ULTRAFAST NONADIABATIC DYNAMICS. THEORETICAL STUDY OF FEMTOSECOND ELECTRON TRANSFER PROCESSES

Joshua JORTNER[1] and Mordechai BIXON[2]

School of Chemistry, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel;
e-mail: [1] jortner@chemsg1.tau.ac.il, [2] bixon@post.tau.ac.il

Received July 6, 1998
Accepted July 13, 1998

Most people say that it is the intellect which makes a great scientist. They are wrong. It is the character.

Albert Einstein, Zurich 1929

Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

This paper addresses the conceptual framework of femtosecond nonadiabatic dynamics involving electron transfer processes on the time scale of nuclear motion. Coupling and relaxation of a manifold of doorway states into a weakly correlated Franck–Condon quasicontinuum reflects the extension of the validity range of nonadiabatic dynamics for large values of the electronic coupling, transcendenting the vibrational period of nuclear motion. The theory is applied to ultrafast femtosecond electron transfer processes in solution.

Key words: Ultrafast femtosecond dynamics; Franck–Condon quasicontinuum; Electron transfer.

Remarkable progress has been made in the experimental and theoretical elucidation of the processes of energy acquisition, storage and disposal in large molecules, clusters, condensed phase and biophysical systems, as explored from the microscopic point of view[1–9]. This broad and important area of nonradiative chemical dynamics, from isolated molecules to biomolecules, played a central role in the development of modern chemistry. A major goal of this diverse and important research area of dynamics pertains to a unified description of structure–electronic level structure–energetic–spectroscopic–dynamic relations and correlations.

In the realm of modern physical and theoretical chemistry, the unification of concepts is imperative. A unified description of nonradiative electronic-vibrational processes in isolated large molecules and supermolecules, in the condensed phase and in the protein medium (Table I), can be provided in terms of nonadiabatic relaxation between two vibronic manifolds corresponding to two different zero-order electronic configurations. In this context, electron transfer (ET) processes[10–15] provide a central case of intramolecular and condensed phase nonradiative dynamics, encompassing ubiqui-

tous and fundamental phenomena in chemistry, physics and biology. A central application of the intramolecular radiationless transitions theory to ET pertains to the new and interesting issues of ultrafast ET dynamics[1,6,8], which is currently actively experimentally explored using femtosecond laser spectroscopy[2,3,7]. Novel aspects of the theory of the dynamics of doorway state(s) coupled to a weakly correlated Franck–Condon quasicontinuum provide the conceptual framework for the elucidation of different facets of population relaxation in the ultrafast dynamics of the total system, without invoking a separation into "system" and "bath" (refs[16–20]). These involve the establishment of the upper temporal limit for ET dynamics, nonexponential decay[15], vibrational coherence[21] and ET *via* bridges[22], laying cornerstones for the fascinating research area of femtosecond chemistry and femtosecond biology.

In this paper we explore the features of the vibrational quasicontinuum (referred to as the Franck–Condon quasicontinuum), which serve as a dissipative channel for nonadiabatic ET (refs[15,21,22]). Such information cannot be inferred from the decay of a

TABLE I
Intermolecular nonradiative processes in condensed phase

Process	Electronic states	Founders	Coupling
Electronic transfer in solids, liquids and biological systems	$DA \rightarrow D^+A^-$ D electron donor A electron acceptor	J. Franck R. A. Marcus	Two-center Coulomb and exchange
Small polaron	$A^-A \rightarrow AA^-$ A neutral molecule A^- negative ion	T. Holstein	Two-center one-electron Coulomb and exchange
Electron-hole recombination in semiconductors	$D^+\|k\rangle \rightarrow D^+\|b\rangle$ $\|k\rangle$ free electron $\|b\rangle$ electron bound to D^+ D^+ positive ion	R. Kubo Y. Toyozawa	Nuclear momentum
Electronic energy transfer in solids, glasses, liquids and biological systems	$D^*A \rightarrow DA^*$ D energy donor A energy acceptor	T. Forster D. Dexter	Intermolecular electrostatic interaction: dipole–dipole, monopole–monopole and also electron exchange
High-spin–low-spin interconversion in transition metal compounds	$M(S1) \rightarrow M(S2)$	M. Bixon	Spin–orbit
Group transfer in hemoglobin	$Fe(S = 2) + CO \rightarrow$ $Fe(S = 0) \bullet CO$	H. Frauenfelder	Spin–orbit

single doorway state and the formalism has to be extended to include correlated effects in the coupling and interference effects in the decay of several doorway states into the common Franck–Condon quasicontinuum[15,21,22]. Novel aspects of the establishment of the upper temporal limit for ET dynamics will emerge from this analysis. These concepts bear on the novel and fascinating issues of ultrafast ET dynamics on the time scale of nuclear motion.

