Chapter 1

Interaction of Theory and Experiment in Reaction Kinetics

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1.1 INTRODUCTION

The interaction of experiment and theory clearly delights John Albery—a colleague and friend to whom this chapter is dedicated. That interaction is the principal theme of this contribution. The examples given below are taken from the experiences of my research group in a number of fields in, or related to, reaction kinetics:

(1) high-resolution spectroscopic studies and intramolecular vibrational energy migration;
(2) long-range electron transfer (ET) in proteins;
(3) ET in a broad range of systems;
(4) ion, atom and group transfers;
(5) photosynthetic reaction center ET;
(6) solvent dynamics and the chemists' delayed use of Kramers' theory;
(7) unimolecular reaction rates and products' distribution of rotational-vibrational quantum states;
(8) unimolecular reaction rates in clusters;
(9) vibrational adiabaticity and reaction coordinates;
(10) graph theory and additivity in delocalized (aromatic) molecules.

New experiments have been very rich in stimulating theoretical ideas and each of the above topics concerns some particular aspect of the interaction between experiment and theory. Comments on the latter are made at the end of each topic treated in this chapter.

Some of the examples involve the derivation of equations, the predictions from which can be tested experimentally. The choice of which particu-

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lar examples to cite was not easy. Others that could have been used include: ETs across liquid-liquid and other interfaces; chemiluminescent ETs; various CH overtone spectra; semiclassical dynamics; reaction path Hamiltonians; and translational energy distribution of the products of unimolecular reactions. Several of the topics described below are also discussed in more detail in Reference [1], a recent survey of transition state (TS) theory and its applications and in Reference [2].

1.2 EXAMPLES OF INTERACTION OF THEORY AND EXPERIMENT

1.2.1 High-resolution overtone spectroscopy of many-atom systems

Some years ago, Scoles and coworkers [3] measured the acetylenic CH overtone spectra ($\upsilon = 0 \rightarrow 1$, $\upsilon = 0 \rightarrow 2$) in $(CH_3)_3$ YC≡CH and in their deuterated methyl counterparts:

$$(CH_3)_3YC{\equiv}CH(\upsilon = 0) + h\nu \rightarrow (CH_3)_3YC{\equiv}CH(\upsilon = 1, 2)(Y = C, Si)\,. \tag{1.1}$$

The spectral lines for $\upsilon = 0 \rightarrow 1$ and for $\upsilon = 0 \rightarrow 2$, were much narrower for the Si than for the C compound. For the C compound, the line was broad enough to determine its shape which was found to be Lorentzian. These results are illustrated in Fig. 1.1.

In one view, the result that the C system has a broader spectrum may seem surprising. The width of a homogeneously broadened line is related, in the real-time domain, to the lifetime of the excited zeroth-order state (here the $\upsilon = 1$, or $\upsilon = 2$ acetylenic CH state): the broader the spectral line the shorter the lifetime, according to the uncertainty principle. According to one view, the CH vibrational quantum transfers its energy more rapidly to the vibrations of the rest of the molecule when there is a greater number of those vibrational acceptor quantum states per unit of energy. The Si compound, because of the larger mass of Si compared with C, has a thirty-fold higher density of vibrational states. However, the paradox is that its acetylenic CH spectrum is much narrower rather than broader.

Another possibility is that the heavier mass of the Si may tend to block the kinetic energy transfer between the two parts of the molecule. (There

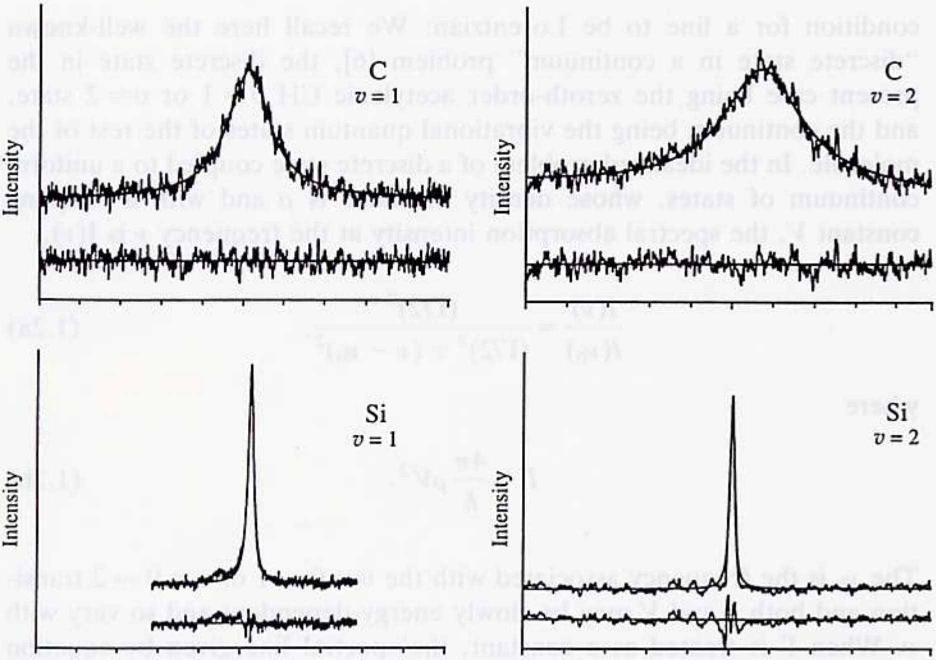

Fig. 1.1. Acetylenic CH overtone spectra of $(CH_3)_3$ C C≡C—H and $(CH_3)_3$ SiC≡C—H. The solid line in the former is the Lorentzian function [3].

had been some earlier controversy on heavy mass blocking, e.g., in the case of a fluorinated tetraallyl tin radical [4].) Some classical and semiclassical calculations were available, but only on a small hypothetical model system. However, a classical trajectory study did not seem desirable for the present system because of the low value of v of the acetylenic CH and the very large number of coordinates. Unphysical results are known to arise for such systems [5]. The system also seemed much too large to undertake semiclassical (semiclassical quantization) studies, our large previous investment in several-dimensional (two- and three-dimensional) semiclassical theory notwithstanding. Accordingly, a quantum mechanical approach seemed best, but the question was how. There are 42 vibrational modes in $(CH_3)_3$ YC≡CH, with potentially millions of zeroth-order acceptor vibrational quantum states.

We consider first the Lorentzian aspect and a sufficient but not necessary condition for a line to be Lorentzian: We recall here the well-known "discrete state in a continuum" problem [6], the discrete state in the present case being the zeroth-order acetylenic CH $\upsilon = 1$ or $\upsilon = 2$ state, and the continuum being the vibrational quantum states of the rest of the molecule. In the idealized problem of a discrete state coupled to a uniform continuum of states, whose density of states is ρ and with a coupling constant V, the spectral absorption intensity at the frequency ν is I(ν).

$$\frac{I(\nu)}{I(\nu_0)} = \frac{(\Gamma/2)^2}{(\Gamma/2)^2 + (\nu - \nu_0)^2}, \tag{1.2a}$$

where

$$\Gamma = \frac{4\pi}{\hbar}\rho V^2. \tag{1.2b}$$

The ν_0 is the frequency associated with the $\upsilon = 0 \rightarrow 1$ or $\upsilon = 0 \rightarrow 2$ transition and both ρ and V may be slowly energy-dependent and so vary with ν. When Γ is treated as a constant, the spectral line given by equation (1.2) is a Lorentzian. A well-known consequence is that if the zeroth-order CH state is prepared optically (by a laser pulse broader than the width Γ), its temporal decay to the states of the rest of the molecule would be a single exponential with a decay constant Γ.

On the other hand, when the density of the "continuum" of vibrational states of the system is small, it would have to be treated as being finite rather than as a continuum. Then $I(\nu)$ would be "spiky" rather than Lorentzian. Two questions that arise are how can such a simple Lorentzian expression characterize the real and very complicated $(CH_3)_3$ $CC{\equiv}CH$ system and why does the Si compound have the narrower spectral line?

In the actual molecule the "bath" of zeroth-order vibrational states does not really form an exactly uniform continuum, each with a constant or at most energy-dependent coupling element. The exact vibrational quantum states of the system of all states but the cited acetylenic state υ are irregularly but extremely closely spaced and can be expected to have quite variable couplings to that state. However, if we divide the relevant energy range of the spectrum into very small cells, each cell containing numerous vibrational states of the system, there will be a mean value of the coupling element V to the cited υ state and a mean density of states in each cell and each mean may vary slowly from cell to cell. With such a coarse-graining we can see how the simple expression in equation (1.2), with an approximately constant Γ, might apply even for this very complicated system. Similar to the case of the statistical mechanics of bulk systems, the sheer number of contributing states can yield a certain simplicity.

To treat the actual problem, an approximate description for the bath was used involving zeroth-order vibrational quantum states of the system of all vibrational coordinates (apart from the state v of the acetylenic CH stretch) [7, 8]. Approximate generic anharmonicities were introduced coupling those modes with each other and with the state v. A tier structure connecting the initial acetylenic CH state v to the first tier of vibrational quantum states was introduced. In turn, this tier was coupled to the next and so on for more than 30 tiers. With an artificial intelligence search method, the most important states in this tier structure could be selected. Most of the coupling occurred via off-resonant vibrational states and we termed the overall coupling process vibrational superexchange, by analogy with the usual electronic superexchange for coupling of two electronic states via off-resonant states.

Ultimately, a Lorentzian lineshape emerged in the calculation for the C compound [7, 8]. It was also found that while the density of states for the Si molecule was indeed some thirty-fold higher than that of the C molecule, the density of the coupled states in the first five or so tiers, which were particularly important in determining the overall spectral width, was substantially greater for the C compound (Fig. 1.2). A variety of other effects were uncovered, such as the need for using enough couplings (e.g., quartics in some cases) to avoid "dead end states", which give rise to spurious peaks. Ultimately, good agreement was obtained without adjustable parameters. Some questions still remain to be investigated, including the detailed vibrational state paths for the transfer. Perhaps, they can be addressed, as Dr. Stuchebrukhov suggested, by using his new method [9] for following *tunneling paths*.

