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The three pillars of photo-initiated quantum molecular dynamics

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Studies of the interaction of light with matter, based on spectroscopy and diffraction, yielded a microscopic view of nature. The detailed structure of molecules and solids emerged from this effort and led to many of the advances of the 20th century, with the 'structure-function' paradigm being perhaps paramount. This static view of Nature is a necessary but insufficient advance and, in the 21st century, we will need to develop microscopic yet dynamical views of Nature. We consider here issues in Photo-initiated Quantum Molecular Dynamics raised by Faraday Discussions 163, in the context of three main categories or 'pillars' of light-matter interaction: energy/time, phase/ coherence, intensity.

1 Introduction

The subject of Faraday Discussion 163 is 'Photo-initiated Quantum Molecular Dynamics'. The topics under discussion range very broadly, from high resolution spectroscopy,^{1,2} to ultrafast dynamics³⁻⁹ and coherence^{10,11} quantum control¹²⁻¹⁵ and strong field attosecond physics.¹⁶⁻¹⁸ Yet underlying this seemingly disparate collection of topics is the unifying theme of light-matter interactions. Why is this an important subject? One hundred years ago, it was studies of the interaction of light with matter which led scientists to a microscopic view of nature. It was spectroscopy and diffraction, combined with quantum mechanics, which led us to understand the detailed structure of matter-the shapes of molecules, biomolecules and solids. It is hard to overstate how significant a step this was. One might fairly call it the 'great leap forward' of the 20th century. From the point of view of molecular sciences, this led to the central paradigm of 'structurefunction relationships', the basis of much of our understanding of chemistry, biochemistry and material science. The canonical example is the structure of double helix DNA, the shape of which clearly determines its function as the template for the storage and transfer of genetic information. As powerful and successful as 'structure-function relations' may be, they remain a necessary but insufficient condition for our understanding of the world around and within us.

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Simply put, this is because Nature is not static. There are dynamical, often fast competing processes which determine the outcomes of many natural phenomena and these cannot be discerned from a static, structural perspective alone.

It is perhaps useful to consider an example. A compelling case is the process of Vision which involves the light-sensitive *trans*-membrane protein rhodopsin, comprised of an opsin protein 'shell' surrounding a photoactive chromophore. The chromophore is the molecular sub-unit retinal which contains a polyene chain that acts, in essence, as the 'light collector'. The first step in Vision, following absorption of a visible photon, is the cis-trans isomerisation of 11-cis retinal about the C11-12 double bond and occurs on the 10⁻¹³ s time scale.¹⁹ Given that the overall visual response is much slower (10^{-2} s) , one could reasonably ask whether this ultrafast time scale is a curiosity or, in fact, is essential for the process of Vision. I argue that it is essential and that if this first step was much slower, Vision would be impossible. The rapid cis-trans isomerisation stresses and 'deforms' the trans-membrane opsin protein, permitting the now 're-shaped' cytoplasmic side of the protein to catalyze many hundreds of transducin proteins to an activated state.²⁰ This leads to a closing of cationic trans-membrane transport channels, hyperpolarizing the cell membrane and affecting a nearby synaptic terminal, thereby converting visual information to an electrical signal. However, the retinal chromophore is surrounded both by protein and by water-a highly dissipative environment. Dissipative processes are typically fast (ps time scale) and eventually lead to the conversion of photon energy to a simple, local temperature increase. In such a case, the energy associated with photon absorption would not lead to 're-shaping' of the protein: there would be no 'signal transduction'. Given that these fast dissipative mechanisms do exist, Nature was left with only one choice: the signal transduction pathway must be much faster than dissipation in order to compete. The first steps in Vision must be ultrafast, otherwise it would be impossible. We can see that a purely static 'structure-function' perspective would not lead to any understanding of the ultrafast functioning of the rhodopsin protein. In this example, and in many others, dynamics is central to the function. I suggest that



Fig. 1 The three pillars of photo-initiated quantum molecular dynamics. The light-matter interactions which underlie much of this subject can be broadly categorized into these three themes.

in the 21st century we will need to develop 'dynamics-function' relationships to augment and amplify our 'structure-function' view of Nature.

In Faraday 163, we are concerned with light-matter interactions. In the following, I will make use of the narrative device illustrated in Fig. 1. I will try to broadly (but perhaps somewhat incorrectly) classify light-matter interactions into three categories or 'pillars': (1) energy/time; (2) phase/coherence; (3) intensity. Modern optics allows for the creation of coherent pulses of light which are only a few cycles in duration. This allows for probing of the fastest events in chemistry. The other side of this coin is the implicit control over optical phase that comes with short pulses. The transfer of this phase control to molecular systems underlies all control scenarios. Finally, modern optics allows for the creation of very precise but high intensity laser pulses which allow the application of strong electric fields, opening up new regimes of light-matter interaction. Hopefully, the device suggested by Fig. 1 will allow us to consider these broad themes which underlie the subject of Faraday Discussions 163.

2 Energy/time

The first pillar of 'photo-initiated quantum molecular dynamics' is that of energy and/or time. Our studies of molecular dynamics benefit enormously from understanding light-matter interactions. Spectroscopy is the study of such interactions from a frequency domain point of view. This subject is so well established and so broadly studied that it needs no further discussion here. Conveniently, modern optical techniques allow for the creation of optical pulses which are on the time scales of dynamical processes within molecules. This has led to a time domain approach to spectroscopy and dynamics. In the following, I will try to connect time and frequency domain forms of spectroscopy, showing their correspondence. Pump-probe spectroscopy involves by definition the use of at least two photons. As such, it is a double resonance technique and, therefore, can be compared and contrasted with frequency domain double resonance spectroscopies.

Time domain techniques make use of spectrally broad, coherent laser pulses, as illustrated in Fig. 2. A laser pulse is described by the set of frequencies which comprise it. For example, two colours ω_j and ω_k within the pulse may have amplitudes A_j and A_k and a fixed phase difference $\phi_k - \phi_j$. A spectrometer measures only the intensities $|A_j|^2$ and $|A_k|^2$, therefore revealing nothing of these



Fig. 2 Ultrashort laser pulses are understood in terms of the Fourier components which comprise them. The amplitudes $A(\omega)$ and phases $\Phi(\omega)$ determine the temporal shape of the pulse. Active control over these functions is now nearly routine.



Fig. 3 Time-resolved experiments involve preparing a non-stationary state (a wavepacket) with an ultrashort pump pulse. Its field-free dynamics is probed by a time-delayed probe pulse which projects it onto a suitable final state. The signal is proportional to the population in the final state at the end of the pump-probe sequence. The choice of final state is critically important.

relative phases. The Fourier synthesis of all frequencies ω having amplitudes $A(\omega)$ and phases $\Phi(\omega)$ determines the temporal pulse shape. For example, when $\Phi(\omega)$ is a constant, the pulse assumes its shortest duration, the so-called transform-limit pulse. The transfer of the coherent properties of light to material systems, *via* dipole interactions, is what underlies all pump-probe and quantum control experiments.

