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Ultrafast processes in chemistry and biology: concluding remarks

By Joshua Jortner

School of Chemistry, Tel Aviv University, Ramat Aviv, 69978 Tel Aviv, Israel

We address the conceptual framework and perspectives of femtosecond chemistry and biology, which rest on intramolecular, cluster, condensed phase and biophysical dynamics on the time scale of nuclear motion.

Keywords: radiationless transitions; Franck–Condon quasi-continuum; coherence effects; cluster dynamic size effects; non-adiabatic dynamics; ultrafast processes

1. How fast is ultrafast?

This Discussion Meeting has been truly stimulating and broad in scope. We are particularly indebted to Professor Graham R. Fleming, Professor Peter L. Knight and Professor John P. Simons, for having arranged this timely and interesting scientific endeavour.

We explored the temporal limits of chemistry and photobiology on the time scale from femtoseconds to attoseconds. Many contributions to this meeting addressed 'ultrafast' or 'ultrashort' processes. It will be appropriate to inquire 'how fast is ultrafast'? This question attracts different answers in different realms of science (figure 1). In the realm of chemical and biological dynamics ultrafast relaxation can prevail on the time scale of nuclear motion. The exploration of ultrafast chemical and biological dynamics stems from concurrent progress in theory and experiment. The advent of fs lasers allows for the real-time interrogation of the intramolecular and intermolecular nuclear motion during chemical and biophysical transformation (Zewail 1994; Chergui 1996). On the theoretical front, the theory and simulations of radiationless processes (Jortner 1996), wavepacket dynamics (Manz 1998), coherence effects (Manz 1998), cluster dynamic size effects (Jortner 1992), non-adiabatic condensed phase dynamics (Jortner 1996) and nonlinear optical interactions (Mukamel 1995) provide the conceptual framework for ultrafast intramolecular, cluster, condensed phase and biophysical dynamics.

2. Facets of intramolecular dynamics: decay channels

Ultrafast radiationless processes in molecular and cluster systems involve:

(i) 'Reactive' non-radiative processes of molecular (rotational, vibrational or electronic) autoionization and predissociation, which involve the decay of a metastable state(s) into dissociation or ionization channels.

(ii) 'Non-reactive' relaxation in a bound level structure of large isolated molecules, e.g. electronic-vibrational relaxation (internal conversion or intersystem crossing) or intramolecular vibrational energy redistribution (IVR), can occur on the time scale of *ca.* 10–10^3 fs (Jortner 1996).

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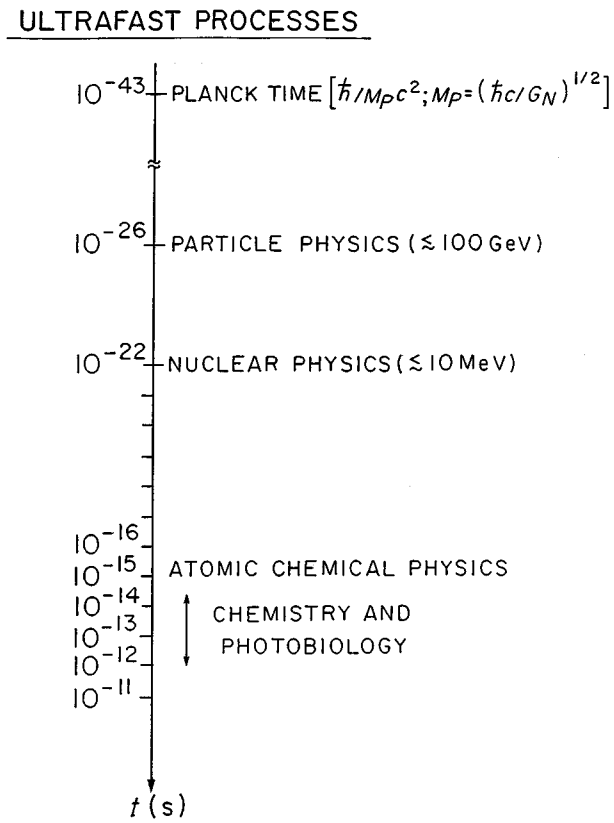

Figure 1. Time scales for ultrafast processes.

