical Franck–Condon region and how the character of this state can be stabilized/manipulated through the addition of electron 'donor' and 'acceptor' groups.

to the  $N(\text{CH}_3)_2$  moiety can lead to the stabilization of ICT in the  $2^1\pi\pi^*$  manifold through the twisting of the  $N(\text{CH}_3)_2$  group relative to the phenyl ring, causing DMABN's classic dual-colour fluorescence.<sup>3</sup> Yet further 'tuning' of this ICT can be seen in the more complex malachite green (MG) system, where a carbocation centre lying *para* to the  $N(\text{CH}_3)_2$  group leads to dramatic ICT stabilization, effectively deactivating the fluorescence and opening the rapid internal conversion to  $S_0$  through conical intersections.<sup>4,5</sup> This seemingly inherent ICT character of the  $2^1\pi\pi^*$  state does not have its origins in the aniline motif, but actually originates from the more fundamental benzene chromophore, whose  $2^1\pi\pi^*$  ( $1^1B_{1u}$ ) state exhibits the same zwitterionic ICT valence bonding structure in the vFC region (see Fig. 2).<sup>6</sup>

These comments/observations feedback more generally into the debate raised throughout this Faraday Discussion of 'predictive rules for photochemical dynamics'. While there may not be a unified set of 'silver bullet' rules on the horizon (as there isn't in organic synthesis), with appropriate theory and experiment, in certain cases trends can clearly be identified, understood and (to some degree) manipulated using ideas borrowed from organic chemistry (*i.e.* donors, acceptors, electron-withdrawing *versus* electron-donating *etc.*). Naturally, there are nuances to this simplified approach, but it can serve as an excellent heuristic starting point, as demonstrated here by a trend series which aims to manipulate an inherent characteristic of a fundamental UV chromophore.<sup>6</sup> This tuning of the ICT character in benzene's  $2^1\pi\pi^*$  ( $1^1B_{1u}$ ) manifold is summarized in Fig. 2, but is by no means an isolated example and other apt demonstrations of tuning organic photochemistry in this manner also exist in the recent literature (see, for example, Ref. 7 and 8).

- 1 G. M. Roberts, C. A. Williams, J. D. Young, S. Ullrich, M. J. Paterson and V. G. Stavros, *J. Am. Chem. Soc.*, 2012, **134**, 12578–12589.
- 2 I. Gómez, M. Reguero, M. Boggio-Pasqua and M. A. Robb, *J. Am. Chem. Soc.*, 2005, **127**, 7119–7129.
- 3 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3889–4031.
- 4 E. Riedle, M. Bradler, M. Wenninger, C. F. Sailer and I. Pugliesi, *Faraday Discuss.*, 2013, **163**, 139–158.
- 5 G. M. Roberts, *Faraday Discuss.*, 2013, **163**, 244–245.
- 6 S. Zilberg and Y. Haas, *J. Phys. Chem. A*, 2002, **106**, 1–11.
- 7 T. N. V. Karsili, A. M. Wenge, S. J. Harris, D. Murdock, J. N. Harvey, R. N. Dixon and M. N. R. Ashfold, *Chem. Sci.*, 2013, **4**, 2434–2446.

8 G. Bassolino, T. Sovdat, M. Liebel, C. Schnedermann, B. Odell, T. D. W. Claridge, P. Kukura and S. P. Fletcher, *J. Am. Chem. Soc.*, 2014, **136**, 2650–2658.

**Michael A. Robb** answered: In addition there is the role of the Rydberg states.

**Daniel Neumark** commented: One of the interesting aspects in the systems you are studying is the competition between dissociation and internal conversion from the  $2\pi\pi^*$  state. My understanding is that you think  $\text{CH}_3$  loss is competitive in *N,N*-DMA but that dissociation is not important in 3,5-DMA. Since your experiment is blind to this channel, what is the basis for this conclusion?