From a time domain perspective, illustrated in Fig. 3, a short pump pulse prepares a non-stationary excited state |ex>, generally called a wavepacket, which evolves as a function of time. The wavepacket dynamics are projected onto a final state |f> as a function of time *via* a suitable probe pulse. The measured signal is proportional to the population in the final state at the end of the two-pulse sequence. The utility of time domain approaches to spectroscopy and dynamics is that the superposition of exact molecular eigenstates—which in general are extremely complicated—constructs, for a short period of time, a zeroth order state



Fig. 4 A frequency domain picture of the preparation and detection of wavepacket dynamics.

which is a solution to a simpler Hamiltonian. One example would be the coherent superposition of exact non-Born-Oppeneheimer molecular eigenstates which, for a short period of time, can behave like a Born-Oppenehimer (BO) state. The latter will, of course, evolve due to the non-adiabatic coupling terms which were neglected in the BO approximation. This leads to the coupled evolution of electronic and vibrational character within the excited molecule, generally termed non-adiabatic processes. It is the time evolution of these zeroth order states which yields information about the coupling terms of interest. Importantly, this perspective applies even at 'chemical' levels of excitation, when bonds are being broken/formed and true continuum channels are open, and no high resolution spectrum exists.

In Fig. 4, we present a frequency domain perspective on such wavepacket measurements. The wavepacket is prepared by an ultrashort pump pulse (black) at time t = 0. The E_n are the excited state eigenenergies. (N.B. This discussion of wavepacket dynamics can be readily extended to include continuum states). The wavepacket $\chi(\Delta t)$, given by eqn (1), subsequently evolves in a field-free manner, governed by relative energy phase factors in the superposition.

$$|\chi(\Delta t)\rangle = \sum_{n} \tilde{a}_{n} |\Psi_{n}\rangle e^{-iE_{n}\Delta t/\hbar}$$
 where $|\Psi_{n}\rangle \in |\alpha\rangle, |\beta\rangle....$ (1)

The a_n complex coefficients determine both the amplitudes and initial phases of the exact (non-BO) molecular eigenstates $|\Psi_n\rangle$ which were prepared by the pump laser $\mathbf{E}_{\text{PUMP}}(\omega_1, t = 0)$. The probe laser $\mathbf{E}_{\text{PROBE}}(\omega_2, t = \Delta t)$, shown in blue, projects the wavepacket onto a specific final state $|\Psi_i\rangle$ at time delay Δt . The time dependence of the differential signal, $S_i(\Delta t)$, the projection onto a *single* final state $|\Psi_i\rangle$, is:

$$S_{i}(\Delta t) = \left| \left\langle \Psi_{i} \right| \vec{\mu} \left(\vec{r} \right) \cdot \vec{E}_{\text{PROBE}} \left| \chi(\Delta t) \right\rangle \right|^{2} = \left| \sum_{n} \tilde{b}_{n} e^{-iE_{n}\Delta t/\hbar} \right|^{2}$$
(2)

where
$$\tilde{b}_n = \tilde{a}_n \langle \Psi_i | \vec{\mu}(\vec{r}) \cdot \vec{E}_{\text{PROBE}}(\omega_2, \Delta t) | \Psi_n \rangle$$

$$S_i(\Delta t) = \sum_n \sum_{m \le n} \left| \tilde{b}_n \right| \left| \tilde{b}_m \right| \cos\{ (E_n - E_m) \Delta t / \hbar + \Phi_{nm} \}$$

The complex coefficients b_n contain both the a_n from eqn (1) and the probe transition dipole moments to the final state $|\Psi_i\rangle$. The differential signal $S_i(\Delta t)$ is the coherent sum over all two-photon transition amplitudes consistent with the pump and probe laser bandwidths and contains interferences between all degenerate two-photon transitions. Therefore, the signal as a function of Δt contains modulations at frequencies $(E_n - E_m)$, the set of excited state level spacings. The wavepacket signal is, in essence, a multi-level quantum beat. The Fourier power spectrum of this signal yields frequencies, related to the set of level spacings in the problem, and their amplitudes (*i.e.* modulation depths), related to the respective overlaps of the wavepacket states with the

specific, chosen final state $|\Psi_i\rangle$. Importantly, different final states $|\Psi_i\rangle$ will generally have differing overlaps with the wavepacket, leading to differing amplitudes in the power spectrum. Choosing an appropriate final state is therefore critical. Finally, in order to avoid losing information due to averaging over final states, differential detection techniques such as dispersed fluorescence or photoelectron spectroscopy may be important.

Excited state dynamics in polyatomic systems generally do not obey the BO approximation. This is because excited state potential energy surfaces of polyatomics intersect, leading to ultrafast radiationless processes such as internal conversion. These electronic degeneracies are termed conical intersections, 3N-8 dimensional hypersurfaces of intersection between potential energy surfaces.²¹ The remaining two dimensions locally lift the electronic degeneracy in linear fashion and therefore have the topography of a double cone, hence the name. Conical intersections play the same role in excited state dynamics as do transition states in ground state dynamics. As such, we might be able to gain some insights into vibrational dynamics at conical intersections by making analogies to vibrational motions through transition states. J. C. Polanyi developed simple rules to help guide our thinking about vibrational motions at transition states for A + BC collisions.²² In particular, the location of the barrier (*i.e.* 'early', 'middle' or 'late') with respect to the col (saddle point) of the potential significantly governs which types of vibrational motions lead to chemical reaction. The effects of the particle masses are also important, determining the skew angle of the potential in a mass-weighted coordinate system. Will there be analogous 'Polanyi rules' for dynamics at conical intersections? The higher dimensionality of the problem renders this non-obvious. An experimentalist's initial approach to this problem might be via phenomenology. Much was learned about 'structure-function' relationships through the use of systematic chemical substitution. Can systematic variation of molecular properties reveal dynamical information about vibrational motions at conical intersections?

One of the most innocuous of chemical substitutions is the replacement of a hydrogen atom by a methyl group. By systematically moving a methyl



Fig. 5 Excited state photophysics of the unsaturated aldehyde acrolien (propenal). Ultrafast non-adiabatic dynamics involve conical intersections between S_2 and S_1 (CoIn 1) and between S_1 and S_0 (CoIn 2).