(iii) Relaxation in electronic quasi-continua. Very high n (= 50–250, where n is the principal quantum number) molecular Rydberg states are characterized by a high density ($\rho \propto n^3/Ry$) of electronic states and by unique intramolecular nl'–$n'l'$ coupling, which involves core multipole and anisotropic polarizability interactions (Bixon & Jortner 1996). A generalization and unification of the theory of intramolecular coupling and dynamics for a Rydberg manifold was provided, establishing the conditions for strong coupling of a doorway Rydberg state and the attainment of the statistical limit within an electronic quasi-continuum (Bixon & Jortner 1996).

The dissipative channels for intramolecular dynamics can be characterized in terms of the state specificity of the matrix elements of the Hamiltonian ($\boldsymbol{H}$), i.e. $V_{sl} = \langle s|\boldsymbol{H}|l\rangle$, for the coupling of the doorway states $|s\rangle$, $|s'\rangle$, $|s''\rangle \ldots$, with the $\{|l\rangle\}$ states of the continuum or quasi-continuum. The state dependence of the couplings is quantified by the correlation parameter (Bixon & Jortner 1997a, b) $\eta_{ss'} = \langle V_{sl}V_{ls'}\rangle/[\langle V_{sl}^2\rangle\langle V_{s'l}^2\rangle]^{1/2}$. The continua and quasi-continua can be segregated into: (i) 'smooth' decay channels, involving slow energy dependence (E_l) of V_{sl}, with $\eta_{ss'} = 1$ for $s \neq s'$, i.e. dissociation and ionization continua and the electronic quasi-continuum, and (ii) 'non-smooth' decay channels, where V_{sl} exhibits a large and irregular energy (E_l) variation, $\eta_{ss'} \ll l$; $s \neq s'$, i.e. the vibrational Franck–Condon quasi-continuum. The distinction between 'smooth' and 'non-smooth' channels does not affect the level structure and dynamics of molecular eigenstates which have their parentage in a single doorway state coupled to a single quasi-continuum. This distinc-

tion is of central importance for interference effects between several doorway states, which exhibit a profound influence on femtosecond intramolecular dynamics in electronically vibrationally excited wavepackets of states of large isolated molecules and in the condensed phase. The correlation parameters $\eta_{ss'}$ determine vibrational coherence in non-radiative dynamics (Bixon & Jortner 1997*a*) and determine the upper temporal limits for relaxation (Bixon & Jortner 1997*b*).

3. 'Non-reactive' intramolecular dynamics on the time scale of nuclear motion

For intramolecular relaxation processes involving a 'smooth' correlated ($\eta_{ss'} \cong 1$), dissipative channel, the temporal constraints on the dynamics can be inferred from the theory of overlapping resonances (Mies & Kraus 1966; McLaughlin *et al.* 1968), which sets an upper limit on the relaxation rate, k. For the population decay of a set of equally spaced (nearest neighbour separation of ω) resonances (of widths $\Gamma = 2\pi V^2\rho$ for an isolated resonance), interference effects set in when $\Gamma \sim \omega$. The intramolecular relaxation rate is $k = (\Gamma/\hbar)/[1 + (\pi\Gamma/\omega)]$. The rate exhibits a transition from $k = (\Gamma/\hbar)$ for an isolated resonance ($\Gamma \ll \omega$) to $k = \omega/h$ for overlapping resonances ($\Gamma \gg \omega$). The overlapping resonance domain provides an upper limit for the non-radiative rates, i.e. $k \leqslant \omega/h$, which is determined by the level spacing, i.e. the vibrational frequency (time scale $t \sim k^{-1} \sim$ 10–1000 fs). This situation prevails for intramolecular dynamics in a 'smooth' nuclear continuum, i.e. electronic and vibrational predissociation. The experimental ultrafast fs electronic predissociation times of diatomics (Lefebvre-Brion & Field 1986) are limited by the overlapping resonances constraint. For dynamics in the 'smooth' electronic Rydberg quasi-continuum the upper limit for the rate is $k \leqslant 2Ry/n^3\hbar$ (i.e. k for $n = 50$ being in the $(\mathrm{ps})^{-1}$ domain).

