SOLVENT DYNAMICS AND RRKM THEORY OF CLUSTERS

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CONTENTS

I. INTRODUCTION

In this chapter we consider the problem of reaction rates in clusters (microcanonical) modified by solvent dynamics. The field is a relatively new one, both experimentally and theoretically, and stems from recent work on well-defined clusters [1, 2]. We first review some theories and results for the solvent dynamics of reactions in constant-temperature condensed-phase systems and then describe two papers from our recent work on the adaptation to microcanonical systems. In the process we comment on a number of questions in the constant-temperature studies and consider the relation of those studies to corresponding future studies of clusters.

A brief review for constant-temperature condensed-phase systems is given in Fig. 1. The field of solvent dynamics has grown so extensively that it is

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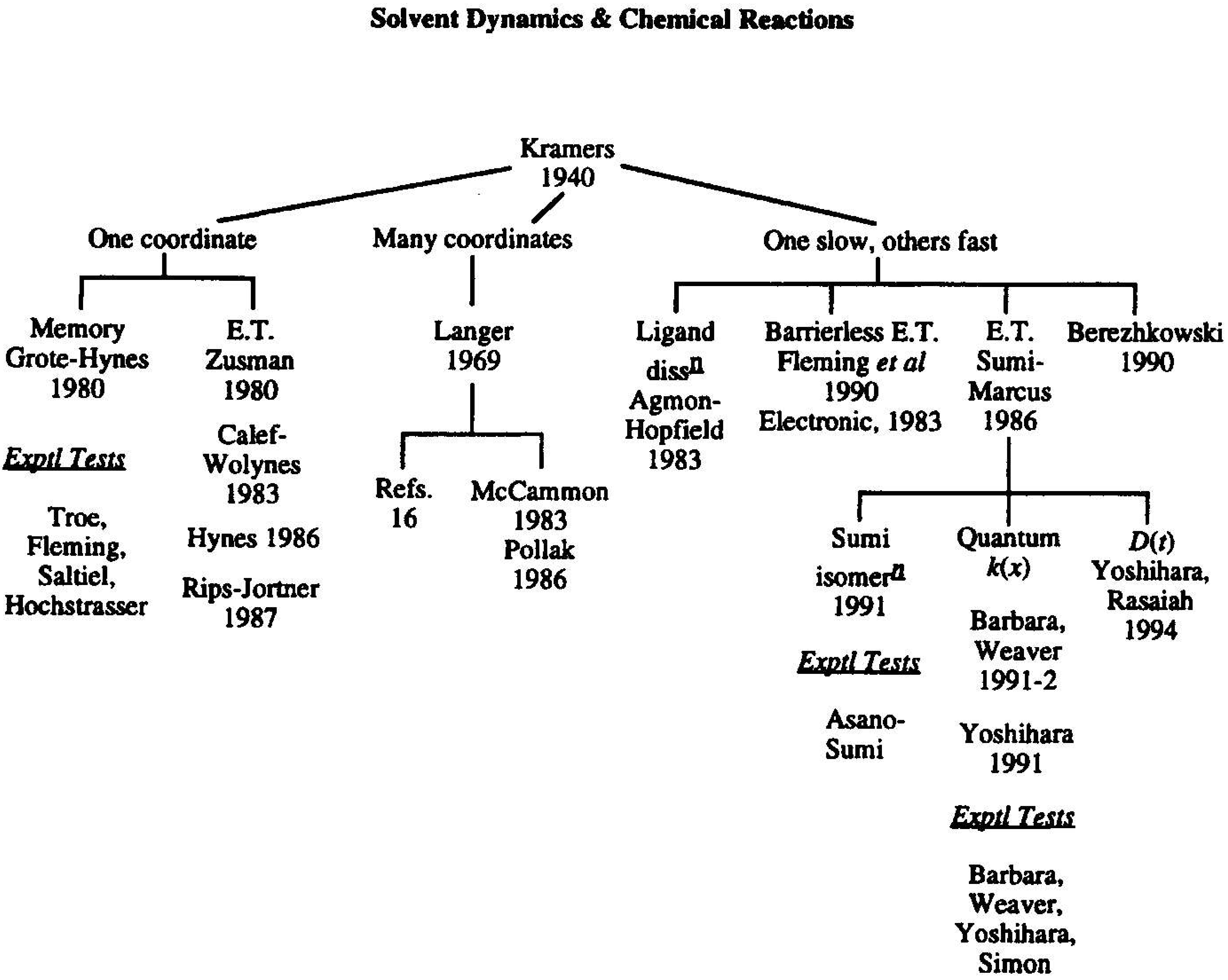