Fig. 6 The competition between intersystem crossing (ISC) and internal conversion to the S_0 ground state depends on vibrational dynamics at the S_1 – S_0 conical intersection. The speed of twisting (torsion) of the terminal methylene group is related to diabatic *versus* adiabatic passage through the conical intersection.

substituent to different locations on the molecular frame, one can alter the relative inertia of certain vibrations with respect to others, while keeping the overall density of states roughly constant. We have been trying to use this approach to discern vibrational dynamics at conical intersections in unsaturated hydrocarbons.²³⁻²⁶ An example is the Norrish Type 1 photoreaction of the unsaturated aldehydes and ketones, the simplest of which is acrolein (propenal). The excited state photo-initiated dynamics of acrolein is depicted in Fig. 5. The UV (200nm) absorbing state is the $S_2(\pi\pi^*)$ state, analogous that in ethylene. The 'bright' S₂ state has a conical intersection with the lower lying but 'dark' S₁($n\pi^*$) state. The excited state lifetime of the S2 state is extremely short and, as in ethylene, is determined by passage through the S_2-S_1 conical intersection via vibrational motions involving large amplitude torsion of the terminal methylene group. Motion on the steep $S_1(n\pi^*)$ potential leads to a second conical intersection, in this case between the S1 state and S0 ground state. Diabatic versus adiabatic passage though this second conical intersection governs the fate of the excited molecule. Diabatic passage preserves the $S_1(n\pi^*)$ electronic character, leading to triplet formation and subsequent α -cleavage photochemistry (HCO and C₂H₃ radical products), typical of aldehydes and ketones. By contrast, adiabatic passage leads to formation of the hot ground state molecule and subsequent singlet state photochemistry and molecular products (e.g. CO, C₂H₄, H_2). We have found that the location of a single methyl substituent greatly affects the excited state lifetime and singlet-triple branching.23 Locating the methyl group on the central carbon atom (i.e. methacrolein) or carbonyl group carbon atom (i.e. methyl vinyl ketone) has only a small effect. Surprisingly, locating the methyl group on the ethylenic end (i.e. crotonaldehyde) simultaneously reduces the excited state lifetime and, amazingly, completely turns off the triplet photochemistry channel. These results cannot be rationalized in terms of slight energetic shifts due to methylation, changes in conical intersection topography or density of states arguments. An explanation for this remarkable result is depicted in Fig. 6. The conical intersection between S1 and S₀ is achieved via large amplitude torsional motions of the terminal methylene group, originating at S_2 - S_1 conical intersection. When this terminal methylene

group contains only hydrogen atoms (acrolein), the 'torsional velocity' is high. This rapid motion leads to a more diabatic passage through the S_1 - S_0 conical intersection. Remaining on the $S_1(n\pi^*)$ potential, spin-orbit coupling leads to triplet state formation and subsequent α -cleavage photochemistry (typical of aldehydes and ketones). In contrast, replacing an ethylenic hydrogen atom with a methyl group adds significant inertia (mass 15 *vs.* mass 1) to this torsional motion. This slows down the 'torsional velocity' and leads to a more adiabatic passage through the S_1 - S_0 conical intersection. This simultaneously reduces the excited state lifetime and turns off the triplet photochemistry channel. These types of studies give some first glimpses of the important role of vibrational motions at conical intersections. From a control point of view, it is remarkable that the location of a methyl group has such a dramatic effect on the excited state dynamics and photochemical branching ratios, a consequence not predictable from a 'structure-function' perspective alone.

As reflected by the topics covered in Faraday 163, an excited state photodynamical process of current interest is photodamage to DNA.^{3,7,27} The photostability (*i.e.* protection against damage) of biomolecules such as DNA is generally determined by a competition between ultrafast excited state electronic relaxation processes. In DNA, UV excitation can lead to singlet excited state photochemistry and potential mutagenic damage. Although intracellular DNA repair mechanisms exist, these are slow and energetically inefficient. Therefore, molecular features that led to any intrinsic photostability will have had an evolutionary advantage. What determines this intrinsic photostability? Generally, excited states of molecules are much more reactive than are ground states. Therefore, electronically excited states are 'dangerous' for biomolecules because their rapid photochemistry can alter their structure and ability to function. Therefore, ultrafast excited state mechanisms which can 'quench' or 'relax' the electronically excited state, thereby competing effectively with excited state chemistry, are important photostabilization mechanisms. Generally, such 'electronic relaxation' processes are



Fig. 7 The UV $\pi\pi^*$ state of the DNA nucleobase adenine is protected against photodamage by ultrafast internal conversion processes involving several excited states. Internal conversion to the ground state converts 'dangerous' electronic excitations to 'less dangerous' vibrational excitations which may then be rapidly cooled in aqueous environments.

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achieved *via* ultrafast internal conversion to the ground state, typically involving conical intersections. This process converts 'dangerous' electronic energy into 'less dangerous' vibrational energy, since the latter will be cooled efficiently in aqueous solution. The UV chromophores in DNA are the aromatic nucleobases themselves and it is their photophysics which determines the outcome of UV absorption.

One nucleobase which has attracted considerable experimental and theoretical attention is adenine. Some of the relevant excited states of isolated adenine are shown in Fig. 7. The UV absorbing state is the $S_2(\pi\pi^*)$ state. The S_2 state has conical intersections with two lower lying excited states, the $S_1(n\pi^*)$ state and the $S_3(\pi\sigma^*)$ state, leading to a very rapid quenching of the S_2 state electronic excitation. Although details of the vibrational motions which govern branching between these competing pathways have yet to be finalized, it seems clear that very rapid non-adiabatic processes can lead to stabilization against excited state photochemistry. Once again, these important dynamical effects are not predictable from a 'structure-function' perspective.

In general, scattering processes are vectorial in nature. Whether they involve photon or particle interactions, scattering or absorption depends on how the molecule is oriented with respect to the direction of approach. For example, transition dipole moments generally differ along different axes (*i.e.* $\mu_x \neq \mu_y \neq \mu_z$), as does chemical reactivity (*i.e.* steric effects). Therefore, the most detailed views of molecular dynamics will obtain from the molecular frame (MF) of reference, avoiding the loss of information due to lab frame (LF) orientational averaging. For time-resolved dynamics in isolated gas phase molecules, there are two general approaches to such MF studies: (i) determine the MF orientation *post facto* on an event-by-event basis using coincidence techniques;²⁸ (ii) pre-align the MF to the LF using laser-induced alignment techniques.²⁹ An example of the first which is based on photoionization detection is the Coincidence Imaging Spectroscopy (CIS) technique, illustrated in Fig. 8. This approach is based on dissociation events which 'label' the MF direction in space. For example, a given



Fig. 8 Coincidence imaging spectroscopy (CIS) measures kinematically complete 3D recoil momentum vectors of both ions and electrons, in coincidence and as a function of time.

photo-initiated reaction $R-XY + h\nu \rightarrow R + XY$ is vectorial in nature, the photofragment angular distribution being referred to the MF. Any LF orientational averaging will blur this angular information, since the parent molecules were randomly oriented before excitation. However, in the so-called axial recoil limit where the emission direction of the R photofragment is along the LF direction of the original R-XY bond, measurement of the 3D fragment recoil vector yields information on the orientation of the MF within the LF. Using time-resolved photoelectron spectroscopy (TRPES), the time-evolution of vibrational and electronic dynamics may be observed.³⁰ In particular, measuring the time evolution of the 3D photoelectron angular distribution (PAD) in coincidence with the 3D photofragment recoil distribution allows the PAD to be transformed from the LF to the MF on an event-byevent basis. The time-resolved MF-PAD yields detailed information on the rearrangement of electronic structure (bonding) within the molecule during a photoinitiated dynamical process. As one example, the CIS approach to photodissociation dynamics studies was applied to the non-adiabatic photodissociation of the nitric oxide dimer:²⁸ (NO)₂ + $h\nu \rightarrow NO(A, 3s) + NO(X)$.