For the decay of weakly correlated ($\eta_{ss'} \ll 1$) overlapping resonances into a 'non-smooth' Franck–Condon vibrational quasi-continuum, interference effects are expected to be much less pronounced than for the case of a 'smooth' channel. This is experimentally manifested in the related context of the lack of interference effects, i.e. Fano antiresonances in the absorption spectra of Rydberg states which overlap $\pi\pi^*$ intravalence excitations in large aromatic molecules. Model calculations of correlation parameters $\eta_{ss'}$ for a doorway state in the vicinity of the electronic origin are considerably lower than unity, with their highest values falling in the range $|\eta_{ss'}| = 0.4$–0.2 for a small number of s, s' pairs differing only by a single vibrational quantum number, while for multimode s, s' changes very low values of $|\eta_{ss'}| < 0.1$ are exhibited (Bixon & Jortner 1997*a*). These propensity rules imply the existence of weak correlations within the Franck–Condon vibrational quasi-continuum, resulting in a partial erosion of resonance interference effects, in some analogy with random coupling models for intramolecular coupling and dynamics (Schek & Jortner 1979; Carmeli *et al.* 1980), where interference effects are completely eroded. Ultrafast intramolecular radiationless transition rates in a bound level structure of overlapping resonances into the Franck–Condon quasi-continuum are expected not to be strictly limited by the level spacing, but rather the temporal upper limit $k \propto V^2 \geqslant \omega/h$ can be realized. Indeed, some of the ultrafast (*ca.* 10 fs) relaxation times of intravalence excitations of isolated aromatic molecules (Jortner 1996) exceed most of the intramolecular frequencies. Such temporal records may be achieved for 'non-reactive'

radiationless transition in large molecules and for non-adiabatic processes in liquids, solids and proteins, providing a unification of intramolecular and condensed phase ultrafast dynamics.

Perspectives for future studies of ultrafast dynamics in large isolated molecules pertain to:

(1) High-energy intravalence and Rydberg excitations of large molecules will constitute a hunting ground for fs intramolecular time-resolved dynamics in electronic origins of jet-cooled isolated molecules (Jortner 1996). Only recently the first time resolved lifetime of *ca.* 40 fs for the S_2 state of isolated benzene was reported by Radloff *et al.* (1996). These data, which approach or exceed the time scale for intramolecular frequencies, are important in the context of intramolecular dynamics in the Franck–Condon quasi-continuum. Temporal records on the time scale for ultrafast interstate dynamics will prevail.

(2) Time-resolved chemistry in isolated supermolecules and model biomolecules, mode selective and coherent single molecule chemistry. Some of the interesting problems involve electrons in a single supermolecule resulting in the formation of a giant dipole, hole transfer in an isolated polypeptide, with the possible distinction between transfer and transport, vibrational coherence in intramolecular chemistry, vibrational mode selectivity in ET and in EET, and coherent versus incoherent electronic energy transfer.

(3) Quantum beats. The time evolution of a coherently excited wavepacket of molecular eigenstates will exhibit interference effects. For large molecules such wavepackets can manifest (i) molecular eigenstates originating from interstate or intrastate coupling; (ii) Jahn–Teller coupled vibronic manifolds in doubly degenerate states of a large molecule, e.g. the E state of triptycene, which bears analogy to the adiabatic–diabatic coupling in IBr studied by Stollow *et al.* (this volume); (iii) electron-vibrational coherence in mediated coupling; (iv) electron-vibrational coherence in intramolecular chemistry.

(4) Dynamics of ultrahigh n (= 50–250) molecular Rydberg states. Time scales for the longevity of molecular Rydberg states in I_2 were explored by Stollow *et al.* (this volume) by nuclear wavepacket dynamics. Of considerable interest is the coherent excitation and interrogation of an electronic wavepacket in high n molecular Rydberg states (Radloff *et al.* 1996).

4. Dissociative dynamics and Coulomb explosion in molecules and clusters

For direct dissociation in molecular systems the dynamics involves the sliding on a repulsive potential surface (Bernstein & Zewail 1989). The characteristic time for dissociation is described in terms of the classical mechanical model of Zewail and his colleagues (Bernstein & Zewail 1989)

$$\tau_{\mathrm{c}} = \int_{R_0}^{R} \mathrm{d}R'/v(R'),$$

where $v(R')$ is the velocity at R'. This simple expression captures the essential features of the dynamics. The typical time scale for direct dissociation is $\tau_{\mathrm{c}} \cong 100$ fs.