Comment: In this example an experimental paradox prompted the theoretical treatment. The simplicity of the experimental lineshape also prompted some thought as to the reason for such simplicity. With an approximate force field, and assumed generic anharmonicities, the method itself can be used to make predictions for other molecules.

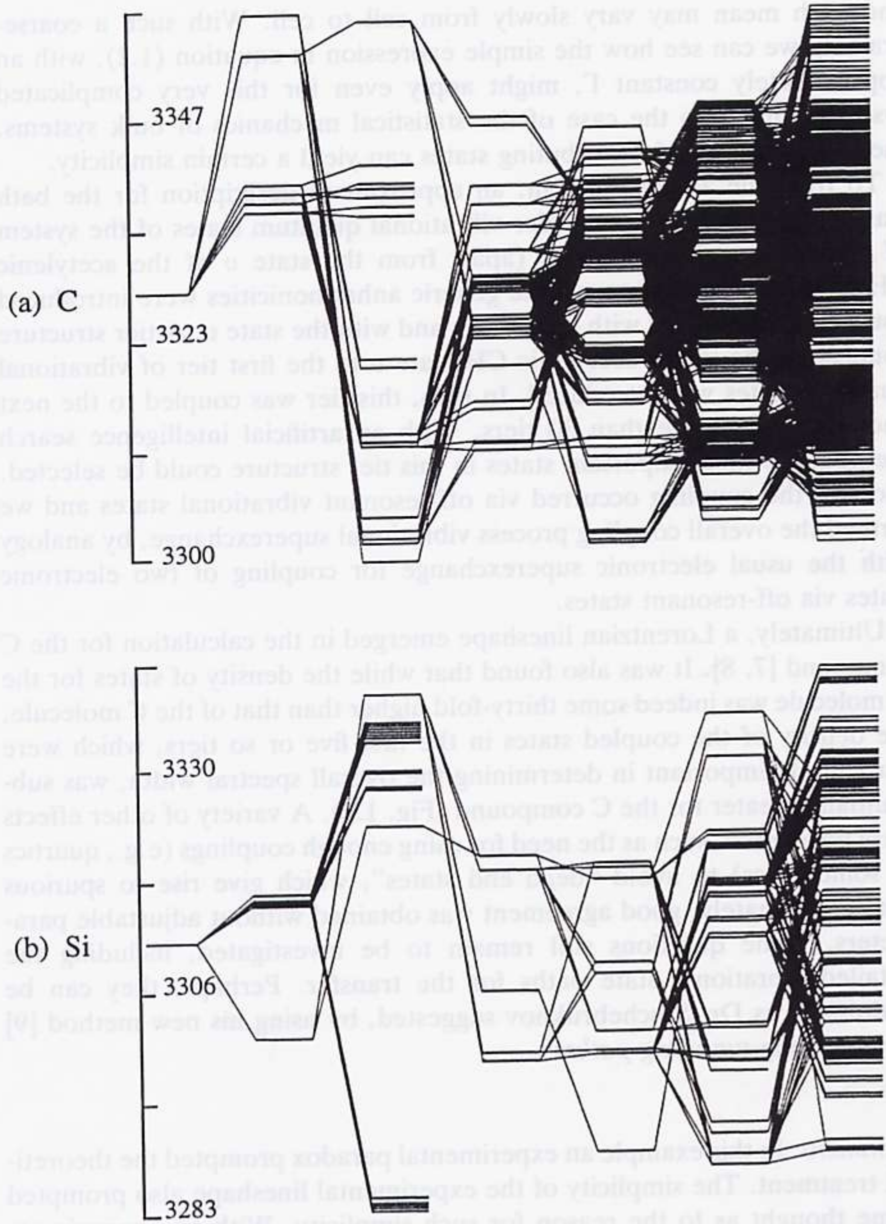

Fig. 1.2. Tier structure connecting zeroth-order vibrational quantum states for the molecules in Fig. 1.1 [7].

1.2.2 *Long-range ET in proteins*

Gray and coworkers described an interesting set of studies on the long-range ET in proteins, such as cytochrome c or azurin [10]. The position of an electron acceptor A relative to that of a donor D, both in the protein, was varied, using site-directed mutagenesis and ET rates were determined. Two factors affect the reaction rate as shown in equations (1.3)–(1.4). One is an activation free energy ΔG^*, and the other the matrix element H_{DA} coupling the donor and acceptor electronic orbitals for long-range electron coupling [11]:

$$k_{\text{rate}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{\exp(-\Delta G^*/k_B T)}{(4\pi\lambda k_B T)^{1/2}}. \tag{1.3}$$

Here, λ is the "reorganization energy" and

$$\Delta G^* = (\lambda/4)(1 + \Delta G^{\mathrm{o}}/\lambda)^2, \tag{1.4}$$

where ΔG^{o} is the standard free energy of reaction, $\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^+ + \mathrm{A}^-$. (The actual ionic charges in this one-ET typically differ from those indicated.)

There is now a well-defined theory-based method for separating these two factors: By using suitable substituents, ΔG^{o} can be varied. Either by extrapolation or otherwise, a condition can be attained where $\Delta G^{\mathrm{o}} \cong -\lambda$, and then the $\Delta G^* \cong 0$. The resulting rate constant in equation (1.3) then provides directly the value of $|H_{\mathrm{DA}}|^2$, after an approximate estimate of λ is made from the data on the ΔG^{o} dependence.

In this way, Gray and coworkers [10] obtained results for $|H_{\mathrm{DA}}|^2$'s for the protein system (containing about 100 amino acids for cytochrome c). Similarly, Dutton and coworkers [12] obtained $|H_{\mathrm{DA}}|^2$'s for quinone reactions in a photosynthetic reaction center. The next theoretical problem was how to calculate the coupling for comparison with Gray's data. The difficulty was that the protein is quite non-uniform in its composition and, being so large, contains numerous electronic orbitals coupling the electron donor and the acceptor. Using the known molecular structure of the protein, we applied a particular molecular orbital method [13] that we had tested previously against experiment for long-range ET in simple systems

[14]. Employing an artificial intelligence search technique to locate the most important amino acid paths, we found the individual amino acids orbitals contributing most to an electronic superexchange (i.e., off-resonant) mechanism [15, 16]. This smaller subsystem was then used to calculate H_{DA} and so compare with the experimental data [15, 16]. Later, a more all-embracing approach was developed by Dr. Stuchebrukhov in our group, in which the entire protein was treated and "pruned" to locate the most important amino acid paths [17]. He has since extended the theoretical analysis further to obtain the distribution of tunneling paths [9]. Theoretical treatments of other ET groups are cited in refs. [15–17].

There is a strong parallel between the vibrational energy coupling in Section 1.2.1 and the electronic state coupling here, as we have already noted. In the former, the zeroth-order states are excited normal mode vibrational quantum states of the molecule, while in the latter they are zeroth-order electronic orbitals of the amino acids. In one case, the mechanism is a "vibrational superexchange", namely, a coupling via off-resonant vibrational states, while in the other case, it is an "electronic superexchange", i.e., a coupling of D and A via off-resonant electronic orbitals of the amino acids. Ultimately, in either case, if the density of the intermediate coupled states were to become very large, the original localized donor and acceptor orbitals would become delocalized and any transfer of vibrational energy or of the electron would become "conductive" rather than being of the off-resonant type [18]. Such a high density of states did not occur in the examples mentioned.

Comment: In this electronic example, the data did prompt the theory but did not pose a paradox in themselves, since off-resonant ET was or could be anticipated. Instead, the problem was how to treat this extremely large electronic system. Ultimately, two ways were found to do this, and comparison of $|H_{\mathrm{DA}}|$'s was then made with the measured ET rates, after an analysis based on equations (1.3) and (1.4) to obtain the $|H_{\mathrm{DA}}|$'s.

1.2.3 ET, an early puzzle

In the late 1940s, the 1950s and later, radioactive isotopic tracers were used extensively to study the mechanistic paths of chemical reactions. One such use was in isotopic exchange reactions [19], such as the reaction, equation (1.5), in an aqueous medium,

$$\mathrm{Fe}^{+2} + \mathrm{Fe}^{+3*} \rightarrow \mathrm{Fe}^{+3} + \mathrm{Fe}^{+2*}\,, \tag{1.5}$$

The ET rate was measured by following the appearance of the isotope (the starred atom) in the other valence state, using selective precipitation or other techniques to separate the two redox forms at various reaction times.

In such studies, it appeared that the larger the reactants the faster the rate [19]. This enhancement was not merely a factor of two or so expected from a larger collision diameter, but much larger. To explain this effect, Libby introduced the Franck–Condon principle [20]: An electron jumps so rapidly from one reactant to the other that the nuclei, being much heavier, have no time to move during that instant. Libby argued that each newly formed ion would, therefore, find itself in the wrong molecular solvent environment—one appropriate to the previous charge of the ion rather than to its new charge. He noted that the resultant high energy of the system would then yield an energy barrier to the ET rate. Since the electrostatic ion-solvent dipole interactions increase considerably with decreasing ionic size (e.g., Born model for the calculation of the ion solvation free energy), such a barrier would be much greater for small rather than for large ions and so the ET rate would be slower, in agreement with the experiment.

In 1955, I happened to read Libby's (1952) paper, which was part of a symposium held at the University of Notre Dame and included isotopic exchange reactions [19]. His use of the Franck–Condon principle caught my eye: I had not seen its application to reaction rates before, although its use in electronic spectroscopy, for which it was originally designed in the mid-1920s, was well known. However, the energy barrier itself in Libby's application seemed mysterious, since the law of conservation of energy would be violated by a sudden apparent increase in potential energy with no change in kinetic energy. (According to the full Franck–Condon principle the nuclear momenta are also unchanged.)