The second MF approach to time-resolved studies of dynamics in isolated gas phase molecules is based on laser pre-alignment of the MF within the LF. Importantly, strong (but non-ionizing) non-resonant laser fields can induce degrees of alignment (\cos^n) much greater than the \cos^2 alignment typically obtainable via single photon absorption. A polarizable molecule in an electric field will have a dipole moment induced by the field. A dipole in a field will feel a torque which induces the dipole to align with the field. This is the origin of the non-resonant laser-induced alignment of molecules. This effect can be used to fix the MF alignment within the LF, thereby minimizing the loss of information due to orientational averaging. While the strong laser field remains on, the induced dipole will feel a pendular potential, maintaining the axis alignment of the MF along the laser polarization direction. However, for the purposes of studying native dynamics in molecules, the presence of a strong laser field will strongly perturb such dynamics. Ideally, the molecule should be aligned but field-free during the dynamical evolution. The field-free alignment of molecules can be achieved via two means: the non-adiabatic or 'kick' approach,³¹ or the adiabatic 'switched wavepacket' approach.32 In either case, a strong non-resonant laser field induces a torque towards alignment, but then the field is rapidly turned off. This leaves the molecules in field-free alignment (FFA), but only for a time short compared to molecular rotation. FFA has even been demonstrated in 3D, where all three MF axes of an asymmetric top are fixed within the LF.33,34 As long as the dynamical process under study is fast compared to rotation, this approach can be used to study time-resolved dynamics in the MF. An illustrative example is the non-adiabatic UV (200 nm) photodissociation dynamics of carbon disulfide:29 $CS_2 + h\nu \rightarrow CS(X) + S({}^{3}P, {}^{1}D)$. Due to its favourable polarizability anisotropy, ground state CS₂ can be readily aligned using the non-adiabatic (kick) approach. This induces rotational wavepacket motion in the ground state. At the revival time $(\sim 75 \text{ ps after the kick})$ of this wavepacket, the initial MF alignment is reproduced but the molecule is now field-free. In CS2, the non-adiabatic photodissociation dynamics is fast compared to rotation and therefore these dynamics may be studied in the MF. At 200 nm excitation, the excited $CS_2(^{1}B_2)$ state is quasi-bound, undergoing compound stretch-bend vibrational motions perpendicular to the dissociation coordinate, leading to vibrational structure in the UV absorption

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Fig. 9 Probing excited state wavepacket dynamics in the CS_2 (${}^{1}B_{u}$) state from the molecule's point of view. A strong, polarized laser field 'kicks' the molecular frame (MF) into alignment. Time-resolved MF photoelectron angular distributions (MFPADs), right, recorded at the time of alignment, are able to directly probe the purely electronic dynamics of the valence electrons.

spectrum. As illustrated in Fig. 9(a), an ultrashort pulse can be used to prepare a coherent superposition of these compound stretch-bend predissocation resonances (here spaced by 33 cm⁻¹). The superposition of compound stretch-bend resonances leads to a quasi-bound vibrational motions which oscillate from stretch to bend during dissociation. Using photoionization as a probe, the MFPAD may be measured as a function of time, as shown in Fig. 9(b). In the $CS_2(^{1}B_2)$ state, bending mixes Π_g electronic character into the initial Σ_u electronic wavefunction, due to Renner–Teller interactions in the next-higher-lying state. This means that vibrational and electronic dynamics are coupled during dissociation. This leads to the observed changes in the MFPAD seen at 500 fs, compared to 100 and 900 fs. Importantly, the MFPAD is able to project out the purely valence electronic dynamics³⁵ even though these are strongly coupled to the nuclear motions.

The most familiar forms of light-matter interactions used in the study of photo-initiated quantum molecular dynamics are those of spectroscopy and photodissociation dynamics. These interactions are typically perturbative in terms of the strength of light-matter coupling. This represents the majority of the cases presented here in Faraday 163. In the next sections, we will also consider what happens as laser fields become stronger and the conventional perturbative picture of spectroscopy fails.

3 Phase/coherence

The second pillar of 'photo-initiated quantum molecular dynamics' is that of phase and/or coherence. As indicated by Fig. 2, laser pulses by definition have a certain degree of phase coherence between the frequencies which make up the pulse. The ability to control these phases and to transfer them to molecular systems *via* dipole interactions is the basis of the field of quantum control. Since electric forces underpin the dynamics of all chemical processes, the use of externally applied electric fields is a natural approach. The catalysis of reactions by metals is an example of externally applied electric fields (due to the surface) being used to suppress the activation barrier along the reaction co-ordinate.



Fig. 10 Quantum dynamics of the non-resonant dynamic Stark effect (NRDSE) in a strong laser field. The time evolution of the superposition in the field is driven by two source terms, one dipole-type and one Raman-type. For details, see the text.

Amplified lasers allow for the application of very precise electric fields, even at strengths which exceed the fields that bind matter. In the perturbative limit, quantum control schemes are based on the interference between degenerate pathways. For examples, interference between coherent 1- and 3-photon transitions, controlling total cross sections, or between coherent 1- and 2-photon transitions, controlling differential cross sections (*i.e.* angular distributions), have been implemented. The interference between coherent 2-photon transitions is even more common and, as can be seen from Fig. 4, is the basis of ultrafast pump-probe experiments. Commonly, control over the amplitudes $A(\omega)$ and phases $\phi(\omega)$ of a laser field, indicated within Fig. 2, is achieved *via* Fourier domain spatial light modulators (*i.e.* pulse shapers). These can be coupled to computer-controlled feedback mechanisms which vary $A(\omega)$ and $\phi(\omega)$ so as to optimize a specific outcome (*e.g.* product branching ratio). As long as perturbation theory applies, this type of quantum control can be understood in terms of interfering transitions between field-free states of the molecule. This picture will hold until perturbation theory fails—*i.e.* when the laser electric field significantly perturbs the eigenstates and the optical transitions can no longer be understood in terms of field-free transitions. One of the first nonperturbative interactions to emerge is the dynamic Stark effect,36 discussed in more detail below.