An ultrafast excitation leading to the localization of energy in polyatomic molecules or clusters can be achieved by a Coulomb explosion. This ultrafast process is charac-

terized by site selective energy acquisition in conjunction with bond-specific energy disposal. The mechanical model for the separation of two positive ions of charges q_1 and q_2 with an effective mass (μ/AM) initially separated at distance (R_0 Å) to the distance (R Å), gives (Last *et al.* 1997) τ_c (fs) $= 1.9R_0(\mu R_0/q_1q_2)^{1/2}Z(\xi)$, where $\xi = R_0/R < 1$ and the numerical function $Z(\xi) \sim 1$ for $\xi = 1/2$. The time scales for Coulomb explosion reflect fs dynamics being shorter by about 1–2 orders of magnitude than the corresponding time scales for molecular dissociation. The pioneering investigation of the dynamics of Coulomb explosion of I_2^{+3} in real-time, reported by Corkum and his colleagues (this volume), should be applicable to more complex molecules and clusters. The mechanisms of enhanced high-order multiphoton ionization, producing the target for Coulomb explosion, are novel and interesting. In molecular systems a two-step non-vertical molecular ionization model was considered, where the ionization enhancement at the stretched intramolecular distance originates from non-adiabatic electron localization near the nuclei (Schmidt *et al.* 1994; Seidman *et al.* 1995). It is still an open question whether this model applies for elemental atomic clusters, where Hutchinson *et al.* (this volume) observed a dramatic enhancement of ionization clusters. It appears that high-order direct multiphoton atomic ionization in an elemental cluster does not occur in view of the observation of highly multicharged species from a cluster beam, but not from an atomic beam (Snyder *et al.* 1996). The ionization ignition model (Rose-Petruck *et al.* 1995) accounts for many features of cluster high-order multiphoton ionization. In this model initial ionization events result in a large and inhomogeneous electric field of ions, lowering the ionization barrier and allowing for subsequent ionization processes to occur. The time scales obtained from the classical model for the explosion of a $(Xe)_n^{+q}$ cluster reveal that $\tau_c^{-1} \propto q$, being borne out by molecular dynamics simulations (Last *et al.* 1997). The use of the ultrafast fs 'chemical clock' of Coulomb explosion of molecules (Jortner & Levine 1990), surface states (Jortner & Levine 1990) and clusters (Last *et al.* 1997; Purnell *et al.* 1994) precludes IVR and shows potential applications for selective chemistry.

5. Dynamic cluster size effects

Clusters, i.e. finite aggregates containing 2–10^9 constituents, provide novel insight into the dynamics of systems with a finite density of states, where separation of time scales can be realized. A key concept for the quantification of the unique characteristics of clusters pertains to size effects (Jortner 1992, 1996). These involve the evolution of structural, thermodynamic, electronic, energetic, electrodynamic and dynamic features of finite systems with increasing cluster size. Several interesting dynamic cluster size effects were explored theoretically by modelling and by simulations.

(1) The 'transition' from molecular-type dissociative dynamics in small clusters to condensed-matter type non-reactive vibrational relaxation in large clusters manifests the bridging between molecular and condensed phase nuclear dynamics (Jortner 1992).

(2) Collective vibrational modes (Jortner 1995). Interior, collective, compression nuclear modes of molecular clusters (He_n, Ar_n) can be treated in terms of the excitation of a liquid drop and were experimentally documented. Complementary to the energetics of these collective modes, their dynamics is interesting. The damping of the

collective motion via the coupling of a 'giant resonance' to non-coherent vibrational modes, constitutes a theoretical and experimental challenge.

(3) Bubble dynamics. The dynamics of large local configurational change are induced by an extravalence excitation of a probe atom (e.g. $^1S_0 \rightarrow {}^3P_1$ excitation of Xe) or molecule (e.g. Rydberg excitation of NO) in a rare-gas cluster. Molecular dynamics simulations of the dynamics of configurational nuclear relaxation around the $^3P_1$ excitation of Xe in $XeAr_n$ clusters (Goldberg & Jortner 1998) reveal: (i) large configurational dilation, i.e. 'bubble' formation on the time scale of $t_B \sim 100$–300 fs; (ii) t_B marking the time scale for ultrafast energy transfer; (iii) multimodal time evolution, with slower time scales of 1–5 ps; (iv) marked impact vibrational coherence excitation. This vibrational coherence characterizes the collective vibrations around the excited probe atom with a long time scale for dephasing of 1–5 ps, considerably exceeding the time scale for initial configurational relaxation.

(4) Ultrafast energy acquisition via high-energy cluster-wall collisions (Schek *et al.* 1995). High-energy impact of atomic or molecular cluster ions (of sizes 10–1000 constituents, with velocities up to $v \sim 20\,\mathrm{km\,s^{-1}}$ and kinetic energies up to *ca.* 100 eV per particle) on insulator, semiconductor or metal surfaces, produces a new medium of extremely high density (up to *ca.* 2–4 times the standard density), high temperature (up to *ca.* 10^5 K) and high energy density (up to 10^2 eV per particle), which is temporarily generated during the propagation of a microshock wave within the cluster on the 10^2–10^3 fs time scale. Chemical applications, e.g. cluster impact dissociation of a probe diatomic molecule, have been attempted (Sheck *et al.* 1995). The dissociation process is limited by the vibrational period of the molecule.