I realized that the answer to this problem was that suitable fluctuations of orientations of the solvent dipoles in the neighborhood of the reactants had to precede the ET. In the TS, the ensemble of configurations of solvent dipoles would then be neither an equilibrium one for the reactants, nor an equilibrium one for the products. Instead, for appropriate configurations of the ensemble of solvent molecules the electron could transfer and satisfy both the Franck–Condon principle and the energy conservation.

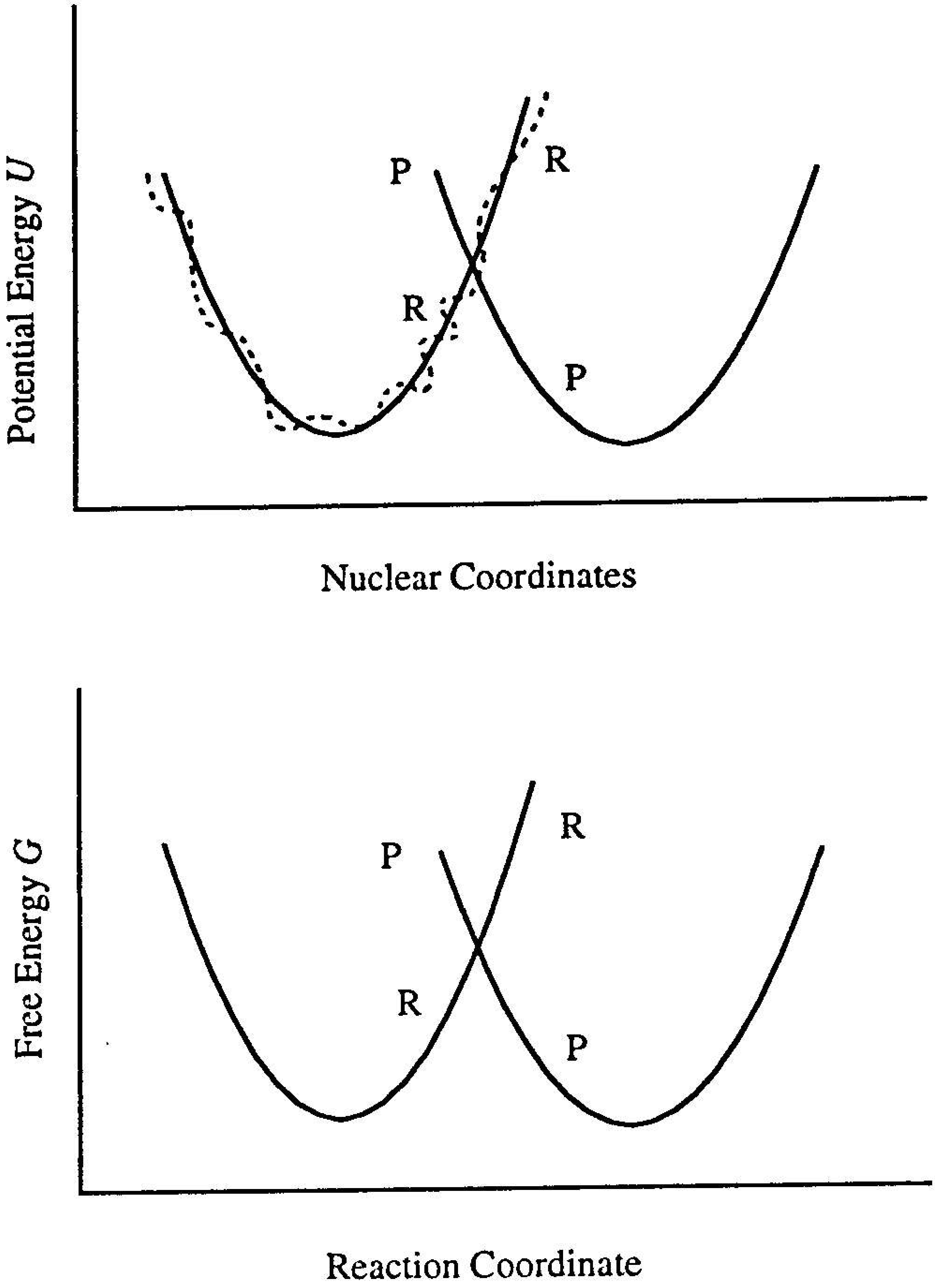

Fig. 1.3. Upper: Schematic view (dotted line) of cross-section of many-dimensional highly anharmonic potential energy surfaces for reactants plus solution (R) and (dotted line omitted) for products plus solution (P). TS occurs at the intersection. Lower: Plot of free energy G for the above R and P systems vs. the reaction coordinate ΔU.

A cross-section of the many dimensional potential energy surface for reactants in solution (R) and that for products in solution (P), is depicted schematically in Fig. 1.3 (upper).

The main task was how to characterize and determine this highly non-equilibrium state of the solvent in the TS, calculate its free energy and, using it, the rate of the ET. In the 1956 papers, these problems were solved by treating the solvent as a dielectric continuum [21]. The corresponding statistical mechanical solution, including changes in reactants' bond lengths [22], was given in the 1960 and 1965 papers [23, 24]. Equation (1.1.3) was obtained in this way, apart from using [21] an "adiabatic" pre-exponential factor instead of the non-adiabatic one appearing in equation (1.3). The non-adiabatic one is appropriate for weak electronic coupling, e.g., long-range ET. Expressions were given for the λ in equation (1.3) in terms of the properties of the reactants and the solvent [21, 23, 24]. Quantum effects for high-frequency vibrational modes were introduced by several authors (e.g., see ref. [25]).

With new developments in technology, increasingly more rapid reactions can be investigated and many chemical, electrochemical and biological systems were studied. Consequently, the ET field developed in many directions as depicted in Fig. 1.4 [2]. Isotopic exchange reactions or, as they are now more generally termed, self-exchange reactions (since non-

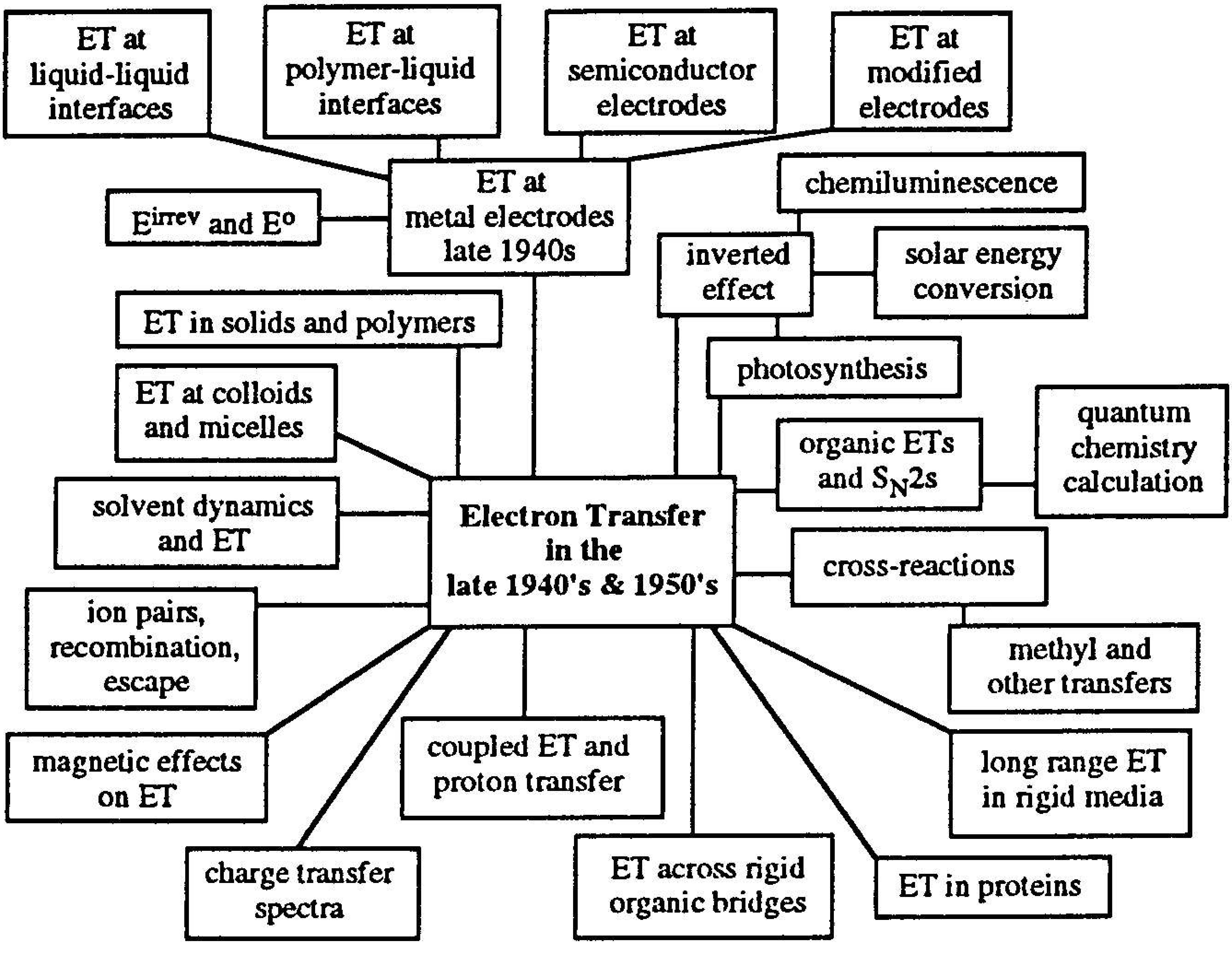

Fig. 1.4. Developments in the electron transfer field [1].

isotopic methods are also used for their study), proved to be particularly important for understanding the factors influencing the rates of ET reactions: Simple ET reactions form the simplest class of reactions in all chemistry, since no chemical bonds are broken or formed. Furthermore, self-exchange ET reactions are the simplest members of this class. In chemical reactions, the products usually differ from the products in their stability, i.e., the ΔG° is usually non-zero and, for any series of reactants, the free energy barrier to the reaction rate usually depends strongly on this ΔG°. For example, there have been numerous scientific conferences on "linear free energy relations" between rate constants and equilibrium, or related constants in a reaction series. Bronsted plots for acid or base-catalyzed reactions form one example. However, for self-exchange reactions this major factor, ΔG°, which can obscure the presence of other factors, is absent. Thus, the effect of other factors, such as the size of the reactants on the ET rate could be observed, with the consequences for theory and interaction with the experiment mentioned above.