In Fig. 10, we consider a molecular Hamiltonian which has the typical band structure of well-separated electronic states, with each electronic state having the smaller level spacing structures of vibrational states. The set of ground electronic states are labelled $\{E_q\}$ whereas the excited states are labelled $\{N_p\}$. Here we are interested in controlling dynamics within the set of electronic ground eigenstates $E_n^{(0)}$ via the application of a strong but non-resonant electric field, indicated by the red arrow. By non-resonant, we mean that the laser frequency is large compared to the small (vibrational) level spacings but small compared to the large (electronic) level spacings, as shown in the figure. We now wish to consider the quantum dynamics of these levels in a strong laser field.

In the optical domain ($\lambda \sim 100$ –1000 nm) where the wavelength of light is much larger than the molecule (\sim 1 nm) and, therefore, its spatial variation across

the molecule can be neglected, the fundamental interaction between light and matter is *via* dipole coupling:

$$V(t) = -\vec{\mu} \cdot \vec{E}(t) \tag{3}$$

where

$$E(t) = 1/2 \varepsilon(t) e^{i\omega t} + c.c.$$

Here $\varepsilon(t)$ is the laser pulse envelope (*e.g.* a Gaussian) and ω is the frequency of light. In order to develop the quantum dynamics of the ground state in a strong laser field, we expand the states in the field free basis but with time dependent coefficients:

$$|\Psi(t)\rangle = \sum_{n} c_{n}(t) \mathbf{e}^{-i\omega_{n}t} |n\rangle$$
(4)

The problem is now to determine the time varying coefficients $c_n(t)$. To do this, we plug the ansatz of eqn (4) into the Schrödinger equation to get the coupled equations of motion for the state coefficients:

$$i\hbar \frac{\partial c_n}{\partial t} = \sum_m e^{-i\omega_{mn}t} V_{mn}(t) c_m(t)$$
(5)

This is the formal solution to the problem and involves a sum over all states: all dipole-coupled states m, whether near or far away, affect the time evolution of the state n. Anything else is an approximation. For the case of strong but non-ionizing non-resonant laser fields of interest here, we can treat the near and far away states differently. We will keep the full quantum dynamics of the near $\{E_q\}$ states but approximate the effect of the far away $\{N_p\}$ states on the nearby states by a derived effective interaction, namely the polarizability. In this case, the equations of motion of the nearby state coefficients take the form:

$$i \frac{\partial}{\partial t} c_n(t) = -\sum_m c_m(t) \left[\varepsilon(t) \cos\left(\omega t\right) d_{mn} + \varepsilon^2(t) \alpha_{mn}(\omega) \right]$$
(6)

It can be seen that there are two source terms driving the state coefficients $c_n(t)$. These represent the two limiting cases for the non-resonant dynamic Stark effect (NRDSE). If the neighbouring states $E_m^{(0)}$ and $E_n^{(0)}$ have dipole allowed transitions between them $(d_{mn} \neq 0)$, then the dominant term in eqn (6) is the first term, the dipole coupling. In this case, the superposition in the field will oscillates at the frequency of light due to the $\cos(\omega t)$ factor. In essence, the state $E_m^{(0)}$ makes a transition to neighbouring state $E_n^{(0)}$ with an off-resonant photon, the large detuning being made up for by the field strength. It is the Rabi cycling of these types of transitions which builds the superposition in the field. In contrast, if the neighbouring states $E_m^{(0)}$ and $E_n^{(0)}$ do not have dipole allowed transitions between them $(d_{mn} = 0)$, then the dominant term becomes the second one, the polarizability coupling. In this case, the state $E_m^{(0)}$ tries to makes a dipole transition to the far away $\{N_p\}$ states but cannot do so since they are too far away. Instead, a stimulated Raman transition back down to the $E_n^{(0)}$ state occurs and it is the Rabi cycling of this process



Fig. 11 Dynamic Stark Control (DSC) of the IBr \rightarrow I + Br/Br* non-adiabatic photodissociation. A strong non-resonant IR field modifies the curve crossing at the time of wavepacket passage, thereby controlling the branching ratio.

which builds the superposition in the field. Since this 'up and down process' represents a difference frequency within the laser pulse, the carrier frequency ω of the light falls out and only the laser pulse envelope $\varepsilon(t)$ remains important. Thus, the superposition in the field follows only the slower pulse envelope and does not oscillate at the frequency of light itself. This polarizability-dominated NRDSE regime is what underlies the laser-induced alignment of molecules (in which case the states $E_m^{(0)}$ are rotational states). The polarizability NRDSE can also be used to control photo-initiated quantum dynamics (*e.g.* photodissociation) in molecular excited states,¹³ and discussed in more detail below.

In Fig. 11, we consider the ultrafast non-adiabatic photodissociation of the diatomic molecule iodine bromide:³⁷ IBr + $h\nu \rightarrow I({}^{2}P_{3/2}) + Br({}^{2}P_{3/2})/Br^{*}({}^{2}P_{1/2})$. The optically bright, bound B-state correlates to I + Br* excited state products. It is crossed by the dark, dissociative Y-state which correlates with I + Br ground state products. The coupling between the B and Y states is in the intermediate strength coupling regime and, hence, neither the diabatic nor adiabatic potential curves apply. This is seen in the field-free Br/Br* branching ratio, which is around 50% at visible wavelengths. Since the B and Y states correlate to products of differing spin multiplicity, the dipole coupling between the B and Y states is small. Therefore, in a strong laser field, the dominant NRDSE is of the polarizability type. Imagine that we excite the B-state with a short visible pump pulse (green), creating a wavepacket. If left to evolve field-free, the expected Br/Br* branching ratio would obtain. However, if we applied a strong, non-resonant field (red) at time delay Δt , as the wavepacket crossed the region of non-adiabatic coupling, we might be able to modify the hopping probability. What type of control should we expect? We can understand the basic effect by considering the Stark effect on the diabatic states. Since the B-state is bound, it has continuous electron density between the atoms. Therefore, we might expect it to have a significant polarizability. In contrast, the dissociative Y-state has a node in the electronic wavefunction between the two atoms and, therefore, it should have a lower polarizability. Therefore, in a strong non-resonant field, the B and Y states should have different Stark shifts, leading to a field-induced change in the crossing point (inset) between the two states. This



Fig. 12 Using the dynamic Stark control scheme of Fig. 11, the Br/Br* branching ratio may be controlled by a strong non-resonant laser field. Importantly, there is no net absorption of photons from the strong control field.

would lead to a change in the surface hopping probability and, therefore, Dynamic Stark Control (DSC) over the Br/Br* branching ratio. This scenario was experimentally demonstrated³⁸ and, as shown in Fig. 12, large fractional changes in the Br/Br* branching ratio were obtained, depending on the timing between the creation of the wavepacket and the application of the NRDSE control pulse. It is important to realize that, in NRDSE control, there is no net consumption of photons. This means that the dynamics remain on the coupled potential energy surfaces to be controlled, rather than making electronic transitions to other states. In this sense, the NRDSE control pulse acts like a catalyst rather than as a reagent. It can also be seen that the field-free Br/Br* branching ratio obtains when the NRDSE pulse is applied too early or too late. This demonstrates that the NRDSE reversibly follows the control pulse envelope, leaving the molecule in its field-free configuration after the Stark interaction is over.