Perspective of future explorations of cluster dynamic size effects pertain to:

(1) Real-time probing of adiabatic nuclear motion on multidimensional potential surfaces. These will involve preparation, e.g. (passive) vibrational mode selectivity and energy storage, e.g. intracluster vibrational energy redistribution. This problem is also central in biophysics, pertaining to protein folding (Zwanzig *et al.* 1992).

(2) Real-time dynamics of nuclear configurational changes. The real-time interrogation of cluster isomerization and of rigid–non-rigid transformation (i.e. 'melting') will be of considerable interest.

(3) Impact-induced vibrational coherence. These are induced by short-range repulsive interactions with intracluster dissociation fragments in I_2Ar_n (Lieman & Zewail 1993) or $I_2^-Ar_n$ (Papanikolas *et al.* 1995) or by Rydberg excitation, e.g. Xe^*Ar_n, and manifest the excitation of a vibrational wavepacket.

(4) Interstate fs dynamics in clusters. Radiationless electronic-vibrational relaxation in $metal_n$ (Baumert & Gerber 1995) clusters will elucidate the interrelations between electronic level structure and dynamics.

(5) Temporal records for nuclear dynamics. These presumably involve the Coulomb explosion of highly charged clusters (Last *et al.* 1997; Purnell *et al.* 1994).

(6) Real-time dynamics of elementary excitations in finite systems. These will involve collective compression nuclear modes and phonons. More esoteric elementary excitations constitute rotons (vortex rings) in quantum boson systems, e.g. $(^4He)_n$ with $n > 100$ or possibly $(H_2)_n$, which can be studied by two-particle excitations in the electronic origin of a probe molecule in the cluster (Hartmann *et al.* 1996).

(7) Thermal fs chemistry. Cluster impact dynamics via high-energy cluster–wall collisions or cluster–cluster collisions open up a new research area of thermal femtosecond chemistry.

6. Condensed phase dynamics

The pioneering studies of Kubo on electron–hole recombination in semiconductors (Kubo & Toyozawa 1955), of Marcus on electron transfer (ET) in solution (Marcus 1956) and of Förster on electronic energy transfer (EET) in the condensed phase (Förster 1959), laid the foundations for the theory of non-adiabatic dynamics in the condensed phase and in protein medium. The isomorphism between condensed phase non-adiabatic dynamics and intramolecular radiationless transitions was addressed (Kestner *et al.* 1974) in the context of the incorporation of quantum effects in ET theory. Both condensed phase and intramolecular radiationless transitions are induced by the coupling of doorway state(s) to a vibronic quasi-continuum. Perspectives of future studies of condensed phase dynamics pertain to:

(1) Real-time dynamics of elementary excitations, e.g. excitons, phonons, vibrons or rotons, in the context of one-particle and two-particle excitations.

(2) Real-time dynamics of configurational relaxation induced by electron solvation in fluids. The interesting adiabatic electron bubble formation equilibrium radius 17 Å at zero pressure in liquid He, Ne or H_2 was theoretically studied (Rosenblit & Jortner 1995, 1997), considering a combination of a quantum mechanical and a hydrodynamic effect, and should be subjected to experimental scrutiny.

(3) Dynamics of medium structure. The exploration of the time-dependent correlation function $g(r,t)$, following the excitation of a probe ion or molecule in a fluid, conducted by Hochstrasser (this volume), is novel and interesting.

(4) Interstate energy and phase relaxation in the Franck–Condon vibronic quasi-continuum. Non-adiabatic fs dynamics is governed by electronic coupling (V) and nuclear Franck–Condon factors. The coupling to the vibronic quasi-continuum is weakly correlated (i.e. small $\eta_{ss'} < 0.3$ for multimode model systems) resulting in high rates ($\propto V^2$) and in phase erosion (Bixon & Jortner 1997*a*, *b*). Further exploration of ultrafast fs electronic energy transfer (EET) and electron transfer (ET) processes (Bradforth *et al.* 1995; Vos *et al.* 1993; Kühn & Sundström 1997) will be of interest.