There were many predictions arising from the theory and its extension to electrochemical and other systems [11, 23, 24]. One such prediction, the "cross-relation", was based on the relation between the λ for reactions between two different redox systems, λ_{12}, to the λ's of the self-exchange reactions, λ_{11} and λ_{12}, for each of the two systems ($\lambda_{12} \cong 1/2(\lambda_{11} + \lambda_{22})$). The result for k_{12}, the rate constant for the cross-reaction, is

$$k_{12} \cong (k_{11} k_{22} K_{12} f_{12})^{1/2}, \tag{1.6}$$

where k_{11} and k_{22} are the rate constants for the two self-exchange reactions; K_{12} is the equilibrium constant; and f_{12} is a known function of them, usually close to unity.

Most of the predictions were confirmed experimentally (apart from some anomalous cases), but one prediction, the "inverted effect", (the decrease of rate constant with increasingly favorable (increasingly negative) ΔG^{0}, when $|\Delta G^{0}|$ is very large) was counterintuitive, but clearly evident in equation (1.4) and took 25 years before it was confirmed [26]. This story has been told many times and so I will not describe it here. However, the inverted effect is believed to have implications for efficiency of solar energy conversion in photosynthetic systems, as discussed elsewhere. Also, the ET theory had spin-offs for ion, atom and group transfer reactions considered in the next section.

One interesting aspect concerns the reason why equation (1.4) is so simple, even though the actual solvent medium for the ET reaction is very complex. In the actual system, the potential energy surface for the pair of reactants and their environment is a function of thousands of molecular solvent coordinates (positions, orientations, vibrations). Furthermore, the interactions of those solvent molecules with each other and with the charged reactants, are highly anharmonic (outside the inner coordination shell). Nevertheless, when the bulk system is in the so-called linear response regime, e.g., when its local dielectric polarization responds linearly to a change in local electric field, the free energy G of the reactants in the complex system becomes a simple quadratic function of a fluctuation coordinate, here the reaction coordinate. A similar remark applies to the products. This simple dependence is depicted in Fig. 1.3 (lower) and led to the simple quadratic expression given by equation (1.4).

The reaction coordinate used as the abcissa in Fig. 1.3 is rather unusual. It is, for any value $\mathbf{q}$ of the entire set of thousands of coordinates of the system, the difference of the products' and reactants' potential energy function, $\Delta U(\mathbf{q})$, both including the solvent's and reactants' coordinates [23, 27]. For each fixed value of ΔU, an equilibrium ensemble of systems of this *constrained* system can be used to calculate the two free energies G that appear in Fig. 1.3 (lower) for the reactants in solution (R) and for the products in solution (P). In this way, the important behavior of the system on each highly anharmonic potential energy surfaces with thousands of coordinates can be re-expressed in terms of a quadratic function, the free energy G, of only one coordinate ΔU, the reaction coordinate. One of the interesting extensions of equation (1.4) was by Savéant to ETs accompanied by the rupture of a chemical bond [28].

Comment: In formulating the theory in 1956, I had no idea as to its wider implications or that it might later be involved in many applications such as those shown in Fig. 1.4. It was merely an interesting problem stimulated by Libby's [20] paper, which in turn was stimulated by experiment.

1.2.4 Ion, atom and group transfers

In the simple ETs just discussed, there are no bond ruptures and usually only a relatively weak electronic coupling of the two reactants, perhaps of the order of k_BT, or even much less when the reactants are far apart.

Since there is no rupture or formation of a chemical bond, the extensive computation normally needed for quantum chemistry calculations for such bond breaking-bond-forming reactions is now absent. For reactions that do involve a concerted bond rupture and formation, the intersecting parabolas of Fig. 1.2 are normally inappropriate.

Only if there were a transfer of, say, an H^+, H^-, or $H^\bullet$ in a reaction, $AH + B \rightarrow A + HB$ (charges not indicated), at a fairly large AB separation distance, would the situation be rather analogous to that of ETs. The H transfer would occur at an approximately fixed position of A and B, fixed because of the substantially larger masses of A and B compared with that of H. That is, an approximate version of the Franck–Condon principle would apply. Under such conditions of an H transfer, the description of the reaction via two intersecting approximate parabolas would be a reasonable first approximation.

The reaction coordinate could again be chosen to be the ΔU of the products' and reactants' many-dimensional potential energy surfaces, each with its own equilibrium distribution of the position of the H. Similar to the ET case, the electron has an equilibrium distribution within a reactant for each value of the coordinates $\mathbf{q}$. The wave functions of H for the reactants, and that for the products at the given $\mathbf{q}$, could each be obtained by solving the respective Schrodinger equation for the H motion at that $\mathbf{q}$. The "splitting" of the two many-dimensional potential energy surfaces in their intersection region could be obtained from the off-diagonal elements of that solution, as could the splitting, $2|H_{\mathrm{DA}}|$, for the electronic system in the ET case. The H in such a system might either tunnel (as the electron does typically in ETs), or surmount the barrier along the H coordinate, depending on the energy.

Next, we consider the more typical case where A and B are close enough so that the interaction is sufficiently strong that the intersecting parabolas description is no longer appropriate. Here, at any $\mathbf{q}$ (and so at any given AB distance significant for the TS), the splitting at the intersection is so large that the barrier height is substantially less than it would have been if the many-dimensional potential energy surfaces intersected. Nevertheless, an approximate the Franck–Condon principle still describes the transfer of the light H particle in this strong interaction case. An example is seen from a classical trajectory in Fig. 1.5 for an H transfer in a simple model collinear AHB system [29], where A and B are substantially heavier than H.

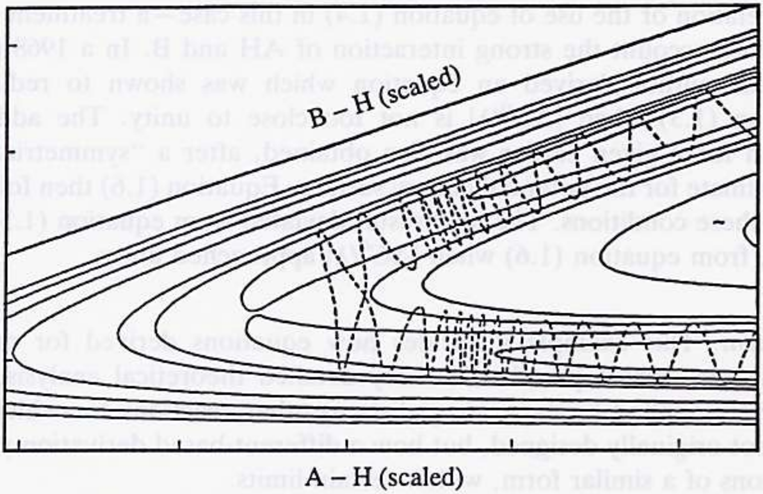

Fig. 1.5. Classical trajectory for an H atom transfer, AH + B → A + HB.

The diagram in Fig. 1.5 is the usual one, with its axes skewed so that the kinetic energy of the three centers has no cross-terms and has a single reduced mass to describe their internal motion [30]. (This single mass can be used even though there are two internal coordinates in this three-center collinear system [30].) One skewed-axis is a scaled AH–B distance and the other is a scaled A–HB distance. When polar coordinates are introduced, with the origin of the skewed axes as center, the polar angle coordinate serves as the H-transfer coordinate, while the radial coordinate is the scaled AB distance. A transfer occurring at a fixed AB distance and so obeying the Franck–Condon principle, occurs at a fixed radius in the symmetric system, B = A. The classical trajectory in Fig. 1.5, which passes over the top of the barrier rather than tunneling through it, is seen to satisfy this approximate Franck–Condon restriction. Although the model system in Fig. 1.5 is symmetric, a Franck–Condon-like behavior can also be expected in asymmetric systems.

The cross-relation (equation (1.6)), has also been applied successfully to transfers of CH_3 [31] and to transfers of H^- [32–33], while equation (1.4) has been used to treat proton transfers [34] and proton bound dimers [34d]. As already noted, the intersecting parabolas of Fig. 1.3 would not be applicable and so some other treatment was needed to understand the cross-relation or the use of equation (1.4) in this case—a treatment which takes into account the strong interaction of AH and B. In a 1968 article [35], the author derived an equation which was shown to reduce to equation (1.3) when $|\Delta G^0/\lambda|$ is not too close to unity. The additivity relation for λ given earlier was also obtained, after a "symmetrization" approximate for the potential energy surface. Equation (1.6) then followed under these conditions. The final result deviated from equation (1.3) and, hence, from equation (1.6) when $|\Delta G^0/\lambda|$ approached unity.

Comment: This example illustrates how equations derived for one set of reactions, which permitted a very detailed theoretical analysis, were intuitively applied by experimentalists to other reactions for which they were not originally designed, but how a different-based derivation yielded equations of a similar form, within certain limits.