As researcher's control over photo-initiated quantum molecular dynamics continues to improve, we may hope to see the range of applications of the NRDSE expand. However, as non-resonant laser fields become only somewhat stronger, ionization becomes the dominant response. This is the subject of the following section.

4 Intensity

The third pillar of 'photo-initiated quantum molecular dynamics' is that of intensity. At laser intensities above 10^{13} W cm⁻², laser electric fields applied to matter start to become comparable to the fields which bind electrons to matter itself. In this regime, a new physics emerges, that of strong field ionization (SFI), tunnel ionization and strongly driven electrons.

A simple quasi-static model³⁹ applies to the SFI of rare gas atoms whereby, for sufficiently long wavelengths, tunnelling of the single most weakly bound electron

(of binding energy I_p) occurs through an essentially static barrier formed by the superposition of the core potential Coulomb electric field with the laser electric field. This model ignores any electronic excitations inside the Coulomb potential, as well as any multi-electron effects. The subsequent evolution of the SFI liberated electron in the strong field leads to a range of important new phenomena. Most significant is that the strongly driven electron can recollide with its parent ion core, emitting a burst of XUV radiation. This process is known as high harmonic generation (HHG). Controlling the recollision electron leads to the formation of attosecond pulses⁴⁰ and the birth of a new field of research: attosecond science.

Implicit in the quasi-static model³⁹ is an approximation that the bound electrons can adiabatically follow the 1-2 fs time scale oscillations of the laser field. This is analogous the BO approximation wherein the bound valence electrons adiabatically follow the time dependent electric field due to the vibrational motions of the charged nuclei. In the rare gas atoms, the electronic level spacings are very large (~ 10 eV) and, therefore, the time scale of electronic motion (the inverse of the level spacing) is very fast compared to optical periods. The adiabatic approximation holds very well for rare gas atoms. A second important approximation in the quasi-static model of SFI is that only a single active electron (SAE) responds to the strong field. This may seem odd for the rare gas atoms such as Ne, Ar, Kr etc. where there are six equivalent outer shell electrons. However, in the rare gas atoms, the first excited state is typically about 2/3 of the way to the ionization potential. This means that there exist no doubly excited states below the first In-Therefore, only single excitations contribute effectively to the strong field polarizability: the rare gas atoms behave in SFI as if they have only a SAE. Finally, we must remember that the inert gases have a pathological electronic structure. Will these approximations hold for polyatomic molecules which generally have extended lengths and doubly excited states existing below the first Ip?

Laser driven electrons in an extended molecular potential suggests a rough analogy with the splashing of water in a periodically tipping bathtub of length *L*. An oscillating electric field causes the potential to periodically tip left and right at the laser frequency ω_L , forcing the electron density to oscillate within the well.



Fig. 13 In a strong ionizing laser field ε , the driven electrons within the molecular potential may adiabatically follow (solid black lines) the applied laser field. However, depending on level spacings, dipole coupling strengths and laser frequency, the system may also make non-adiabatic transitions (dashed black lines) at the zero crossings of the laser field. In such a case, the tunnelling picture of strong field ionization will not apply.

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In the low frequency limit (adiabatic dynamics), the 'bathtub' tips very slowly and the 'surface of the water' remains flat at all times: this is the quasi-static picture. As the frequency of the tipping motion increases, the water no longer remains flat—splashing (non-adiabatic dynamics) occurs. As the amplitude increases, water is splashed out of the bathtub. This is non-adiabatic multielectron ionization dynamics, which we have termed NME.^{41,42}

A simple model can be used to estimate when NME becomes important. Referring to Fig. 13, we consider a Hückel-type molecular potential of characteristic length L and field-free electronic level spacings Δ_0 subjected to a strong oscillating electric field $E = \varepsilon \sin \omega_L t$. We allow for a typical dipole coupling between states to have value μ . For laser frequencies $\omega_L \ll \Delta_0$, the level shifts adiabatically follow the field (solid black lines) and populations remain in their Stark shifted states at all times. As the laser frequency increases, however, the probability of Landau–Zener (LZ) type non-adiabatic transitions (dashed black lines) significantly increases. These transitions will occur when the laser field is changing most rapidly (near the zero crossings $\varepsilon = 0$), rather than when the field is strongest (near the maxima $\pm \varepsilon$). The strongest transition dipoles will have the greatest influence. In molecules, these would likely be the charge transfer transitions, where the dipole $\mu \equiv d_0 \approx L$. The probability P_{LZ} of non-resonant LZ transition during one-half of a laser cycle will be:

$$P_{\rm LZ} \approx {\rm e}^{-\pi\Delta_0^2/4\omega_L\varepsilon\mu} \tag{7}$$

When $\omega_L \varepsilon L \sim {\Delta_0}^2$, there will be strong non-resonant absorption by all delocalized electrons. This non-adiabatic electronic 'ladder climbing' ionization



Fig. 14 Failure of the strong field adiabatic approximation. SFI mass spectra of linear, conjugated hydrocarbons of increasing length, hexatriene, decatetraene and β -carotene, at wavelengths of 800 and 1450 nm. Hexatriene shows characteristics of quasi-static tunnel ionization. The longer decatetraene has a fragmentation pattern which varies with wavelength, exhibiting a transition to complete fragmentation by 800 nm. This is a failure of the adiabatic approximation. The much longer β -carotene shows extensive fragmentation at all wavelengths studied.

mechanism (NME) represents a complete failure of the quasi-static picture. As a specific example, we consider a linear polyene-type molecule with L = 13.5 Å, $\Delta_0 = 4$ eV, and $\lambda = 700$ nm. In this case, $\omega_L \varepsilon L \sim {\Delta_0}^2$ is achieved at an intensity $I \sim 5 \times 10^{12}$ W cm⁻², a situation which occurs in many strong field experiments on molecules.