Figure 1. Brief survey of some developments in the solvent dynamics field.

difficult for recent reviews [3–5] to keep pace. Only some representative articles are cited below. The classic paper is solvent dynamics, due to Kramers, appeared in 1940 [6]. Subsequently, apart from some isolated works in the physics literature, such as Langer's generalization to many coordinates in 1969 [7], there was relatively little follow-up, and particularly little in the chemical literature, until around 1980. The subsequent developments can be classified as being largely of three types: (1) those, like Kramers's, that are one-coordinate treatments; (2) their many-coordinate extensions; and (3) treatments having one slow coordinate, the remainder being fast coordinates, appropriately averaged.

Kramers's equation, it may be recalled, is [6]

$$\frac{\partial P}{\partial t} = \frac{\partial U}{\partial q} \frac{\partial P}{\partial p} - p \frac{\partial P}{\partial q} + \zeta \frac{\partial}{\partial p}\left(pP + k_B T \frac{\partial P}{\partial p}\right) \tag{1.1}$$

where $P(p, q, t)$ is the probability density in phase space, q the reaction coordinate, p its conjugate momentum, $U(q)$ the potential energy function, and ζ the frictional coefficient. Kramers's theory for reactions in liquids, which includes both the inertial and the overdamped limits, was extended by Gröte and Hynes [8] to include a memory effect, namely, a frequency-dependent friction $\zeta(\omega)$. A number of other one-dimensional extensions have also been made [9]. Some of the ideas were tested experimentally by many investigators 4, 5, 10, 11. Another pioneering one-coordinate extension of Kramers's analysis was made for electron transfer reactions by Zusman [12] and Alexandrov [12] (1980), and further illuminating developments were made by a number of researchers [13–15]. When there are no relevant "vibrationally assisting" coordinates (examples are mentioned later), a one-coordinate approach suffices.

The second approach, a multidimensional one, was given by Langer [7]. Other multidimensional developments were many [16–18]. McCammon [17] discussed a variational approach (1983) to seek the best path for crossing the transition-state hypersurface in multidimensional space and discussed the topic of saddle-point avoidance. Further developments have been made using variational transition state theory, for example, by Pollak [18].

The third, and perhaps now the currently major, approach for treating the experimental data on electron transfer reactions assumes that there is one slow coordinate, with the remaining coordinates being fast. The equation used, or coupled with one for the back reaction or further extended by making D a $D(t)$, is

$$\frac{\partial P}{\partial t} = D \frac{\partial}{\partial X}\left(\frac{\partial P}{\partial X} + \frac{P}{k_B T}\frac{\partial G}{\partial X}\right) - k(X)P(X) \qquad (1.2)$$

and is obtained by an averaging over or *adiabatic elimination* of the fast (vibrational) variables. Here, $P(X)$ is the probability density along the slow coordinate X, D is a diffusion constant in this X space, $G(X)$ is the free energy to reach any X from the equilibrium value of X, $X = 0$ for the reactant, and $k(X)$ is a rate constant at any given X for crossing the barrier. The motion along X is, as seen in (1.2), treated as overdamped.

Using Eq. (1.2) Agmon and Hopfield (Ref. 19; cf. Ref. 23) treated the dissociation of a ligand from a heme in a protein (1983), and Sumi and Marcus [20] treated electron transfer reactions (1986). For electron transfers the previous (one-coordinate) treatments neglected the very common case that solute vibrations play a major role (*vibrational assistance*) in the transfer when there are significant changes in vibrational geometry, for example, in bond lengths. The use of Eq. (1.2) removes that defect. Beginning around 1990 Berezhovskii, Zitserman, and co-workers introduced a number of treatments of the type based on Eq. (1.2) [21].