**Dave Townsend** answered: The basis for this interpretation stems from the fact that, in contrast to *N,N*-DMA, the  $S_2(3s/\pi\sigma^*)$  state of 3,5-DMA exhibits no signatures of internal conversion to the lower-lying  $S_1(\pi\pi^*)$  state (*i.e.* there is no negative amplitude in the DAS assigned to the decay of the  $S_2(3s/\pi\sigma^*)$  state). The  $S_2(3s/\pi\sigma^*)$  state of 3,5-DMA does, however, still exhibit an extremely short lifetime. Population within this state must therefore be rapidly decaying *via* another route. The  $S_2(3s/\pi\sigma^*)$  state is only very weakly bound along the N–H coordinate (see Fig. 6) and so direct dissociation to yield H atom photoproducts is the obvious alternative – especially since this pathway has been observed to occur in the related species aniline (see, for example, Ref. 1 and 2). We suggest that, in principle, following 240 nm excitation both the internal conversion and direct dissociation pathways are energetically possible in both *N,N*-DMA and 3,5-DMA and, in the former, both are actively taking place. In the latter case, however, dissociation kinetically out-competes internal conversion to an overwhelming extent due to methylation of the aromatic ring system slowing the non-adiabatic decay pathway (relative to the dissociation pathway) to a much greater extent than methylation of the amino group in *N,N*-DMA. The temporal evolution of the anisotropy parameters presented in Fig. 5 also appears to be consistent with this picture, providing a particularly illustrative example of the interplay between structure and dynamics, as well as the power of the angle resolved data afforded by the TRPEI approach to reveal these effects.

1 G. A. King, T. A. A. Oliver and M. N. R. Ashfold, *J. Chem. Phys.*, 2010, **132**, 214307.

2 G. M. Roberts, C. A. Williams, J. D. Young, S. Ullrich, M. J. Paterson and V. G. Stavros, *J. Am. Chem. Soc.*, 2012, **134**, 12578–12589.

**Andrew Orr-Ewing** asked: Are there reported quantum yields for photofragments from aniline and the methylated anilines you have studied with which you might compare your deductions about competition between dissociative and non-dissociative pathways? Might a transient absorption spectroscopy measurement of the efficiency of parent recovery following UV excitation of the molecules dissolved in a weakly interacting solvent be instructive because it can quantify fragmentation pathway yields?

**Dave Townsend** replied: As highlighted in the response to Daniel Neumark's question, experimental schemes interrogating excited state dynamics using energy- and angle-resolved measurements of time-resolved photoreactant ionization provide a particularly powerful approach for revealing very subtle details of specific non-adiabatic pathways that may (or may not) operate within a given



molecular system. One inherent problem, however, is that in instances where various competing pathways are present, techniques employing photoreactant ionization are not able to reliably differentiate which pathway is dominant. This issue with determining branching fractions stems from changes in relative detection sensitivity as the population evolves non-adiabatically over multiple potential energy surfaces and is an effect that is a convolution of several factors. These include changes in relative (electronic) photoionization cross-sections, variation in associated Franck–Condon factors for ionization (a particular problem for seeing any ground state recovery), excited state alignment effects and also the relative excited state lifetimes. Although some of these can be accounted for fairly easily, the issue of the electronic photoionization cross-section (which may vary between different excited states by an order of magnitude or more) is, at present, a notoriously challenging problem to address either experimentally or computationally. We have previously presented some speculative thoughts on how one may begin to address this issue,<sup>1–2</sup> although this only (potentially) serves as a rough guide for qualitative discussion. Any complementary measurement that may be able to shed light on this issue (such as the one Andrew Orr-Ewing suggests) would therefore be extremely valuable. This is not only important in terms of direct relevance to the specific problem under consideration here, but also more generally in providing data that may ultimately be used, in conjunction with that from ionization-based studies, to provide useful benchmarks for theoretical developments related to the accurate determination of excited state photoionization cross-sections.

1 J. O. Thompson, L. Saalbach, S. W. Crane, M. J. Paterson and D. Townsend, *J. Chem. Phys.*, 2015, **142**, 114309.

2 M. M. Zawadzki, J. O. F. Thompson, E. A. Burgess, M. J. Paterson and D. Townsend, *Phys. Chem. Chem. Phys.*, 2015, **17**, 26659.

**Oliver Schalk** remarked: In Fig. 5 (left panels), you show the time-dependent behavior of the  $\beta$ -parameters. It looks like there would be a change on a 1.5 ps timescale which would agree with the timescale you assign to IVR. Why would the  $\beta$ -parameters change if IVR is present?

**Dave Townsend** responded: The timescales for the evolution of the  $\beta$ -parameters in Fig. 5 are not really that well-matched to the timescales assigned as IVR in Fig. 4. In principle, IVR could lead to changes in the  $\beta$ -parameters but, without this process then inducing additional associated changes in the electronic state character through induced electronic coupling, it seems unlikely this would lead to the increase in the  $\beta$ -parameters that is observed. We therefore assume that Fig 5 is predominantly reflecting a change in the electronic character of the  $S_1(\pi\pi^*)$  state as the molecule assumes the required geometry to couple efficiently to other low-lying states and (at least in principle) facilitate non-adiabatic population transfer – although as discussed in the paper, other energetically open pathways may (and in some cases do) effectively out-compete this mechanism if they occur on a faster timescale.