In Fig. 14 we show the SFI mass spectra of linear, fully conjugated *all trans* hydrocarbons of increasing length, hexatriene, decatetraene and β -carotene, using intense 40 fs pulses at the wavelengths of 800 and 1450 nm.⁴¹ (We remind that the quasi-static model is frequency independent). Hexatriene (upper) shows the formation of several charge states of the parent molecule, with little fragmentation (no excited ionic states) and little variation with wavelength (frequency independence). This is characteristic of quasi-static tunnel ionization. The longer decate-traene (middle) shows a similar result at 1450 nm, forming singly, doubly and triply charged parent ions. However, its fragmentation pattern varies greatly with wavelength dependence indicates a complete failure of the quasi-static picture and is due to the emergence of NME. The longer β -carotene (bottom) shows extensive fragmentation at all wavelengths. These results suggest that, for polyatomic systems, the adiabatic approximation upon which the quasi-static model rests can fail dramatically, depending on both molecular and laser properties.

Even in the longer wavelength adiabatic limit, there can still be multielectron effects in SFI. The SAE picture of SFI assumes that only a single electron is driven by the strong laser field and that all other bound electrons remain unaffected by this field. This would be strictly true only if the ion core had zero polarizability. Were ion core polarizable, the remaining bound electrons would displace in the field, affecting the Coulomb potential barrier for the active electron. One can get a sense for this issue by considering a classical, perfectly conducting shell in a static external electric field. The electrons on the surface of the shell will arrange in such a way so as to counteract (screen) the applied field. Due to the exponential dependence of tunnelling rates on the properties of the barrier, dynamic multielectron screening will have significant effects on ionization rates.

In order to characterize dynamic screening effects in SFI, we studied the ionization rates of transition metal atoms⁴³ and clusters⁴⁴ in strong infrared ($\lambda =$



Fig. 15 Failure of the single active electron (SAE) approximation. The strong field ionization response of transition metals clusters, here of niobium, reveals a dramatic suppression of ionization as compared to the expectations of SAE theories such as ADK. This is due to the dynamic screening of the applied field by the polarisable electrons of the ionic core.

1.5 μ m) laser fields. In Fig. 15, we show results for the case of Niobium clusters. The saturation intensity, I_{sat}, a measure of the SFI response, is plotted (upper panel) as a function of the Nb_n cluster size n. In order to compare with the expectations of a non-polarizable core model, we used the well established Ammosov-Delone-Krainov (ADK) theory⁴⁵ which considers only the I_p of the species in question and neglects any electronic dynamics inside the potential. ADK theory accurately describes the SFI rates of the rare gas atoms. The ratio of the experimental I_{sat} to the I_{sat}(ADK) is plotted in the lower panel. If the Niobium clusters experienced SFI as do rare gas atoms, this ratio would have a value equal to one. Instead, it can be seen that this ratio can be an order of magnitude larger. This represents a several order of magnitude suppression of SFI rates for the Niobium clusters as compared to an artificial 'rare gas atom' of the same I_p. The origin of this suppression is the dynamic polarization of the core, screening the applied laser field felt by the 'active' electron. A simple model (left) which treats the cluster as a metal sphere by including the polarizability, the image charge and laser field interactions, is largely able to capture the essential physics.⁴⁴ Although metal clusters are expected to be more polarizable than many molecules, these results show that even in the quasi-static limit, there are important multielectron effects in the SFI of polyatomic molecules.

The failures of the adiabatic and SAE approximations have important consequences for the study of polyatomic molecular dynamics using strong laser fields. In SFI, the driven multielectron response occurs on the sub-cycle (attosecond) time scale. There is considerable interest in probing coherent electron dynamics in atomic and molecular systems, using both strong and weak laser fields. This is the domain of the emerging field of attosecond science.⁴⁶

Attosecond science is based on the strong field process of high harmonic generation (HHG). Since its origins⁴⁰ in 1994, it was understood that attosecond time scale measurements could probe the dynamics of electrons in a manner analogous to the femtosecond probing of vibrational and vibronic dynamics. Isolated attosecond pulses as short as 80 as have been created. In terms of timeresolved measurements, both strong and weak field approaches have been proposed, although to date all attosecond measurements have involved the use of at least one strong laser field. As discussed above, the physics of multi-electron polyatomic molecules in strong laser fields is complex. As such, SFI-based processes such as HHG may not be the most direct probes of native electronic dynamics in molecules. However, by analogy with femtosecond wavepacket experiments, the generation of isolated attosecond pulses will allow for attosecond pump-probe studies of electronic wavepacket dynamics. For reference, a Gaussian 100 as laser pulse has a bandwidth of \sim 18 eV, spanning many electronic states, and a central frequency in the XUV range. What are the consequences of this? Well, 'wavepackets are wavepackets' and much of the intuition that we have developed in understanding wavepacket dynamics using narrower bandwidth femtosecond pulses should be translatable, adjusting level spacing and time scales, to attosecond wavepacket dynamics. This idea is discussed a little further, below.

On sub-femtosecond time scales, the atoms are essentially frozen and the dynamics is purely electronic. (N.B. The fastest molecular vibration, that of H_2 , has a frequency of 4155 cm⁻¹, corresponding to a period of ~8 fs). What kind of electronic wavepackets will very broad attosecond pulses prepare? For simplicity, we will restrict ourselves to bound states, the extension to electronic continua

being straightforward. With a frozen core electronic Hamiltonian, the exact fieldfree eigenstates are stationary, many-body solutions to the Schrödinger equation—*i.e.* the exact *n*-body electronic wavefunction for all electrons. These wavefunctions implicitly contain all static and dynamic electron correlations. (Artificial single particle functions such as molecular orbitals are certainly not solutions to this Schrödinger equation.) We may not be able to calculate exact electronic wavefunctions, but the molecule knows them. One may be tempted to think of an electronic state as composed of electrons whizzing about the molecular core at near-relativistic velocities. However, this is not what the Schrödinger equation tells us. The eigenstates are stationary solutions: the *n*-body electronic density is time-independent. Field-free dynamics (time dependence) therefore obtains only *via* the coherent superposition of eigenstates—in other words, formation of a wavepacket.

Using the broad bandwidths of attosecond pulses, we could create a coherent superposition of exact *n*-body electronic wavefunctions. This superposition may, for a short time, appear like the solution to a simpler Hamiltonian wherein certain couplings (*e.g.* electron correlation) are neglected. For example, a specific coherent superposition of exact *n*-body wavefunctions could behave, for a short period of time, like a molecular orbital—a single particle excitation. Electron correlation would, of course, eventually convert this single particle excitation into many-body excitations. Analogous to the fs wavepacket dynamics case discussed above, the time-resolved study of this process would yield information about the electronic couplings which evolve charge distributions on the molecular frame.