1.2.5 Photosynthetic reaction center ET

Nature has constructed an efficient mechanism for the conversion of solar energy into useful chemical energy. At the heart of this process is the photosynthetic reaction center [36]. It is known from picosecond laser experiments that upon excitation of the special pair $(BChl)_2$ of bacteriochlorophylls in the bacterial reaction center, for example, the electron transfers to a pheophytin BPh occurs within 3 ps, indicating a strong electronic coupling between $(BChl)_2^*$ and BPh. (In the next 200 ps the electron transfers from this BPh^- to a quinone Q near the other side of the membrane.) However, in a different kind of measurement, the effect of small magnetic fields on a competitive reaction for the BPh^-, $BPh^- + (BChl)_2^+ \rightarrow BPh + (BChl)_2$ (triplet) in the absence of Q, indicated that the electronic coupling between $(BChl)_2^+$ and BPh^- was very weak. To reconcile these two conflicting results on the coupling between the (BChl) and BPh centers, it was postulated [37] that there was an intermediate site for the electron, which we denote here by X, and that the transfer from $(BChl)_2^*$ to BPh was a two-step process, first forming an intermediate X^-, which then underwent an ET with BPh to form BPh^-.

The X^- has since been identified as an accessory BChl, situated more or less between the $(BChl)_2$ and the BPh, but off to one side. The determination of the crystal structure of the photosynthetic reaction center

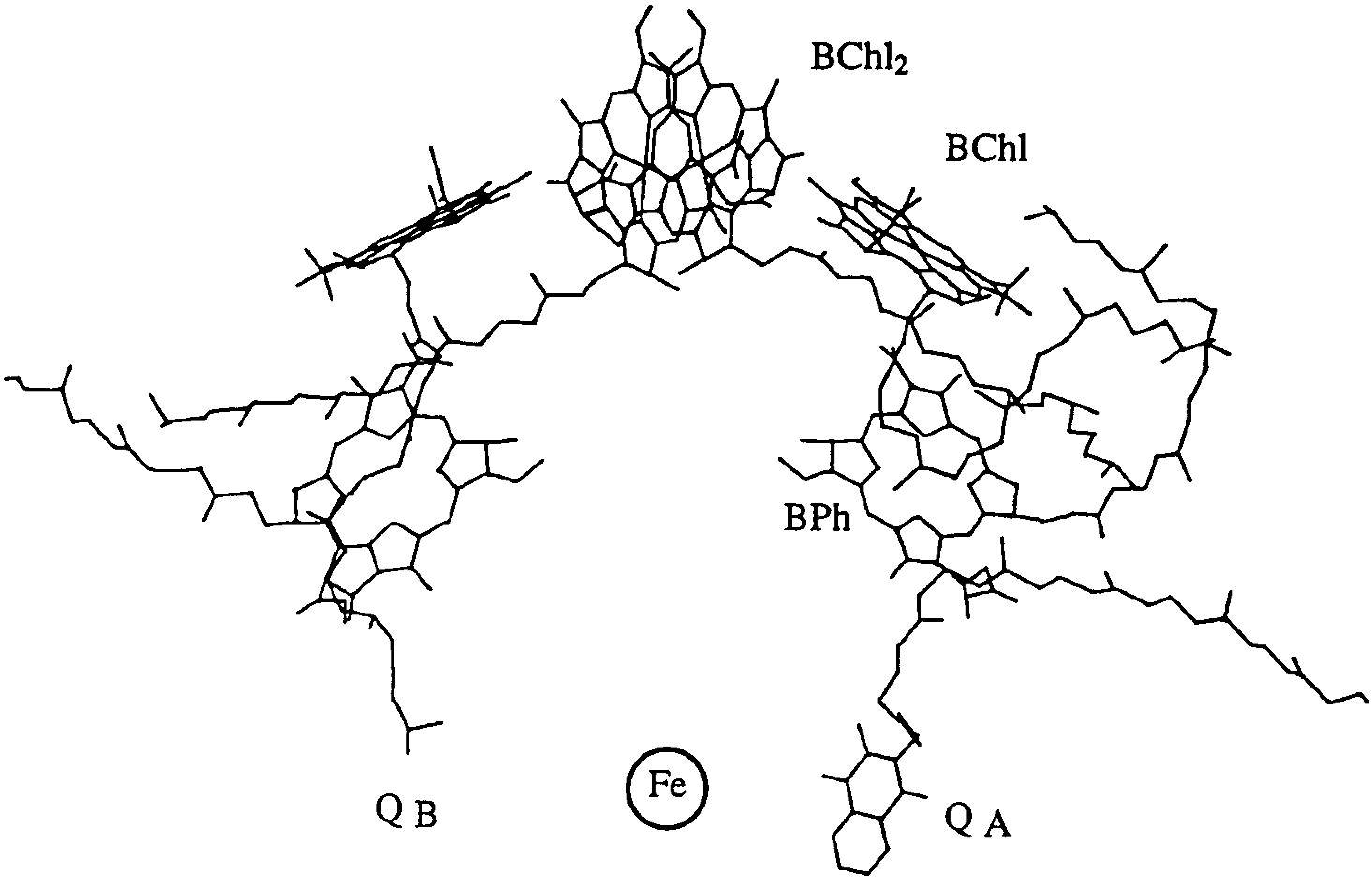

Fig. 1.6. Photosynthetic bacterial reaction center for *Rsp. viridis*. The chromophores are indicated but not the protein part of the structure, helices, etc., holding the whole unit together within the membrane.

(Fig. 1.6) defined the physical positions of each of these components more precisely [38]. For the past decade or more, there has been some dispute as to whether the accessory BChl serves as an actual intermediate, or as an off-resonant site, for the ET from $(\mathrm{BChl})_2^*$ to BPh. At present, the data favor the physical intermediate, BChl^-, over the superexchange mechanism [39].

Comment: In this system, it was again experiments that stimulated theoretical treatments of the reaction center and, they in turn, stimulated further experiments. It is also an example where the simple ET theory found application in biological systems.

1.2.6 Solvent dynamics and the delayed recognition of Kramer's theory

With the advent of picosecond and subsequently femosecond laser techniques, it became possible to study increasingly fast chemical reactions, as well as related rapid solvent relaxation processes. In 1940, the famous Dutch physicist, Kramers [40], published an article on frictional effects on chemical reaction rates. Although the article was occasionally cited in chemical kinetic texts, it was largely ignored by chemists until about 1980. This neglect was perhaps due mostly to the absence or sparsity of experimental data to test the theory. Even computer simulation "experiments" for testing the theory were absent for most of the intervening period.

The situation changed dramatically with the application of picosecond and, later, faster techniques. One stimulating study was that of Kosower and Huppert [41]. They found that the reaction time for a particular intramolecular charge transfer in a series of alcoholic solvents was equal to the respective slowest longitudinal dielectric relaxation time of the solvent. It was later pointed out that this equality of the reaction and dielectric relaxation times would apply for barrierless reactions ($\Delta G^* \approxeq 0$) or, more precisely, for the reactions where the relevant solvent dielectric relaxation, or its fluctuation, are the slow step, i.e., slower than the reaction would be in the absence of any slow solvent relaxational process.

Beginning in 1980 or earlier, numerous theoretical and experimental investigations were undertaken. Kramers' theory was also extended in several ways, such as introducing a frequency-dependent friction to replace a constant one [42] and introducing multidimensional effects [43–46]. Both of these effects caused deviations from Kramers' theory, but his work remained the seminal paper.

Electron transfer reactions are accompanied by significant solvation changes contributing to the reorganization energy term λ, and frequently also by changes in the reactants' vibrational bond lengths and, sometimes, bond angles [11]. Vibrational relaxation is expected to be a fast motion, while the reorientation of solvent molecules is typically slower [47]. This separation of timescales was made in the two-dimensional extension of Kramers' theory for ligand dissociation [43], and for ET [44, 45]. The extension for ETs has been extensively applied to experiments and extended further by including a quantum treatment for the high-frequency vibrational coordinates (see e.g. [48–50]). The latter extension is needed