**Jan Verlet** remarked: In general,  $\beta$ -parameters derived from reconstructed images in time-resolved photoelectron imaging are convoluted. In the time domain, changes in  $\beta_2$  often only probe changes in population of two states with

differing photoelectron angular distributions (PADs).<sup>1</sup> In the energy domain, photoelectron peaks tend to be broad and overlapping so that the PADs are a convolution of the detachment from these overlapping bands. Therefore, although the global fitting of the reconstructed images provides insight into the dynamics through the decay-associated spectra, it does not provide reliable information about PADs. To overcome this limitation, we have shown that the global fitting can be performed directly on the raw time-resolved photoelectron images. This yields decay-associated images. Reconstruction of the decay-associated image provides identical decay-associated spectra, but also provides the PAD associated with a decay-associated spectrum.

1 J. Lecointre, G. M. Roberts, D. A. Horke and J. R. R. Verlet, *J. Phys. Chem. A*, 2010, **114**, 11216.

**Dave Townsend** replied: This is a very interesting approach. Although we do not currently employ such a scheme in our present data evaluation, it would certainly be an interesting avenue for future investigation – especially in instances where photoelectron bands strongly overlap, as Jan Verlet highlights. In the case of the *N,N*-DMA and 3,5-DMA work presented here, the photoelectron signals in the low kinetic energy region originating from ionization of the  $S_1(\pi\pi^*)$  state are, however, reasonably well separated energetically from those due to the other states participating in the overall dynamics. This is important to stress, as it is the (consistent) temporal evolution of the anisotropy parameters within this region that provides strong support to our conclusions about the relative timescales of internal conversion processes and the impact this then has on the overall multipathway dynamics.

**Russell Minns** asked: Picking up on R. J. Dwayne Miller's earlier comments, having performed a systematic study of photochemical dynamics in similar systems, do you find any generalities in their photochemistry and do you think such generalities are likely in broader chemical systems?

**Dave Townsend** replied: Using site-selective methylation to systematically alter a basic molecular motif such as aniline can reveal a great deal of photochemical insight relating to specific relaxation pathways. Methylation (as opposed to substitution with strongly electron-withdrawing or -donating groups) tends not to alter the relative electronic state energies too significantly, although it can profoundly alter dynamical timescales. As such, it is an approach that we would advocate, where possible, as a route to gaining more mechanistic information. In particular, it is the dynamical changes that such an approach may induce that often serve to reveal additional information about the starting motif itself. This is certainly the case in aniline, where the dynamics are slightly too fast (given our present experimental time resolution) to pull out all of the information we would like to access. This is especially true in regard to the photoelectron angular distributions. By studying *N,N*-DMA and 3,5-DMA, we are able to slow the dynamics down sufficiently to learn a great deal of information about not only these specific systems, but also about aniline itself. There are some clear similarities between the dynamics operating in these systems, but also some important differences. Critically, however, some of these observed differences are not

what might be predicted prior to conducting the experiments – a good example of this would be the apparent lack of significant change in the decay lifetimes of the  $2\pi\pi^*$  state within *N,N*-DMA and 3,5-DMA when compared to aniline, even though the out-of-plane motion of the amino group and ring distortions have been implicated theoretically as key coordinates in potentially facilitating relevant non-adiabatic decay pathways in this system.<sup>1–2</sup> More generally, there has been considerable discourse at this Faraday Discussion regarding the desire to ultimately develop generalized predictive rules for excited state photochemical dynamics. Although others may disagree, my feeling is that as a community we are still a very long way from achieving this goal. The excited states of polyatomic molecules are extraordinarily complex and, in my opinion, each is essentially unique in terms of dynamical subtleties. New experimental and theoretical studies on seemingly related species consistently yield unexpected and surprising results, clearly reflecting the present lack of predictive insight. This, of course, should serve as a strong impetus to continue pushing at the boundaries of our understanding in the hope that a clearer picture will materialize, but it seems unlikely to me that this will be forthcoming in the near future. A major part of the problem here is that, in order for rules to be useful, they have to predict a measurable photochemical outcome – *i.e.* product branching ratios – and correlate this with specific key features of any given starting species. Although there are a wide variety of experimental strategies (with different associated observables) available to study the excited state dynamics operating in molecular systems, each only reveals a small piece of the overall “photochemical jigsaw”, making the task of developing such rules rather incoherent and therefore extremely challenging. Although a somewhat obvious statement, it would therefore be highly desirable to develop a universal approach that is able to fully map the entire reaction coordinate connecting photoreactants to all photoproducts in a manner that is fully quantitative and yet also sufficiently differential to reliably extract such correlations for a wide range of systems. This still represents one of the major challenges to this community.