(5) Temporal records on rates for non-adiabatic dynamics. Recent experimental studies on ET dynamics (Zinth, this volume) established time scales of 80–100 fs, while studies of EET between prosthetic groups in the photosynthetic reaction centre and EET in photosynthetic antennas (Vos *et al.* 1993; Kühn & Sundström 1997; Fleming, this volume) established time scales of 50–100 fs. These ultrafast time scales for ET and EET (τ = 50–100 fs) correspond to vibrational frequencies of $(c\tau)^{-1} \cong$ 300–600 cm^{-1}, i.e. being on the time scale of the intramolecular frequencies and considerably exceeding the frequencies of medium (or protein) modes. The theory of radiationless transitions in the (weakly correlated) Franck–Condon quasi-continuum indeed predicts that the characteristic times can exceed the vibrational period (Bixon & Jortner 1997*a*, *b*).

(6) The ubiquity of vibrational coherence effects ranging from small to huge systems (Bradforth *et al.* 1995; Vos *et al.* 1993; Kühn & Sundström 1997; Wynne *et al.* 1996) raises the conceptual question of the distinction between the experimental condition of the preparation and interrogation on one hand, and the intrinsic aspects of relaxation and dephasing dynamics on the other hand. The manifestation of quantum beats is determined by (i) spectroscopic information, i.e. transition moments and periods, and (ii) dynamic information, i.e. modulation amplitudes and (low) correlation parameters $\eta_{ss'}$. For the excited state population probability, weak

modulation reflects dynamics information, while the quantum beats in the photon counting rates from the bacteriochlorophyll dimer in the photosynthetic bacterial reaction centre just provide spectroscopic information.

(7) Homogeneous versus heterogeneous broadening. These pertain to spatial effects, e.g. diagonal Anderson-type and off-diagonal disorder, which result in localization (Mukamel, this volume), and to temporal effects, which are reflected in the spectral density (Fleming, this volume).

7. Digression on biophysics

Remarkable progess has been made in biophysical ultrafast dynamics, with the experimental and the theoretical microscopic exploration of the primary processes of EET in photosynthetic antennas (Bradforth *et al.* 1995; Kühn & Sundström 1997) and ET in photosynthetic reaction centres (Bixon *et al.* 1995). The ultrafast EET processes (time scales from *ca.* 100 fs to ps) in different (non-universal) antenna structures effectively preclude energy waste. The basic issues which pertain to the mechanism and unidirectionality of the primary charge separation in the (universal) reaction centre (RC) structure of photosynthetic bacteria and photosystem II are not yet fully elucidated. These involve:

(1) Optimization principles for the primary ET process.

(2) Kinetic redundancy for the primary ET process. This will insure the stability of the photosynthetic apparatus with respect to mutagenesis, chemical modifications and environmental perturbation.

(3) Structural redundancy. This is manifested in the unique symmetry breaking, i.e. the unidirectionality of the primary charge separation across the 'active' A branch of the RC. ET transfer theory implies that unidirectionality is dominated by cumulative effects, i.e. electronic coupling and energetic modification of the energy gap across the 'inactive' B branch. Breaking of the symmetry breaking, i.e. inducing charge separation across the inactive branch, was accomplished by chemical modification of the energetics, which retards the ET process across the active branch (Michel-Beyerle, personal communication).

(4) Dynamic information complements and transcends structural data in photobiology. Structural information alone is not sufficient to understand the function of the RC, which rests on ultrafast dynamics. We should strive towards the unification of structure–dynamics–function relations in ultrafast biophysical and chemical dynamics.

8. Epilogue

We explored the rich and fascinating world of chemical and biological dynamics on the time scale of nuclear motion. Have we reached the temporal borders of the fundamental processes in chemistry and biology? The time scales of intermolecular and intramolecular nuclear motion definitely provide the relevant temporal limit for biological transformations. For chemical transformations even shorter time scales of femtoseconds to attoseconds (i.e. 1–0.1 fs) for electron dynamics will be unveiled. Examples which come to mind pertain to condensed phase bulk and surface electron–electron collisions and plasmon dynamics, electron–metal surface image state dynamics (Hertel *et al.* 1996; Wolf 1997), incipient excess electron localization in liquids,

electron–hole coherence of Wannier excitons and exciton wavepacket dynamics in semiconductor clusters and quantum dots, electron tunnelling from internal 'bubble' states in large $(He)_n$ clusters, and electron tunnelling microscopy in real-time (Botkin *et al.* 1996). Such chemical transformations involve changes in electronic state(s) without the involvement of nuclear motion, bypassing the constraints imposed by the Franck–Condon principle.

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