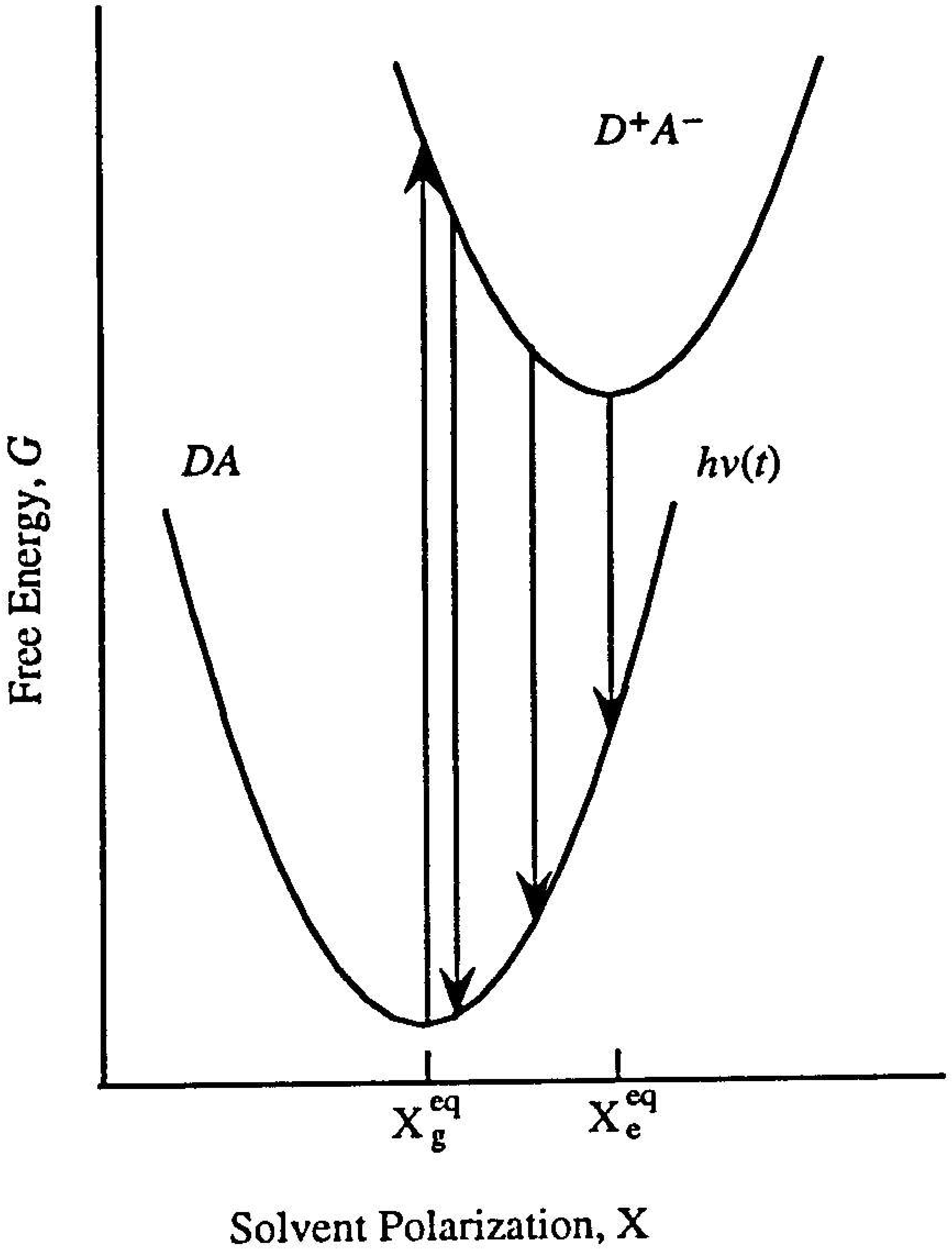

Fig. 1.7. Solvent relaxation and time-dependent fluorescence.

whenever high vibrational frequency modes are important contributors to crossing the TS region, particularly in the inverted regime [51].

A more direct way of exploring the dynamics of polar solvent in the presence of a solute is by the optical excitation of a solute to an intramolecular charge transfer state and then observing the time-dependent fluorescence, as shown in Fig. 1.7 [47, 52]. To follow the time-dependent fluorescence at short times, faster than the usual fluorescent lifetime of nanoseconds, lasers plus an up-conversion technique were used. A quantity frequently measured is the dynamic Stokes shift S(t),

$$S(t) = [\nu(t) - \nu(\infty)]/[\nu(0) - \nu(\infty)] , \tag{1.7}$$

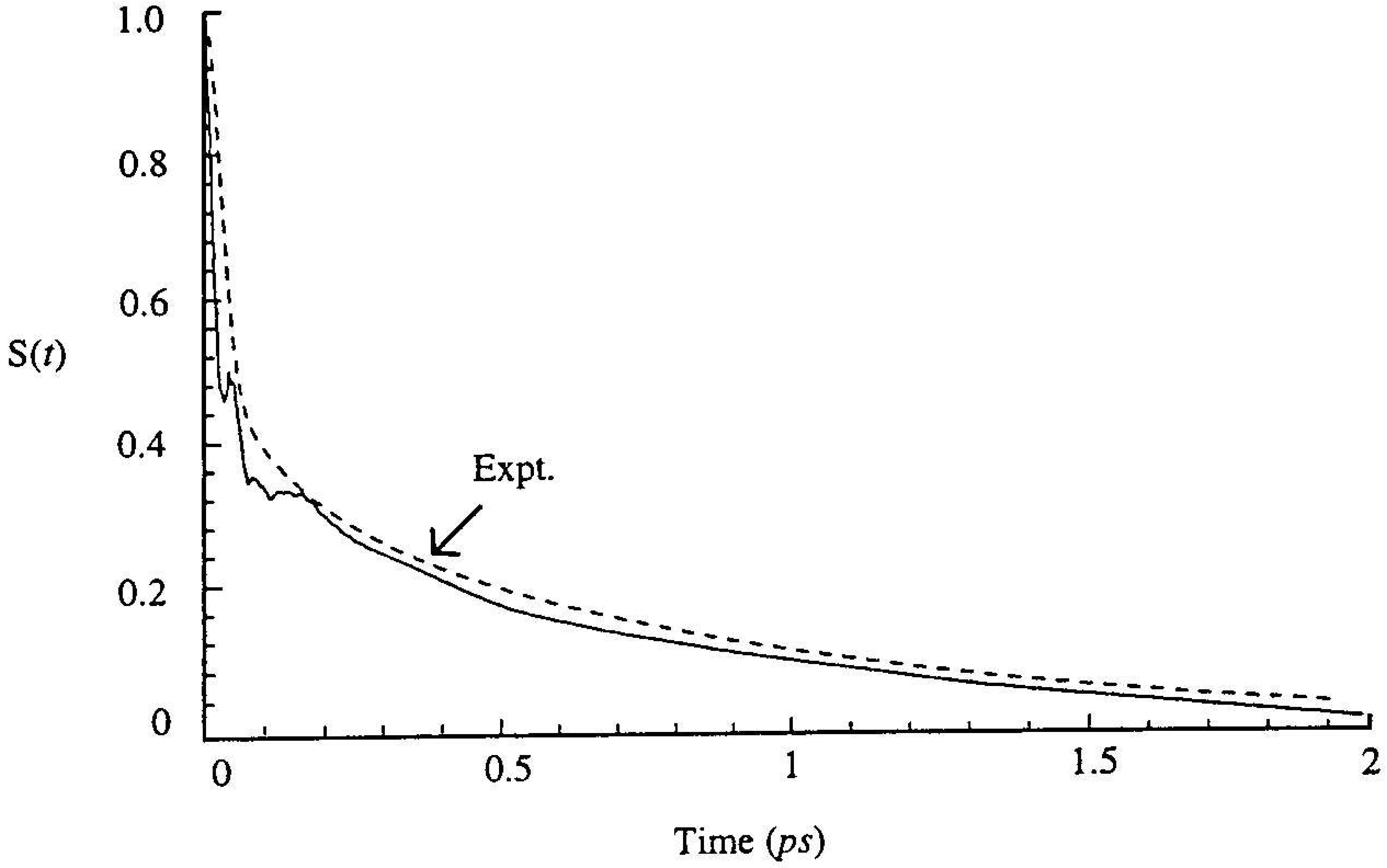

Fig. 1.8. Dynamic Stokes shift S(t) vs. time t for coumarin 343 in water. The theoretically calculated quantity is indicated by a solid line.

where $\nu(t)$ is the frequency at the maximum of the fluorescence spectrum at time t. Typically, the behavior of S(t) is not a single exponential (cf. Fig. 1.6). In one expression for S(t), a dielectric continuum treatment was used for the solvent and S(t) was expressed in terms of its dielectric constant function $\epsilon(\omega)$ [52–54]. Experimental results for coumarin 343 in water are compared in Fig. 1.8 with a theoretical calculation that contains no adjustable parameters [53]. There are other types of experiments, such as photon echoes and the Raman-induced Kerr effect, in which further information is obtained on the dynamics [55]. (Extensive references to the literature are given in refs. [53, 54].) Computer simulations have also played a significant role in the interaction of theory and experiment. However, these are limited mainly by the quality of the model Hamiltonian used for the solvent. Several limitations of some of the models have been noted [56].

Comment: In the case of solvent dynamics in chemical reactions, the theory of Kramers was already available, but there were no experiments for its application at that time and perhaps as a result the theory remained largely unused by chemists for many decades. Later, however, experiments did lead to extensions of the theory. In the related field of solvent relaxation in a photoexcited system, some early experimental work was available in the nanosecond (fluorescence lifetime) [57] and tens of picosecond [58] regimes. Ultrafast (subpicosecond, femtosecond) lasers have now permitted its extension to very short times where interesting multiexponential relaxation properties of the solvent are observed and accompanied by further theoretical developments.

1.2.7 Unimolecular reaction rates and products' quantum states distribution

The field of unimolecular reaction rates had an interesting history beginning around 1920, when chemists attempted to understand how a unimolecular decomposition N_2O_5 could occur thermally and still be first-order, $A \rightarrow$ products, even though the collisions which cause the reaction are second-order ($A + A \rightarrow$ products). The explanation, one may recall, was given by Lindemann [59], i.e., that collisions can produce a vibrationally excited molecule A^*, which has a finite lifetime and can form either products ($A^* \rightarrow$ products), or be deactivated by a collision ($A^* + A \rightarrow A + A$). At sufficiently high pressures of A, such a scheme involving a finite lifetime produces a thermal equilibrium population of this A^*. The reaction rate is proportional to A^*, which would then be proportional to A and so the reaction would be first-order. At low pressures, the collisions of A to form A^* are inadequate to maintain an equilibrium population of A^*, because of the losses due to reaction. Ultimately, the reaction rate at low pressures was predicted to become the bimolecular collisional rate for formation of A^* and, hence, second-order.

The development of a theory of unimolecular reactions proceeded rapidly in the mid-1920s, initiated by Hinshelwood with an A^* whose collision-free lifetime for reaction was approximated by an energy-independent one. The analysis was much elaborated by Rice and Ramsperger [60] and Kassel [61], known later as the RRK theory, where now the lifetime was, as it is in modern times, energy-dependent [62]. These theoretical works of the 1920s stimulated many measurements of the unimolecular rates of dissociation of organic compounds as a function of the gas pressure. Within a few years, however, this entire field collapsed or, more precisely, evolved into a new field: It was shown experimentally that the "unimolecular reactions", assumed originally to consist of only one chemical step, involved the formation of free radical intermediates instead, which in turn reacted with the parent compound, or decomposed, or recombined. In this way, the new field of gas-phase free radical chemistry evolved. Even the N_2O_5 dissociation ultimately shared a similar fate [63]. Photochemical techniques were subsequently extensively used to prepare free radicals and study the individual elementary steps of their reactions.

As a post-doctoral researcher in E.W.R. Steacie's laboratory in the National Research Council of Canada in the late 1940s, I was involved in experiments on several such free radical reaction steps [64, 65] and the data prompted me to wonder about their theoretical interpretation. A second post-doctoral under the tutelage of Oscar Rice led to the formulation in 1951–1952 of what later became known as the RRKM theory [62, 66–68]. Here, I blended the statistical ideas of the RRK theory of the 1920s with the concepts of the TS theory of the mid 1930s.