The various treatments in the literature based on Eq. (1.2) have differed primarily in two respects: (1) the expression for the rate constant $k(X)$ in Eq. (1.2) is specific for the process and so may differ from process to process and (2) the technique for solving Eq. (1.2) differs. For example, Agmon and Hopfield [19] solved Eq. (1.2) numerically, as did Nadler and Marcus [22], Agmon and co-workers [23], and others. Sumi and Marcus [20] introduced, instead, a decoupling approximation, which depended on there being a difference in time scales for the reaction and for the solvent fluctuations. (An excellent summary and an extension of their work is given in Rasaiah and Zhu [24].) Berezkhovskii et al. introduced an approximation that divided the X space into two parts, separated by a value of X at which the escape time $\tau_{\text{esc}}(X)$ equals the solvent relaxation time $\tau_{\text{rel}}(X)$ [21]. Fleming and co-workers treated barrierless electronic energy transfer (1983) [25] and the corresponding barrierless electron transfer (1990) [26].

For electron transfers various extensions and experimental tests of the Sumi–Marcus treatment have been introduced. They include a quantum version for $k(X)$ (of particular importance in the "inverted region") [24, 27, 28], inclusion of forward and reverse reactions [24], and the use of a time-dependent $D(t)$ to allow for several relaxation times [24, 27, 29]. Other experimental tests or extensions have also been introduced [30]. In experimental tests, effects such as the dynamic Stokes shift of fluorescence in these polar systems have been especially invaluable in providing necessary data for relaxation in these electron transfer systems [31]. Numerical solutions by Yoshihara and co-workers [29] and by Barbara and co-workers [27], permitting the inclusion of a $D(t)$, have been important. Use of a $D(t)$ in general had been made in the work of Hynes [14] (cf. Ref. 32). Analyses of solvent dynamics, accompanied by computer simulations, of Chandler and co-workers [33] and of Maroncelli, Fleming, and their co-workers [34] have provided further insight. Inertial effects on solvent dynamics, using a formalism of Mukamel and co-workers [35], have been incorporated by Barbara and co-workers [36]. Further relevant solvent dynamics theoretical analyses [37] and measurements using ultrafast laser spectroscopy have also been described [38]. Earlier theoretical studies of dynamical spectral shifts of solutes had been made by Bakhshiev, Mazurenko, and their co-workers [39] and references cited therein.

In the case of electron transfer reactions, besides data on the dynamic Stokes shift and ultrafast laser spectroscopy, data on the dielectric dispersion $\epsilon(\omega)$ of the solvent can provide invaluable supplementary information. In the case of other reactions, such as isomerizations, it appears that the analogous data, for example, on a solvent viscosity frequency dependence $\eta(\omega)$, or on a dynamic Stokes fluorescence shift may presently be absent. Its absence probably provides one main source of the differences in opinion [5, 40–43] on solvent dynamics treatments of isomerization.

In the next section we summarize two treatments of microcanonical systems [2, 44], one of the steady-state Kramers' one-coordinate type and one including vibrational assistance. An earlier approach to the problem was given by Troe [45].

II. MICROCANONICAL SOLVENT DYNAMICS MODIFIED RRKM THEORY

A. One-Coordinate Type Treatment

The Kramers-type equation corresponding to Eq. (1.1) and adapted in Ref. 2 to the microcanonical case for a system with coordinate q and its conjugate momentum p is

$$\frac{\partial P}{\partial t} = -T_v\left(\frac{\partial S_v}{\partial q}\right)\frac{\partial P}{\partial p} - p\,\frac{\partial P}{\partial q} + \zeta\,\frac{\partial}{\partial p}\left(pP + k_B T_v\,\frac{\partial P}{\partial p}\right) \tag{2.1}$$

where $S_v(q)$ is the local vibrational entropy at q, $T_v[=1/(\partial S_v/\partial E_v)]$ is the local microcanonical vibrational temperature and is a function of q, and P is the probability distribution in (q, p) space. The adaptation was such as to permit the equilibrium microcanonical phase-space distribution function to satisfy the equation identically [2].

In the steady-state approximation, solving Eq. (2.1) for the rate constant at the given total energy E yields [2]

$$k_{\text{rate}} = \frac{1}{\omega^{\dagger}}\left(\sqrt{\left(\frac{\zeta}{2}\right)^2 + \omega^{\dagger 2}} - \frac{\zeta}{2}\right)k_{\text{RRKM}} \tag{2.2}$$

where $\omega^{\dagger 2}$ denotes $T_v d^2S_v/dq^2$ at $q = q^{\dagger}$ and is an effective barrier frequency. The k_{RRKM} is the RRKM (microcanonical) rate constant at the given energy E.