Using the principle that "the same equations have the same solutions", I speculate that we can map the problem of attosecond electronic wavepackets in molecules onto a well known femtosecond time scale problem related to intramolecular vibrational energy redistribution (IVR). The problem I have in mind is that of local modes, an example of which is the C–H stretch in benzene, C_6H_6 . Remarkably, the C–H overtone absorption spectrum of benzene looks like that of a diatomic Morse oscillator. It seems as if an H atom were vibrating against a structureless particle of mass C_6H_5 . However, the linewidths of the overtones increases with C–H vibrational quantum number. This is because the ' C_6H_5 particle' is not really structureless and, as the energy in the C–H stretch increases, it couples ever more strongly into the internal modes of the benzene ring. This flow of vibrational energy from a C–H local mode to the set of ring modes is called IVR.

We can construct a wavepacket picture of these local mode dynamics, referring to the tier model diagram in Fig. 16. The exact molecular vibrational eigenstates (which are generally not the harmonic normal modes) in principle exist, even if we cannot calculate these very well. These necessarily involve the coupled motions of all C and H atoms within the molecule. As such, they are exact *n*-body stationary solutions to the vibrational Schrödinger equation. These exact states are shown in the middle panel. In frequency domain language, the oscillator strength for these vibrational transitions comes from the C–H stretch local oscillator mode, shown left. The vibrational spectrum, shown right, would have this oscillator strength distributed over all coupled modes. A spectrally broad, coherent laser pulse could prepare a superposition of exact *n*-body states such that, for a short time, they behave like a localized zeroth order state – in this case, the 'one-particle' C–H stretch. This phased superposition would initially look like a single particle excitation - an H atom vibrating against a structureless particle of mass C_6H_5 .



Fig. 16 A localized zeroth order state such as a local mode or molecular orbital can be created by the coherent superposition of exact many-body states. Energy or charge redistribution is understood in terms of the dephasing of this superposition. For details, see the text.

However, due to their differing energy phase factors, this superposition will evolve and the interference which initially cancelled out the ring modes will be spoiled. This dephasing of the vibrational wavepacket will lead to energy flow into the ring (a many-body excitation).

This same picture can be applied to attosecond electronic dynamics in molecules. If we make the mapping "local mode" ↔ "molecular orbital" and "exact vibrational wavefunction" \leftrightarrow "exact *n*-body electronic wavefunction", then a very similar discussion of wavepacket dynamics ensues, provided one translates the time scales and level spacings involved. Referring again to Fig. 16, the middle panel now corresponds to the exact *n*-body electronic wavefunctions. The localized zeroth order state is now the single particle molecular orbital. (The coupling would now be electron correlation rather than anharmonic vibrational couplings). Once again, a spectrally broad coherent (attosecond in this case) laser pulse could prepare a coherent superposition of exact n-body electronic states which, for a short time, could look like a single particle excitation-a molecular orbital. Again, the phased superposition will evolve and the localized electronic motion will become a more generalized many-body excitation. Energy flows from the single excited electron to all other coupled electrons in the molecule. This attosecond charge redistribution would represent the real-time observation of electron correlation in molecules.

Finally, I would like to address the issue of "attosecond chemistry". A coherent superposition of many bound electronic states of a molecule, such as illustrated in Fig. 16, would indeed exhibit attosecond time scale electronic motions and one might discern electron correlation in molecules. Chemistry, however, requires that the atoms move: each electronic state in the superposition represents a different potential energy surface for these motions and likely correlates to different product channels. Conventionally, we would call these different chemical reactions (*e.g.* ground state *vs.* excited state reactions). What would be seen in an attosecond wavepacket experiment once the atoms start to move? In general, molecular potential energy surfaces are not parallel to each other and their electronic structure will vary with nuclear coordinates in differing ways. Due to this variation of both electronic level spacings and structure with coordinates, the electronic coherences prepared on attosecond time scales will appear to irreversibly dephase once the atoms start to move.

A given chemical reaction occurs on a given potential energy surface and, by definition, involves the making and breaking of chemical bonds. This requires



Fig. 17 Time scales of electronic dynamics during chemical reaction. One of the fastest processes in chemistry is passage through a conical intersection. An attosecond pulse creates a coherent superposition of two electronic states $|\alpha\rangle$ and $|\beta\rangle$. This oscillating electronic coherence will slow down as the nuclei move towards the conical intersection, where they finally achieve the time scales of nuclear motions.

the concerted motions of both atoms and electrons. This concerted motion may be either adiabatic or non-adiabatic, depending on whether or not the electrons can 'follow' the nuclei. In the adiabatic case, the time scales of electron motion during a chemical reaction are clearly the same as the time scale of atomic motions (femtosecond). The non-adiabatic case, passage through a conical intersection for example, is more interesting because it is one of the fastest processes in chemistry and requires a bit more analysis. For this purpose, we refer to Fig. 17. We consider two electronic states, $|\alpha\rangle$ and $|\beta\rangle$, of a polyatomic molecule which exhibit a conical intersection at some geometry. We imagine that, at the Franck–Condon geometry of the ground state (not shown), the states $|\alpha\rangle$ and $|\beta\rangle$ are well separated with spacing ΔE , as shown on the left side of the figure. An attosecond pulse would prepare a coherent superposition of these two states. At short times, the atoms are stationary and a purely electronic two-level quantum beat is created wherein the charge distribution on the molecular frame oscillates between the sum and difference of the two electronic wavefunctions, at a time scale given by the inverse level spacing ΔE . Until the atoms move, nothing else can happen. Let us now let the atoms move, in this case towards the conical intersection, and ask what happens to the time scale of electron dynamics. As the two surfaces approach, the electronic energy level spacing diminishes, meaning that the electron dynamics slows down. Close to the conical intersection, the electronic level spacings become comparable to the vibrational ones and, therefore, the time scale of electron motion has slowed down to the time scale of vibrational motions. In fact, this is the reason why the BO separation fails. Therefore, at conical intersections, the dynamics of electron motions becomes comparable to the time scale of vibrational motions. The above simple arguments seem to suggest, perhaps more generally, that the time scale of electron dynamics during a chemical reaction is femtoseconds, the time scale of the motions of the atoms.

5 Conclusion

The interaction of light with matter underlies many important areas of research, ranging from fundamental physics and chemistry to medicine and engineering.

As new optical tools continue to become available, our ability to apply them will depend on our understanding of the nature and range of light-matter interactions. Using the narrative device of the 'three pillars' shown in Fig. 1, we have attempted to classify light-matter interactions as they apply to photo-initiated quantum molecular dynamics, the subject of Faraday Discussion 163.

New light sources will lead to new regimes of resolution in both the time and frequency domains. In particular, non-linear optics will become an increasingly useful tool due to the commercial availability of appropriate lasers. The consequences of this are that understanding and controlling optical phase, important only in non-linear optics, will open broad new avenues for studying molecular dynamics, life sciences and engineering. The ability to apply precise yet strong laser fields offers novel routes to controlling or modifying molecular systems. The three pillars of photo-initiated quantum molecular dynamics will continue to offer new opportunities for science and technology for the foreseeable future.

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