In the RRKM theory, the microcanonical rate constant $k(E, J)$ at a given E and total angular momentum quantum number J is given by [62, 68],

$$k(E, J) = N^{\dagger}(E, J)/h\rho(E, J)\,, \tag{1.8}$$

where $\rho(E, J)$ is the density of vibrational states of the dissociating molecule at the given E and J. When there is a distribution $p_0(J)$ of J's in the given experiment, the microcanonical rate constant $k(E)$ is given by

$$k(E) = \sum_J k(E, J)p_0(J)\,. \tag{1.9}$$

Although the theory was initially developed in 1952 and had been partly prompted by my prior experimental work, there were very few experimental data to which it could be applied. Around 1959 and subsequent years, B.S. Rabinovitch and coworkers used this theory to interpret their data on chemical activation [62, 69]. It may be recalled that chemical activation produced a narrower energy distribution of dissociating molecules than that in thermal unimolecular reactions and, hence, is better for testing the theory.

Since that time, laser and other techniques were introduced for producing molecules with high vibrational energy [70, 71] and this unimolecular

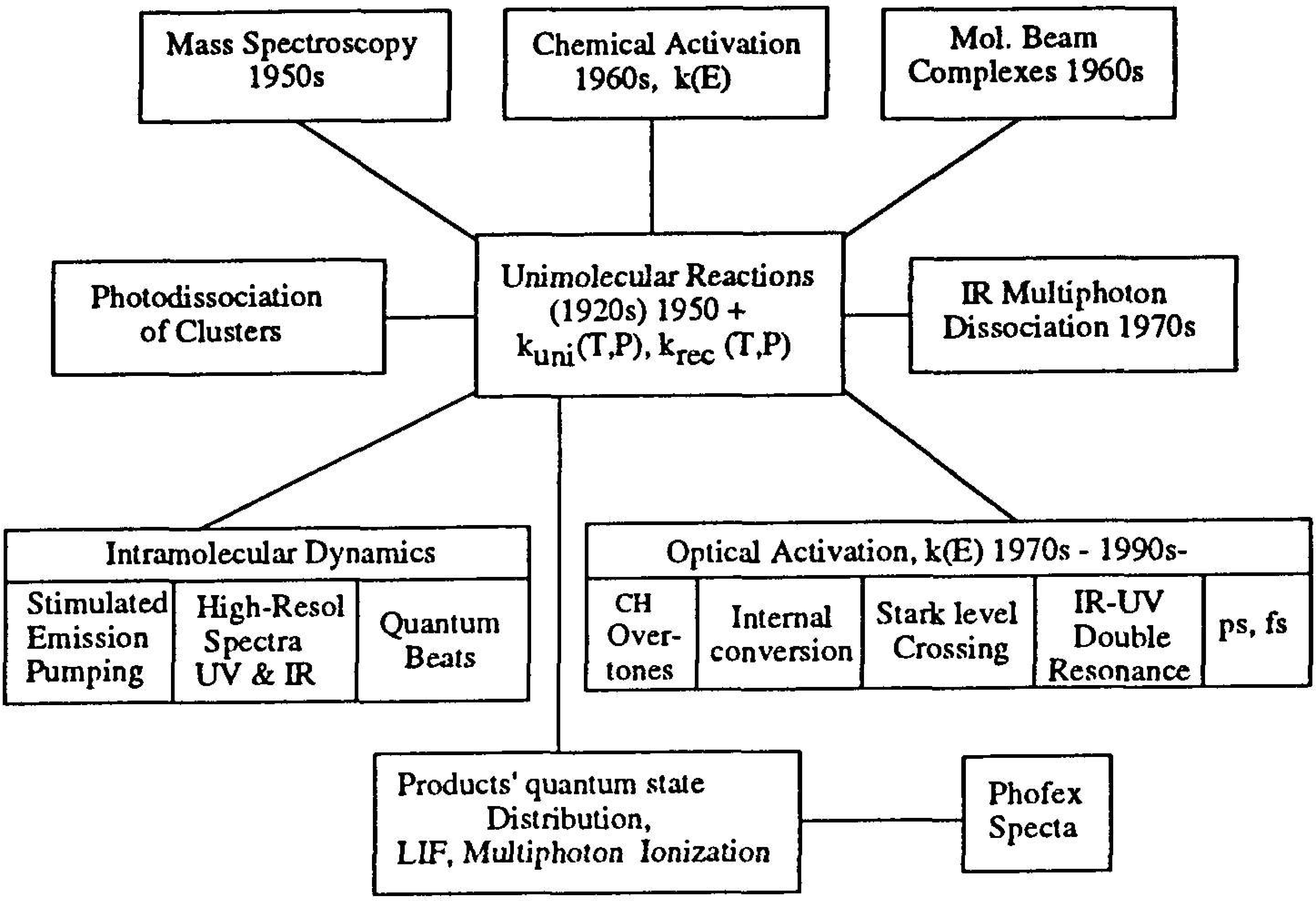

Fig. 1.9. Developments in unimolecular reaction rates and related areas [1].

field expanded in many different directions, as shown in Fig. 1.9. This figure also includes related areas such as that described earlier in Section 1.2.1. One theoretical development was a variational form of the RRKM theory [68, 72]. This theory was prompted by the need to treat experimental data for reactions that had no potential energy maximum to define the position of the TS. The TS occurs where the reactive flux (and thereby the number of states) is a minimum for any given energy E and total angular momentum quantum number J [68, 72–74]. Furthermore, by a convolution of a Monte Carlo evaluation of an expression for the density of classical states of the low frequency modes of the TS with a summation over high-frequency modes, the N^{+} in equation (1.8) could be determined, even with highly anharmonic hindered rotations occurring in the TS [68].

The introduction of laser technology also permitted the determination of related data, such as the distribution of rotational-vibrational quantum states of the products of the unimolecular dissociation [75, 76]. It was found that in the threshold energy region of a unimolecular dissociation, a region where no vibrationally excited products could form, phase space theory (PST) [77] provided an excellent description of the rotational quantum state distribution of the products [76, 78]. In PST, the rotations of two fragments of the dissociating molecule are assumed to be free in the TS. The puzzle was that although PST gave good agreement for the rotational quantum state distribution of the products, the calculated unimolecular rate constant at typical energies was much larger by a substantial factor [79]. The reconciliation of these two sets of observations became the stimulus for a development in the theory, namely, an extension of the RRKM theory, so as to calculate the products' quantum state distribution in addition to calculating the rate constants $k(E, J)$ or $k(E)$ [80, 81].

Extending the theory to interpret or predict the rovibrational state distribution of the products of the unimolecular dissociation, requires some postulate about the nature of the motion after the unimolecularly dissociating system leaves the TS on its way to form products. For systems with no potential energy maximum in the exit channel, the higher frequency vibrations will tend to remain in the same vibrational quantum state after leaving the TS. That is, the reaction is expected to be "vibrationally adiabatic" for those coordinates in the exit channel (we return to vibrational adiabaticity in Section 1.2.9). The hindered rotations and the translation along the reaction coordinate were assumed to be in statistical equilibrium in the exit channel after leaving the TS until an outer TS, the "PST TS", is reached. With these assumptions, the products' quantum state distribution was calculated. (After the system leaves the PST TS, there can be no further dynamical interactions, by definition.)

The results served to explain the paradox described above and led to the prediction that a PST-calculated distribution of states would show discrepancies with experiment when the energy was high enough that vibrationally excited products could form. This latter result also agreed with subsequent data and predictions were made and tested on the distribution. The ideas were extended to treat photofragmentation excitation spectra of Moore and coworkers [75]. A two-TS description (the inner TS and the PST TS) in the threshold region [82] played a significant role in this description [81]. While the PST TS was dominant in the immediate threshold region, the inner TS dominated at higher energies.

For a different system $HO_2 \rightarrow H + O_2$, a very interesting model was introduced [83], in which the distribution in the products was assumed to be the projection of the distribution in the (inner) TS on the states of the products. It would be interesting to explore this model for other mass arrangements also—this one being light + (heavy – heavy), while the previous system was heavy + (heavy – heavy).

Comment: In this section we have seen that unimolecular reaction rate theory was prompted by experiment and earlier theoretical work, which in turn, was prompted by experiment. In the case of the products' quantum state distribution, an extension of the theory was stimulated by a seeming paradox involving existing data and both the agreement and disagreement with a very useful theory, PST, appropriate for a "loose TS". Although the actual system is not loose at typical energies, the TS does move outward in the exit channel when the energy E is reduced and the TS then becomes loose. This explains the applicability of PST in the immediate threshold region.

1.2.8 Unimolecular reaction rates in clusters

In experiments on the isomerization of *cis*-stilbene in clusters of n-hexane molecules (n varying from 1 to 4), the microcanonical rate constant at any given energy outside of the threshold region was observed to decrease with increasing number n [84]. Two effects may enter. First, there is extra frictional effect exerted by the hexane molecules on the *cis-trans*-torsional motion (the reaction coordinate). A second effect is the sharing of the excess vibrational energy by the extra coordinates due to the solvent molecules—at least due to the solvent molecules' librational coordinates. This sharing reduces the possibility of a critical energy becoming localized in the twisted configuration, the TS, of the double bond. In terms of equation (1.8), the ρ increases, as usual, much more than the $N^\dagger$ when extra coordinates are introduced. A treatment was given which combined the RRKM theory with an adaptation of solvent frictional models to this microcanonical system [85, 86]. Two limits, net transfer of energy to the solvent molecules and no such transfer, were included. Since the reaction time at a typical energy ($\sim 3000\,\mathrm{cm}^{-1}$) is of the order of 500–1000 ps for $n = 2$ or 3 and the expected time for transfer of energy to the librations of the solvent molecules is expected to be of the order of several ps, this energy sharing has to be an important source of the smaller rate constant at a given E.