1 G. M. Roberts, C. A. Williams, J. D. Young, S. Ullrich, M. J. Paterson and V. G. Stavros, *J. Am. Chem. Soc.*, 2012, **134**, 12578–12589.

2 M. Sala, O. M. Kirkby, S. Guérin and H. H. Fielding, *Phys. Chem. Chem. Phys.*, 2014, **16**, 3122.

**Russell Minns** asked: The advantage the organic chemists have is that they are often dealing with rules about systems in equilibrium. In photochemistry this is not the case, excitation leads to non-equilibrium systems with very different electronic structure and levels of vibrational excitation dependent on the particularly wavelength used. It seems that making generalities in these situations would be particularly challenging.

**Dave Townsend** responded: I would strongly agree with this statement. Even very subtle changes in molecular composition (for example, simple deuteration of H atom sites) can have a profound effect on the dynamics exhibited by a specific system at the same excitation wavelength. In some cases this may be in a manner that can be predicted based on prior knowledge of dynamics operating in the system before any changes are introduced – but even then, perhaps not always. More generally, and as already outlined in my previous answer, it does not

therefore seem that at present we are close to a more general set of useful predictive rules for excited state photochemistry. Being slightly more tongue-in-cheek, I might also argue that in some respects the analogy that is often made with rules in organic chemistry is something of a distraction and, as a community, we perhaps shouldn't start to obsess over this too much – my own experience of organic chemistry was always that “rules” get introduced in the first couple of lectures and the rest of the course was then devoted studying all of the “exceptions” – and as Russell Minns points out, this is for systems in equilibrium.

**R. J. Dwayne Miller** commented: I agree with Dave Townsend regarding whether or not general guidelines/rules might be found for photochemistry using the aniline derivatives as a case in point. The specific details and the exact timescales for non-radiative relaxation do depend exquisitely on the specific molecular structure. This implies that we are dealing with molecular “snow flakes” in terms of trying to find common features. However, if one focuses on the nuclear motions that are involved in coupling the electronic surfaces, there are great similarities even if the dynamics are very different. The case in point involves motion along the N–C coordinate for the methylated aniline systems. There is strong coupling along this coordinate as a common feature even though the magnitudes vary. The prospect for finding common, dominant modes, in the reaction dynamics is best exemplified with simple photoisomerization. We saw in Albert Stolow's paper (DOI: 10.1039/C6FD00117C) that the isomerization of ethylene involves a bond softening of the C=C mode, followed by torsional motions along this axis, and pyridinalization involving out-of-plane motions. These are clearly localized modes as we are using a very small system without any prospect of alternative pathways or spatial delocalization of the reaction forces driving isomerization. How curious then is the photoisomerization of rhodopsin and bacteriorhodopsin? We just showed<sup>1</sup> that the photoisomerization of rhodopsin involves the localized bond softening, torsions, and out-of-plane motions at the C<sub>11</sub>–C<sub>12</sub> location, effectively the exact same localized motions as in ethylene. The isomerization occurs within 30 fs (difficult to assign a precise number as we are dealing with timescales of half periods of the key modes, <50 fs) such that even the dynamics are not so different than ethylene. The primary vision in relation to rhodopsin involves a huge biological molecule where there are innumerable ways to spatially delocalize or distribute the forces. Yet, there is enormous reduction in dimensionality during motion through the conical intersection where the strongly anharmonic potential leads to localized motions of primarily 3 key modes - the very same modes as in ethylene as the targeted location for isomerization. Similarly bacteriorhodopsin (bR) undergoes photoisomerization but an order of magnitude slower. The process is not *cis* to *trans* at the C<sub>11</sub>–C<sub>12</sub> position but rather *trans* to *cis* at the C<sub>13</sub>=C<sub>14</sub> position. The same highly localized motions are involved in the same class of reaction. Nature found two different solutions for the same class of reaction in which the potential is clearly different in the bR and rhodopsin case. The details regarding dynamics vary by an order of magnitude but the key reaction modes do not. From a theory standpoint, these issues are understood on a case-by-case basis but the focus is on differences not on general relationships.

This point expands upon my comment that there may be a means to cast out the key modes to provide a dynamic reaction mode basis for understanding

chemistry. The details are critical to a detailed understanding of the photo-physics. However, there are clearly localized motions involving the most strongly coupled modes to the reaction coordinate and these likely are general for a given reaction type. This concept would scale to large systems as can be nicely traced in the family of rhodopsin proteins.