THE FRANCK–CONDON QUASICONTINUUM

A basic concept pertaining to the unification of ET with the theory of radiationless transition involves the quantification of the quasicontinuum both for intramolecular and for medium dynamics. The dissipative vibronic quasicontinuum for ET and for other intramolecular and medium coupled nonadiabatic relaxation processes was referred to by us as the Franck–Condon quasicontinuum[15,21,22] and its properties were explored by us. The dissipative channels for intramolecular and/or condensed phase dynamics can be characterized in terms of the state specificity of the matrix elements of the Hamiltonian (H), *i.e.*, $V_{sl} = \langle s|H|l\rangle$, for the coupling of the doorway states $|s\rangle$, $|s'\rangle$, $|s''\rangle$, ..., with the $\{|l\rangle\}$ states of the dissipative continuum or quasicontinuum (Fig. 1). The state dependence of the couplings was quantified by the correlation parameters[21,22]

$$\eta_{ss'} = \langle V_{sl}\, V_{ls'}\rangle / [\langle V_{sl}^2\rangle \langle V_{s'l}^2\rangle]^{1/2} \quad , \qquad (1)$$

where $\langle\ \rangle$ denotes an average over the relevant finite energy range. In the theory of intramolecular and condensed phase dynamics dissipative channels, constituting the continua and quasicontinua, can be segregated into: (i) "smooth" decay channels, involving slow energy dependence (E_l) of S_{sl}, with $\eta_{ss'} \cong 1$ for $s \neq s'$, *i.e.*, dissociative and ionizative continua[6,8], and the electronic quasicontinuum for ultrahigh Rydberg states[23]

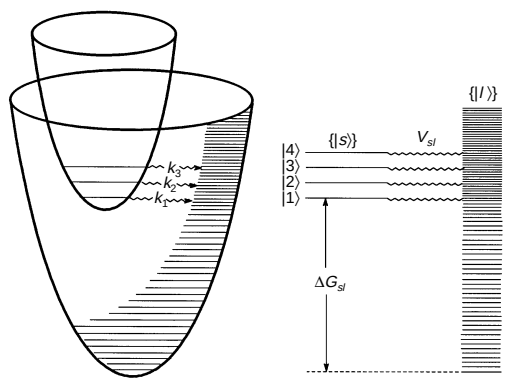

FIG. 1
Energy levels scheme for nonadiabatic ET dynamics. The vibronic manifold of the doorway states $\{|s\rangle\}$ is coupled to the dissipative quasicontinuum $\{|l\rangle\}$

and (ii) "nonsmooth" decay channels, where V_{sl} exhibits a large and irregular energy (E_{sl}) variation, with $\eta_{ss'} << 1$ and $s \neq s'$; *i.e.* the vibrational Franck–Condon quasicontinuum. This is the case for nonadiabatic intramolecular and/or condensed phase dynamics, *e.g.*, ET, which is of interest to us.

The distinction between "smooth" and "nonsmooth" 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 quasicontinuum. This distinction 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 in the condensed phase.