B. Vibrational Assistance Treatment

A second procedure, based on the vibrational assistance model for calculating the solvent-dynamics-modified rate, is given in Ref. 44. The reaction–diffusion equation, adapted from Eq. (1.2), is, for the case where the back reaction is neglected, given by (2.3). The more complete treatment, where the back reaction (recrossings) is included, is given in Ref. 44:

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial X}\left(\frac{\partial P}{\partial X} - \frac{P}{k_B}\frac{\partial S_v(X)}{\partial X}\right) - k(X)P(X) \tag{2.3}$$

The adaptation is such as to permit the equilibrium microcanonical distribution for the slow coordinate X to be a solution (2.3) when $k(X) = 0$. The $S_v(X)$ in Eq. (2.3) is the vibrational entropy change needed to reach X from $X = 0$:

$$S_v(X) = \frac{k_B \ln \rho(X)}{\rho} + \text{const} \tag{2.4}$$

[the constant does not affect the $\partial S_v/\partial X$ appearing in Eq. (2.3)]; ρ is the density (i.e., the number per unit energy) of quantum states of the reactant, and $\rho(X)$ is that density at X per unit X. It is given by [44]

$$\rho(X) = \sum_m \frac{2}{h|P_X|} \qquad P_X = [2(E - U(X) - E_m)]^{1/2} \tag{2.5}$$

where P_X is the momentum conjugate to X. Throughout we use a mass-weighted unit for X for notational brevity. Here, E_m is the energy of the mth quantum state of the reactant for all coordinates but X and $U(X)$ is the potential energy at X at the local equilibrium value of the remaining coordinates. It is readily verified [44] that (2.5) satisfies $\int \rho(X)dX = 1$, where the integral is over the reactant's region of X space.

We give in Fig. 2 a schematic plot showing contours on which a vibrational entropy $S_v(q,X)$ is constant, q is a fast coordinate, and the line C is the transition state in the (X, q) space. This $S_v(q,X)$ can be defined as in an equation similar to (2.4) in terms of a $k_B \ln \rho(q,X)$, $\rho(q,X)$ being the local density of study, that is, the number per unit energy per unit q and per unit X. While this plot is not used in the derivation, it can be visually helpful.

The $k(X)$ in Eq. (2.3) is given by an RRKM-like expression for the given X [44]:

$$k(X) = \frac{N(X)}{h\rho(X)} \tag{2.6}$$

where $N(X)$ is the local number of quantum states (per unit X) for the given X, along the transition state, with energy equal to or less than E and is given by (2.7), and x is a coordinate that is a projection (defined in Ref. 44) on