Comment: Experiments point to a gap in the existing theory, namely, the need for a microcanonical theory which takes some account of the solvent frictional effects. What is desirable next is a detailed comparison of theory and experiment.

1.2.9 Vibrational adiabaticity and reaction coordinate

The term "vibrational adiabaticity" was introduced [87] to describe some results of the "computer experiments" of Wall *et al.* [88]. They were pioneers in the use of classical mechanical trajectories of the atoms to study chemical reactions theoretically, using electronic computers. Using classical trajectories for the collinear transfer of an H atom, $H + H_2 \rightarrow H_2 + H$, they found that when the vibrational energy of H_2 was equal to $(v + 1/2)h\nu$, and the energy barrier to reaction decreased by an amount $(v + 1/2)(h\nu - h\nu^{+})$, where v is 0 or unity; ν is the H_2 vibration frequency; and ν^{+} is the symmetric stretch H—H—H frequency in the TS. The question was how to explain this quantum-like result in a purely classical trajectory calculation.

Had the calculations been quantum mechanical rather than classical, the above result would have implied that somehow a vibrational quantum number v remained constant during the motion along the reaction coordinate, even though the nature of that vibrational motion changed drastically, from an H_2 vibration to a symmetric stretch in the H_3 TS and then to an H_2 vibration in the product H_2.

The classical counterpart of v is the action variable I, which equals $\oint p\,dq$, where the integral is over one vibrational cycle of the vibration. In old quantum theory (or, later, the WKB theory), I is related to v by $I = (v + 1/2)h$. Thus, it occurred to me that the above lowering of the energy barrier for the motion along the reaction coordinates could be rewritten as $I(\nu - \nu^{\ddagger})$ and so the results of Wall imply that the classical vibrational action I was constant along the reaction coordinate in this system.

It seemed appropriate to term this behavior "vibrational adiabaticity". Indeed there were also earlier quantum mechanical results for this reaction [89], for which I found a similar behavior [87]. Furthermore, many years before, Hirschfelder and Wigner [90] suggested the equivalent of a vibrational adiabaticity for reactions. The main question, however, was how to treat this approximate dynamical behavior in a physical way. For this purpose, I introduced a coordinate system which passed smoothly from

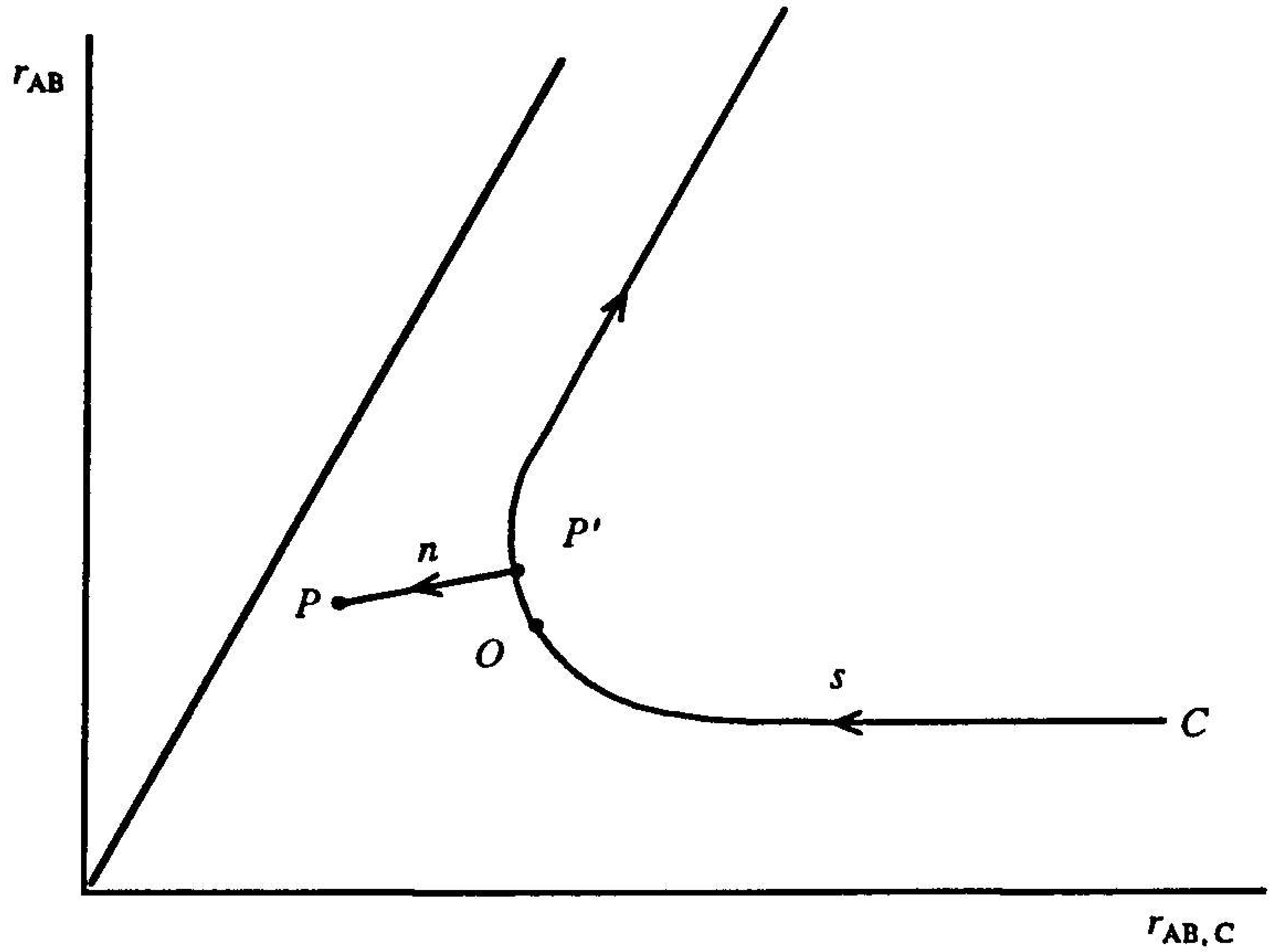

Fig. 1.10. Description of "natural collision coordinates" for a reaction AB + C → A + BC, s and n, for the collinear case. (Those for the three-dimensional problem are described in ref. [53].) The s is the reaction coordinate, measured from any fixed point O on C to the foot P' of the perpendicular from the point P. The n is the vibrational coordinate, i.e., the distance from P to P'.

reactants through the TS and on to products [91–94]. Such a curvilinear coordinate system is shown in Fig. 1.10 and the corresponding Hamiltonian was also introduced. The zeroth-order solution, when the curvature of the curve C in Fig. 1.10 is not large, was, indeed, the desired vibrationally adiabatic solution. Non-adiabatic corrections could then be calculated. There have been various extensions, e.g., the reaction path Hamiltonian [95] and the applications of this approach.

These coordinates in Fig. 1.10, or their extension [53] to three dimensions, are appropriate when the curvature of C is small. Non-adiabatic vibrational transitions then arise from both the curvature and from any rapid change of vibrational frequency as the system moves along the reaction coordinate s [91, 92]. However, in reactions such as the H transfer in AH + B → A + HB in Fig. 1.5, the curvature is so large that there is a tendency for the H to cross from one valley (reactants) to the other (products) at a constant AB distance (the Franck–Condon principle) and even bypass the saddle point [29]. For a symmetric reaction (B = A), the υ of the product HB would equal that of AH. However, if the reaction is largely exothermic and the depth of the well in the products' valley is much more than that in the reactants' at the typical AB distance in the TS, the υ for BH would be much larger than that for AH, as a result of this application of the Franck–Condon principle. Such a reaction is highly vibrationally non-adiabatic.

Comment: These systems provide two markedly different examples of chemical dynamics and coordinate systems suited to their dynamics can be selected. For one of these systems it was computer experiments, rather than real experiments, that served as the stimulus for some of these theoretical ideas.

1.2.10 Graph theory and additivity in delocalized (aromatic) molecules

In some early applications [96] to ETs involving compounds with quinone-like compounds Q, $Q \xrightarrow{e} Q^{-} \xrightarrow{e} Q^{=}$, it was necessary to examine some data on the formation constants of the semiquinone $QH^{\bullet}$, $Q + QH_2 \rightarrow 2QH^{\bullet}$. (The H is typically attached to an O or an N.) My impression, after looking at available data, was that the equilibrium constant was approximately the same, provided all three species had the same charge. Looking at the structures, one could see that every atom in a molecule on the left in this reaction corresponded to one on the right that had the same nearest and next nearest neighbor. I then looked at many examples of other pairs of compounds, which I termed conformal pairs and found that the total of heat of combustion of a pair was approximately the same as its conformal pair [97].

To gain some insight into this type of additivity I examined the results of LCAO calculations for these aromatic compounds [97]. Although individual orbital energies in one conformal pair showed no similarity to those in the other pair, the total energies of the occupied orbitals of the two pairs were approximately equal. Using a contour integral formula for the three total energies and relating the secular determinant appearing in it to the numbers of self-returning random walks, it was possible to gain some insight into this approximate additivity of the conformal pairs, their high delocalized (aromatic) nature notwithstanding. A recent survey of developments in graph theory, with a discussion of the above results, is given in ref. [98].

Comment: In chemistry it is nice to see generalizations from experiment and to find them in unexpected places. The approximate additivity of delocalized systems, described above, provides one such example. With new developments in electronic structure treatments, such as density functional methods, one might hope for a yet deeper insight.

ACKNOWLEDGMENTS

It is a real pleasure to dedicate this article to John Albery and to recognize his influential and joyous contributions to this interaction of experimentalists and theorists. It is a pleasure too to acknowledge the many contributions of my coworkers whose work is described in this chapter. This research was supported by the National Science Foundation and by the Office of Naval Research and I am very pleased to acknowledge that support.

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