Model calculations for correlation parameters were conducted[21] for a Franck–Condon quasicontinuum in a multimode harmonic system of two displaced potential surfaces. The input parameters are the harmonic modes $\underset{\sim}{\omega} = (\omega_1, \omega_2, ..., \omega_n)$, the reduced displacements $\underset{\sim}{\Delta} = (\Delta_1, \Delta_2, ... \Delta_n)$, the couplings $\underset{\sim}{S} = 1/2\ (\Delta_1^2, ..., \Delta_n^2)$ (the reorganization energy being $\lambda = \underset{\sim}{\omega} \cdot \underset{\sim}{S}$), the electronic energy gap ΔE and the electronic coupling V. Scaling laws for the energy gap and for the vibrational frequencies (for constant coupling strengths) can be advanced in terms of an additional energetic scaling parameter ξ. Keeping the reduced displacements $\underset{\sim}{\Delta}$ (or $\underset{\sim}{S}$) fixed, the scaled parameters $\xi\underset{\sim}{\omega}$, $\xi\lambda$, $\xi\Delta E$ and ξV will yield invariant results for the level structure and for the spectral density. With these scaled parameters the time is scaled as t/ξ. The correlation parameters were expressed by the vibrational overlap integrals $f(s;l) = \langle \chi_s | \chi_l \rangle$ between the nuclear wave functions χ_s and χ_l in the $\{|s\rangle\}$ and $\{|l\rangle\}$ vibronic manifolds, respectively, being presented in the form

$$\eta_{ss'} = \frac{\langle f(s;l) f(l;s') \rangle}{[\langle f(s;l)^2 \rangle \langle f(s;l')^2 \rangle]^{1/2}} \quad . \tag{2}$$

The input parameters taken for these model calculations were the frequencies $\underset{\sim}{\omega}$ (in cm^{-1})= (117, 75, 35, 27) and the (reduced) couplings $\underset{\sim}{S}$ = (1.0, 1.1, 2.0, 3.0), which give λ = 350 cm^{-1} and the energy gap ΔE = 500 cm^{-1}. The highest vibrational mode is close to the intermolecular vibrational motion in the D-A charge transfer complex, while the lower vibrational frequencies mimic solvent modes. The energetic parameters were chosen to insure the attainment of a vibrational quasicontinuum, *i.e.*, $\Delta E >> \omega_\mu$ for all vibrational frequencies. The averaging $\langle\ \rangle$ over the density of states in Eqs (*1*) and (*2*) is taken over the relevant energy range δE, where the density of states is ρ, *i.e.*,

$$\langle V_{s,l}\, V' \rangle = \left(\frac{1}{\rho \delta E} \right) \sum_l V_{sl}\, V_{s'l} \ , \qquad E_s, E_{s'} \in \delta E \ . \tag{3}$$

The energy range δE includes the energies of the doorway states E_s and $E_{s'}$ and has to span the E_l domain of the relevant $\{|l\rangle\}$ states which contribute to interference between $|s\rangle$ and $|s'\rangle$. It should be noted that if $\delta E \to \infty$ and the sum over the $\{|l\rangle\}$ states includes the entire manifold, then $\langle V_{sl} V_{ls'}\rangle = 0$ ($s \neq s'$). The energy range δE has to be taken as finite, to include the subset of the relevant $\{|l\rangle\}$ states, *i.e.*, $\delta E > |E_s - E_{s'}|$. We shall take $\delta E = d|E_s - E_{s'}|$, where $d \cong 5$. Numerical calculations show that the average product $\langle V_{sl} V_{ls'}\rangle$ taken over the energy range δE is not sensitive to the magnitude of the parameter d specified above.

The zero-order basis set consisted of $n_s = 100$ doorway states $\{|s\rangle\}$ and $n_l = 3\,000$ quasicontinuum states[21]. From this analysis we conclude that the absolute values of all the correlation parameters are considerably lower than unity (Fig. 2). Their highest values fall in the range $|\eta_{ss'}| \cong 0.4$–0.2. The relatively high values of $|\eta_{ss'}|$ correspond