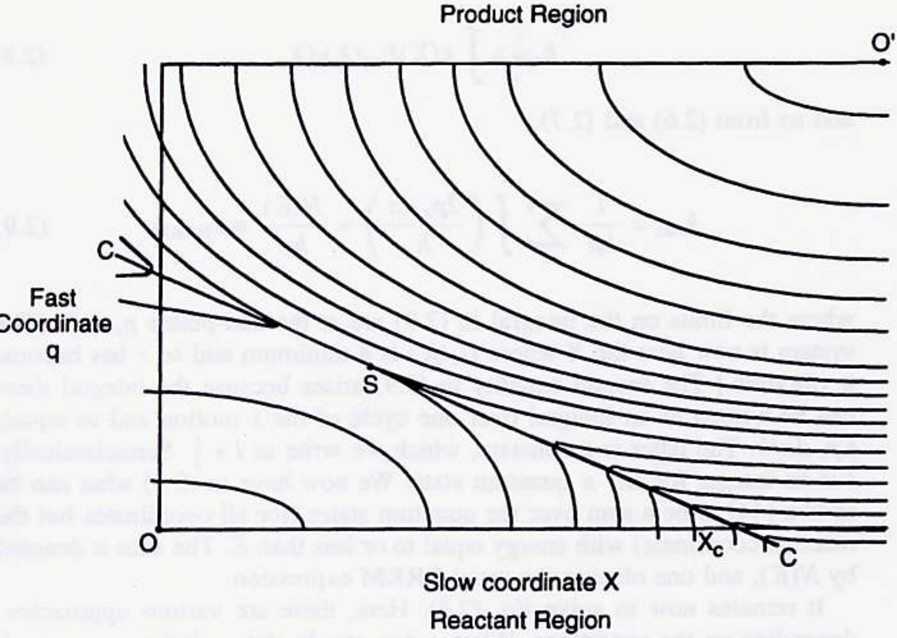

Figure 2. Schematic entropic surface as a function of a slow coordinate X and a fast coordinate q. Here, S is a saddle point, the line C is the transition state in this (X, q) space, and X_c lies at its intersection with the X axis.

the transition state space. We have

$$N(X) = \sum_n \frac{2p_x|dx/dX|}{h} \qquad p_x = [2(E - E_n - U_c)]^{1/2} \tag{2.7}$$

Here, E_n is the energy of the nth quantum state of the transition state for all coordinates but X and Q, the reaction coordinate, $U_c(X)$ is the potential energy in the transition state at the point X and at the position of minimum potential energy with respect to all *other* coordinates in the transition state, and p_x is the momentum conjugate to x.

From the expressions for $k(X)$ and $N(X)$ it can be shown that the usual RRKM expression obtains when the diffusion along X is rapid, that is, when $P(X)$ has its equilibrium value $P_{\text{eq}}(X)[= \rho(X)/\rho]$: We have

$$k_{\text{rate}} = \int k(X)P_{\text{eq}}(X)dX \tag{2.8}$$

and so from (2.6) and (2.7)

$$k_{\text{rate}} = \frac{1}{h\rho} \sum_n \int \left(\frac{2p_x\, dx}{h} \right) = \frac{N(E)}{h\rho} \equiv k_{\text{RRKM}} \tag{2.9}$$

where the limits on the integral in (2.9) are at the end-points $p_x = 0$. [The system is now near the X where $U_c(X)$ is a minimum and so x has become a vibration.] The second equality in (2.9) arises because the integral there can be written as an integral over one cycle of the x motion and so equals $\oint p_x\, dx/h$. The latter is a constant, which we write as $l + \frac{1}{2}$. Semiclassically, l is an integer for any x quantum state. We now have in (2.9) what can be shown [44] to be a sum over the quantum states (for all coordinates but the reaction coordinate) with energy equal to or less than E. The sum is denoted by $N(E)$, and one obtains the usual RRKM expression.

It remains now to solve Eq. (2.3). Here, there are various approaches, depending on the conditions. When a non-steady-state solution is required, one can introduce the decoupling approximation of Sumi and Marcus, if there is the difference in time scales mentioned earlier. Or one can integrate Eq. (2.3) numerically. For the steady-state approximation either Eq. (2.3) can again be solved numerically or some additional analytical approximation can be introduced. For example, one introduced elsewhere [44] is to consider the case that most of the reacting systems cross the transition state in some narrow window $(X_1, X_1 \pm \frac{1}{2}\Delta)$, narrow compared with the X region of the reactant [e.g., the interval (O, X_c) in Fig. 2]. In that case the $k(X)$ can be replaced by a delta function, $k(X_1)\Delta\delta(X - X_1)$. Equation (2.3) is then readily integrated and the point X_1 is obtained as the X that maximizes the rate expression. The Δ is obtained from the width of the distribution of rates in that system [44].

A simple expression for the rate constant results:

$$k_{\text{rate}}(E) = k_{\text{rate}}(X_{\text{max}}) \tag{2.10}$$

where X_{max} is the X that maximizes $k_{\text{rate}}(X)$ and hence minimizes the reaction time $1/k_{\text{rate}}(X)$. That time appears in the final expression in Ref. 44 as

$$\frac{1}{k_{\text{rate}}(X)} = \frac{1}{k_{\text{diff}}(X)} + \frac{1}{k_{\text{act}}(X)} \tag{2.11}$$

where the diffusion-controlled and activation-controlled rate constants are given by

$$k_{\rm diff}(X) = \frac{D}{\int_0^X [\rho/\rho(X')]dX'} \tag{2.12}$$

and

$$k_{\rm act}(X) = \frac{N(X)\Delta}{h\rho} \tag{2.13}$$

[When $X_{\rm max}$ occurs at the end-point X_c, there is a minor change in procedure, and the system now crosses the transition state in the interval $(X_c, X_c - \Delta)$, Equations (2.11)–(2.13) are again obtained.]