1 P. J. M. Johnson *et al.*, *Nature Chem.*, 2015, 7, 980–986.

**Hans Jakob Wörner** presented a comment: I presented the results of our recent work on time-resolved X-ray absorption spectroscopy with a water-window high-harmonic source.<sup>1</sup> Using high-harmonic generation from a 1.8  $\mu\text{m}$  driver, we have generated soft-X-ray spectra covering the range of 100 to 350 eV. We have used this source to observe the photodissociation dynamics of  $\text{CF}_4^+$  to  $\text{CF}_3^+ + \text{F}$ , induced by strong-field ionization from neutral  $\text{CF}_4$ , by monitoring transient absorption at the K-edge of carbon. The single resonance that dominates the carbon K-edge absorption spectrum of  $\text{CF}_4$  was found to split into multiple lines as a consequence of symmetry lowering during the dissociation. We have performed similar measurements at the L-edges of sulfur, where we have studied the photodissociation of  $\text{SF}_6^+$  to  $\text{SF}_5^+$  and F.

1 Y. Pertot, C. Schmidt, M. Matthews, A. Chauvet, M. Huppert, V. Svoboda, A. von Conta, A. Tehlar, D. Baykusheva, J.-P. Wolf and H. J. Wörner, to be published, 2016.

**Kiyoshi Ueda** answered: A very impressive work! As we discussed in person, you should be able to map the delay time to the distances between F and the rest, referring to kinetic energy release. Also you should be able to extract the vibrational excitation of the fragment  $\text{CF}_3^+$  (less for  $\text{SF}_5^+$ ) since off-plane vibrational motion should be highly excited *via* recoil between F and C.

**Jon Marangos** commented: How many cycles are there in the HHG drive pulse? If it is multicycle then it would be a remarkable combination of parameters to lead to an isolated pulse generation (*e.g.* through ionisation gating). Can the spectrum alone (without careful characterisation of the spectrometer resolution) be enough to confirm an IAP?

**Hans Jakob Wörner** replied: The number of cycles was 5–6 as in Ref. 1, but we worked in free-focusing conditions similar to Teichmann *et al.*<sup>2</sup> Chen *et al.*<sup>1</sup> performed a linear auto-correlation measurement and concluded from this that an isolated attosecond pulse had been generated. Whereas this conclusion cannot be made directly without any information about the spectral phase of the pulse, the linear auto-correlation measurement establishes the generation of a continuous spectrum. The existence of “phase-matching gating” invoked by Chen *et al.*<sup>1</sup> has been confirmed theoretically by Teichmann *et al.*,<sup>2</sup> where it was additionally demonstrated experimentally. Teichmann *et al.*<sup>2</sup> observed continuous spectra for all values of the CEP, instead of the harmonic structure expected for a CEP close to  $\pi$  when two identical attosecond pulses should be generated. They attributed this effect to phase-matching gating. Hence, there is both experimental and theoretical evidence for the existence of phase-matching gating. Nevertheless, it is clear that a measurement sensitive to the spectral phase must be performed to definitely establish the generation of an isolated pulse. Such

experiments relying on the attosecond streak camera have been done in our laboratory.

1 M. C. Chen *et al.*, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 8329.

2 S. Teichmann *et al.*, *Nat. Comm.*, 2016, **7**, 11493.

**Allan Johnson** commented: I think the supercontinuum above 200 eV in your carbon K-edge spanning HHG spectrum may be due to resolution limits. The small amount of carbon contamination should show a clear  $\pi^*$  signature before the main edge if the resolution is sufficient to resolve harmonics with spacing around 1.4 eV.

**Hans Jakob Wörner** replied: We can exclude this possibility. We have experimentally determined the resolving power  $E/\Delta E$  of our spectrometer to be 308, *i.e.* a resolution of better than 1 eV at 300 eV. This would be sufficient to resolve the harmonic structure beyond 300 eV.

**Michael Minitti** commented: Knowing how hard it is to perform absorption measurements in the soft X-ray regime, and how critical it is to know your pulse intensity before and after it interacts with the sample. How do you normalize your intensities in the XUV regime?

**Hans Jakob Wörner** replied: Our soft-X-ray source is based on high-harmonic generation of a 1.8-micron pulse in neon. It appears to have a few advantageous properties that simplify the task of recording absorption spectra. These are (i) a high pulse-to-pulse stability, (ii) a good long-term stability over a few hours and (iii) a high photon flux that enables us to record spectra with  $S/N > 100$  in 5 s integration time and detailed pump-probe scans in 45 min. The presented data were obtained by dividing the transmitted spectra at each delay by the average of the spectra without absorption before and after the measurement.