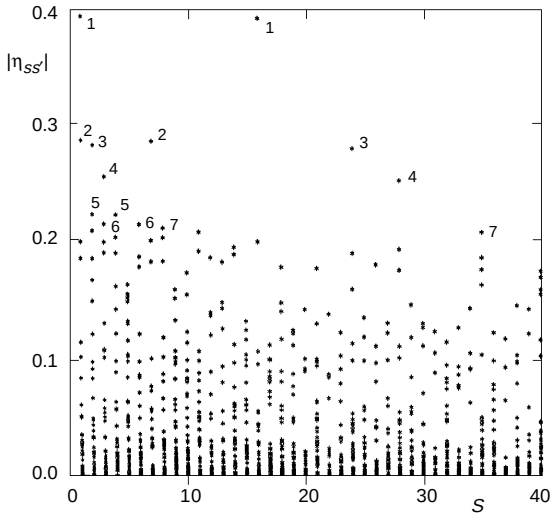

FIG. 2

Absolute values of the correlation parameters $|\eta_{ss'}|$, Eq. (*1*), between doorway states s,s'. Data for the four-mode Franck–Condon system are given with the frequencies $\nu_1 = 27$ cm^{-1}, $\nu_2 = 35$ cm^{-1}, $\nu_3 = 75$ cm^{-1}, $\nu_4 = 117$ cm^{-1}, with the coupling parameters specified in the text. The s and s' states are labeled by the index $s = 1, 2, 3, ..., N$ in the order of increasing energy. Each s state is correlated with the states $s' = 1, ..., N$ and *vice versa*, so that for each s,s' two identical correlation parameters $\eta_{ss'}$ and $\eta_{s's}$ are presented (which allows for the easy identification of s and s'). The larger correlation parameters are labeled by numbers, which represent the corresponding values of s and s', each labeled by the combination of the quantum numbers $\sum_j \kappa_j \omega_j$ ($j = 1$–4 and κ_j are integers) and being given by $s,s' = [\sum_j \kappa_j \omega_j, \sum_j \kappa_j' \omega_j']$, while 0 corresponds to the electronic origin. $\Delta E = 500$ cm^{-1}. The energy range $\Delta E - 200$ cm$^{-1} \leq E \leq \Delta E + 250$ cm^{-1} contains $N = 40$ states and 1 560 values of $\eta_{ss'}$. The pairs of states with the largest values of ($\eta_{ss'} > 0.2$), which are labelled as 1–7, are: 1 [0, ν_4]; 2 [0, ν_3]; 3 [ν_1, $\nu_1 + \nu_4$]; 4 [ν_2, $\nu_2 + \nu_4$]; 5 [ν_1, $2\nu_1$]; 6 [ν_2, $2\nu_2$]; 7 [$3\nu_1$, $3\nu_1 + \nu_4$]

to members of a vibrational progression with s and s' differing by a single quantum number. For multimode changes between s and s' very low values of $|\eta_{ss'}| < 0.1$ are exhibited (Fig. 2). From this analysis we infer that weak but nonvanishing correlations, which are subjected to propensity rules, exist for the coupling of a manifold of doorway states to a Franck–Condon quasicontinuum. The existence of weak correlations for coupling to the Franck–Condon quasicontinuum results in (partial) emission of resonance interference effects, in analogy with random coupling models[24–29] for intramolecular coupling and dynamics, where interference effects are completely eroded. The low values of the correlation parameters exhibit the following important implications:

1. For resonance DA–D^+A^- (or DBA–D^+B^-A) coupling the weak correlation parameters for the Franck–Condon quasicontinuum provide a phase erosion mechanism for the dynamics. In particular, resonance coupling between a doorway state and two coupled Franck–Condon quasicontinua results in sequential DBA $\rightarrow$ D^+B^-A $\rightarrow$ D^+BA^- kinetics, with the chemical mediation *via* the bridge originating from phase erosion due to weakly correlated couplings[22].

2. Preservation of partial interference effects, being manifested in vibrational coherence in the ET dynamics[21].

3. The weak correlations will determine the time scale for ultrafast relaxation into the Franck–Condon quasicontinuum. We shall now address this central issue of the temporal limits for relaxation in the Franck–Condon quasicontinuum.

ULTRAFAST ET DYNAMICS ON THE TIME SCALE OF NUCLEAR MOTION

For 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[30,31], which sets an upper limit on the relaxation rate k. For the population decay of a set of equally spaced (nearest neighbor 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 ($\Gamma << \omega$) to $k = \omega/h$ for overlapping resonances ($\Gamma >> \omega$). The overlapping resonance domain provides an upper limit for the nonradiative rates, *i.e.*, $k \leq \omega/h$, which is determined by the level spacing, *i.e.*, the intramolecular vibrational frequency, with the time scale $t \geq h/\omega$, *e.g.*, $t \geq 33$ fs for $\omega = 1\ 000$ cm^{-1} and $t \geq 330$ fs for $\omega = 100$ cm^{-1}. This situation prevails for intramolecular dynamics in a "smooth" nuclear continuum, *i.e.*, electronic and vibrational predissociation[2–9]. The experimental ultrafast fs electronic predissociation times of diatomics[8,9] are indeed limited by the overlapping resonance constraints. The situation is different for the decay of weakly correlated ($\eta_{ss'} << 1$) overlapping resonances into a "non-smooth' Franck–Condon vibrational quasicontinuum, when interference effects are expected to be much less pronounced than in the case of a "smooth" correlated channel. Weakly correlated coupling with a Franck–Condon quasicontinuum is expected to pre-

vail for nonadiabatic ET. In this case of weakly correlated overlapping resonances decaying into a common Franck–Condon quasicontinuum (Fig. 3), inteference effects are eroded to a large extent. Accordingly, with increasing the coupling strength V so that the situation of overlapping resonances is realized, one expects that the (averaged) radiationless transition rates will not be limited by the level spacing, *i.e.*, by the vibrational frequency. Rather, the temporal upper limit $k \propto V^2 \geq \omega/h$ can be realized for decay into the Franck–Condon quasicontinuum ET dynamics. These expectations are born out by model calculations for the decay dynamics into a Franck–Condon quasicontinuum in a four-mode harmonic system (Fig. 3). For large values of V, when the limit of overlapping resonances is attained, the population probability of the doorway state (corresponding to the electronic origin of the doorway state's manifold) exhibits a pronounced nonexponential decay. The mean lifetimes τ_{ET} (corresponding to the population decay e^{-1} of the initial value) roughly exhibit the $1/\tau_{ET} \propto V^2$ relation with a rather small deviation (30%) even for large values of V (Fig. 3). The mean lifetimes for large values of V are considerably shorter than the characteristic vibrational periods for all the modes (Fig. 3). These characteristics of the Franck–Condon quasicontinuum extend the limits for the applicability of the nonadiabatic ET theory. We infer that the range of nonadiabatic ET dynamics (with microscopic rates $k \propto V^2$) is expected to prevail for stronger coupling than previously realized. For a sufficiently strong coupling the tem-

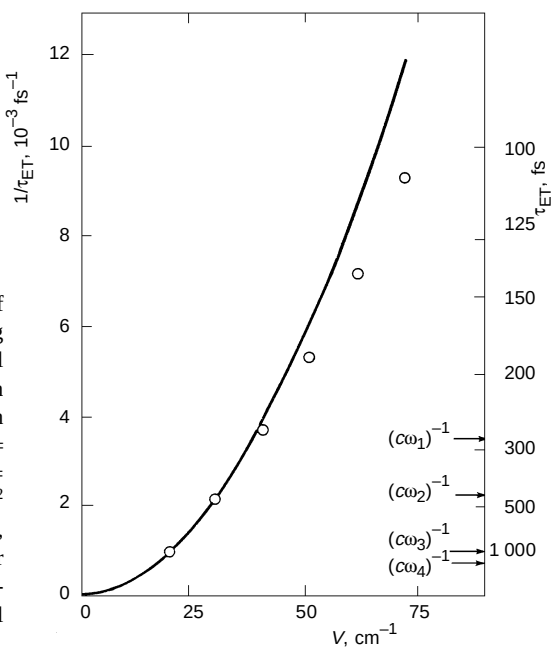

FIG. 3

Model calculations of the V dependence of the (mean) lifetime for ET (corresponding to the population decay of e^{-1} of the initial value). The open points are obtained from calculations for a four-mode system with the following input parameters: $\underset{\sim}{\omega}$ (in cm^{-1}) = (117, 75, 35, 27); $\underset{\sim}{S}$ = (1, 1.2, 3, 3); $-\Delta E$ = 465 cm^{-1}; λ = 500 cm^{-1}. The $1/\tau_{ET} \propto V^2$ dependence is represented by the solid line, and spans a broad range. Note that for strong V the (mean) ET lifetimes are considerably shorter than the vibrational periods of all the modes

poral upper limits for (mean) ET rates will be realized on a time scale which is comparable to, or even shorter than, the relevant vibrational periods.

Temporal records for ET dynamics are of considerable interest. Recent experimental studies of ET dynamics in solution established ultrafast time scales in the region <100 fs. Photoinduced ET in the asymmetric mixed-valence compound $(NH_3)_5Ru^{+2}CNRu^{+3}(CN_5^-) \rightarrow (NH_3)_5Ru^{-3}CNRu^{+2}(CN_5^-)$ in water or formamide occurs[32–37] on a time scale shorter than 100 fs. This system is characterized by a large exoergic energy gap corresponding to the inverted ET region, so that the radiationless transitions theory for the description of ET is definitely applicable, as curve crossing does not occur in the relevant energy region. The characteristic metal–ligand frequencies of this compound, which effectively contribute to the ET dynamics, are in the range $\omega \approx 250$–600 cm^{-1} (ref.[38]) with the characteristic vibrational times 130–55 fs, whereupon ET occurs on the time scale comparable to, or shorter than, that for the vibrational period. Another interesting example pertains to ultrafast photoinduced ET in the oxazine 1/*N*,*N*-dimethylaniline system which occurs on the time scale of 80 fs, with an indication of a shorter 30 fs component[39]. The 30–80 fs ET time marks the same time scale as the vibrational motion of the 562 and 602 cm^{-1} S_1 modes of oxazine 1 in its electronically excited state (≅55 fs), which are accessible by optical excitation[39]. This observation is in accord with our theoretical predictions for radiationless transitions in the (weakly correlated) Franck–Condon quasicontinuum, which predicts that characteristic ET times can exceed the vibrational period. The fastest room temperature ET rates are recorded to date in synthetic supermolecules with $k \cong (30\text{ fs})^{-1}$–$(80\text{ fs})^{-1}$ (ref.[39]). In the photosynthetic bacterial reaction center[40–43], the rates for primary charge separation in the wild-type system of *Rps. viridis* $^1P^*BH \rightarrow P^+B^-H \xrightarrow{k_2} P^+BH^-$ are $k_1 \approx (3\,000\text{ fs})^{-1}$ and $k_2 \approx (800\text{ fs})^{-1}$ at $T = 300$ K, while at 50 K $k_1 \cong (1\,000\text{ fs})^{-1}$, with an increase of the rate at a lower temperature reflecting activationless ET (refs[40–43]). These ET lifetimes $\tau_{ET}^{(1)} = k_1^{-1}$ and $\tau_{ET}^{(2)} = k_2^{-1}$ are still lower than the maximal ET rates in a system where the coupling to a $\omega \approx 100$ cm^{-1} frequency (*i.e.*, the bacteriochlorophyll dimer frequency[15] with a vibrational period of ≅330 fs) dominates the ET dynamics. Recent studies of the L168H → F mutant (where a histidine in the vicinity of the dimer is replaced by a phenylalanine) gives $\tau_{ET}^{(1)} = 200 \pm 100$ fs for the low temperature range from 50 to 150 K (ref.[44]). This short ET lifetime can be attributed to the enhancement of V in the mutant relative to the wild-type system (*e.g.*, by a numerical factor of ≈1.8 at 50 K). This value of $\tau_{ET}^{(1)}$ for the mutant is shorter than the characteristic vibrational period of ≅330 fs for this system, reflecting the extension of the validity range of nonadiabatic dynamics in the Franck–Condon quasicontinuum for large values of V transcendenting the vibrational period of nuclear motion.

REFERENCES

1. Jortner J.: *Discuss. Faraday Soc.* **1997**, *108*, 1.
2. Manz J., Woste L. (Eds): *Femtosecond Chemistry*. VCH, Weinheim 1995.
3. Chergui M. (Ed.): *Femtochemistry*. World Scientific, Singapore 1996.
4. Zewail A. H. (Ed.): *Femtochemistry*. World Scientific, Singapore 1997.
5. Lethokov V. S.: Ref.[3], p. 25; and references therein.
6. Jortner J.: Ref.[3], p. 15; and references therein.
7. Sundstrom V. (Ed.): *Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic Scale Resolution*. Nobel Symposium 101. Imperial College Press, London 1997.
8. Jortner J.: Ref.[7], p. 235.
9. Jortner J.: *Philos. Trans. R. Soc. London* **1998**, *356*, 447.
10. Marcus R. A.: *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
11. Levich V. G. in: *Physical Chemistry – Advanced Treatise* (H. Eyring, D. Henderson and W. Jost, Eds), 9B. Academic Press, London 1970.
12. Kestner N. R., Logan J., Jortner J.: *J. Phys. Chem.* **1974**, *78*, 2148.
13. Bixon M., Jortner J.: *Faraday Discuss. Chem. Soc.* **1982**, *74*, 17.
14. Marcus R. A.: *Rev. Mod. Phys.* **1993**, *65*, 599.
15. Bixon M., Jortner J.: *Adv. Chem. Phys.*, in press.
16. Tang J., Lin S. H.: *Chem. Phys. Lett.* **1996**, *254*, 6.
17. Jean J. M., Friesner R. A., Fleming G. R.: *J. Chem. Phys.* **1992**, *96*, 5827.
18. Jean J. M., Fleming G. R., Friesner R. A.: *Ber. Bunsen–Ges. Phys. Chem.* **1991**, *95*, 253.
19. Wolfseder B., Domcke W.: *Chem. Phys. Lett.* **1996**, *259*, 113.
20. Domcke W., Stock G.: *Adv. Chem. Phys.* **1997**, *100*, 1.
21. Bixon M., Jortner J.: *J. Chem. Phys.* **1997**, *107*, 1470.
22. Bixon M., Jortner J.: *J. Chem. Phys.* **1997**, *107*, 5154.
23. Bixon M., Jortner J.: *J. Phys. Chem.* **1996**, *100*, 11914.
24. a) Wigner E. P.: *Ann. Math. Lpz.* **1955**, *62*, 548; b) Wigner E. P.: *Ann. Math. Lpz.* **1958**, *67*, 325.
25. Kommandeur J., Jortner J.: *Chem. Phys.* **1978**, *28*, 273.
26. Nitzan A., Jortner J.: *J. Chem. Phys.* **1979**, *71*, 3542.
27. Jortner J.: *Adv. Laser Spectrosc.* **1977**, *113*, 88.
28. Schek I., Jortner J.: *J. Chem. Phys.* **1980**, *72*, 2054.
29. Carmeli B., Schek I., Nitzan A., Jortner J.: *J. Chem. Phys.* **1980**, *72*, 1928.
30. Mies F. H., Kraus M.: *J. Chem. Phys.* **1965**, *45*, 4453.
31. Rice S. A., McLaughlin I. J., Jortner J.: *J. Chem. Phys.* **1968**, *49*, 2756.
32. Yoshihara K., Tominaga K., Nagasawa Y.: *Bull. Chem. Soc. Jpn.* **1995**, *68*, 696.
33. Barbara P. F., Meyer T. J., Ratner M. A.: *J. Phys. Chem.* **1996**, *100*, 13148.
34. Kliner D. A. V., Tominaga K., Walker G. C., Barbara P. F.: *J. Am. Chem. Soc.* **1992**, *114*, 8323.
35. Tominaga K., Kliner D. A. V., Johnson A. E., Levinger N. E., Barbara P. F.: *J. Chem. Phys.* **1993**, *98*, 1228.
36. Levinger N. E., Johnson A. E., Walker G. C., Barbara P. F.: *Chem. Phys. Lett.* **1992**, *196*, 159.
37. Walker G. C., Barbara P. F., Doorn S. K., Dong Y., Hupp J. T.: *J. Phys. Chem.* **1991**, *95*, 5712.
38. Doorn S. K., Hupp J. T.: *J. Am. Chem. Soc.* **1989**, *111*, 4704.
39. Seel M., Engleitner S., Zinth W.: *Chem Phys. Lett.* **1997**, *275*, 363.
40. Deisenhofer J., Norris J. R. (Eds): *The Photosynthetic Reaction Center*. Academic Press, San Diego 1993.
41. Michel-Beyerle M. E. (Ed.): *The Reaction Center of Photosynthetic Bacteria. Structure and Dynamics*. Springer, Berlin 1995.

42. Holzapfel W., Finkele U., Kaiser W., Oesterhelt D., Scheer H., Stilz H. U., Zinth W.: *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *7*, 5168.
43. Bixon M., Jortner J., Michel-Beyerle M. E.: *Chem. Phys.* **1995**, *197*, 389.
44. Zinth W., Huppmann P., Penzkofer H., Arlt T. in: *Ultrafast Phenomena X* (P. F. Barbara, J. G. Fujimoto, W. H. Knox and W. Zinth, Eds), p. 330. Springer, Berlin 1997.