The result in (2.11) that the reaction time is the sum of two other times is fairly common in the general reaction–diffusion literature, in which a steady-state approximation is used and there is a diffusion toward a sink followed by reaction at that sink. For example, in the scheme $A \rightleftharpoons B \rightarrow C$, with forward and reverse rate constants k_1 and k_2 for the first step (equilibrium constant $K = k_1/k_2$) and rate constant k_3 for the last step, a steady-state approximation for B yields $1/k_{\rm rate}(1/k_3K)+(1/k_1)$, which has the same functional form as (2.11). The more complete expression, which allows for the back reaction (recrossings), has a slightly more complicated structure [44].

III. DISCUSSION

At present the body of data on reactions in clusters is insufficient to test the above two microcanonical approaches. For electron transfers *in solution* it seems clear that the vibrational assistance approach, stemming from Eq. (1.2), with its extensions mentioned earlier, is the one that has been the most successful [27–30]. For slow isomerizations Sumi and Asano have pointed out that an analysis based on Eq. (1.2) was again needed [40]. An approach based on Eq. (1.1) or on its extension to include a frequency-dependent friction, they noted, led to unphysical correlation times [40]. In investigations of fast isomerizations the most commonly studied system has been the photoexcited *trans*-stilbene [5, 41–43, 46]. Difficulties encountered by a one-coordinate treatment for that system have been reported [4, 8]. Indeed, coherence results for photoexcited *cis*-stilbene have shown a coupling of a phenyl torsional mode to the torsional mode about the C=C bond [42, 47].

Other investigators have used systems that are more apt to represent a one-coordinate-like behavior, for example, the isomerization of "stiff-stilbene," where the phenyl groups are tethered further to the respective carbon atoms of the double bond [48], and the conformational change of binaphthyl [10]. In the last study a microviscosity was introduced into the Kramers formula to obtain the friction coefficient ζ, instead of using the bulk viscosity of the solvent, and was inferred from rotational relaxation or translational diffusion coefficient ($\zeta = k_BT/D$ in mass-weighted units). In that case the expected Kramers function of η (via the Stokes–Einstein equation) was obeyed for the one-coordinate model. Use of the bulk viscosity led, instead, to an observed fractional dependence on η [10]. A microfriction inferred from a rotational or translational relaxation time has been similarly successfully used by various other investigators [41, 43, 49, 50]. An approximate molecular expression ("ballpark") for a ζ for a cluster was given in Ref. 2.

Many questions in the analysis of solvent dynamics effects for isomerizations in solution have arisen, such as (1) when is a frequency-dependent friction needed; (2) when does a change of solvent, of pressure, or of temperature change the barrier height (i.e., the threshold energy), and (3) when is the vibrational assistance model needed, instead of one based on Eq. (1.1) or its extensions?

In the case of electron transfers in solution there appears to be a greater cohesiveness of views, and the need for vibrational assistance is well established for reactions accompanied by vibrational changes (e.g., changes in bond lengths). A detailed analysis of the experiments could be made because of the existence of independent data, which include X-ray crystallography, EXAFS, resonance Raman spectra, time-dependent fluorescence Stokes shifts, among others.

One may inquire as to what this experience with solutions suggests for the study of reactions in clusters. In the case of electron transfers supplementary information, such as time-dependent fluorescence Stokes shift in clusters, would again be helpful. Equation (2.3) can be modified to include a $D(t)$, as in the isothermal case, if needed from the results of such data. For isomerizations, also, it would be useful to have, for solutions or clusters, detailed analogous data such as the above Stokes shift. However, because of the low intensity of such a fluorescence in this case, such data appear to be absent or scarce.

The questions that have arisen in regard to isomerizations in solution also apply to isomerizations in clusters. One of these questions, which has now been addressed, is the threshold energy and its variation with size of the cluster. Data on the threshold energies were obtained in the microcanonical study by Heikal et al. [1]. New questions, however, also arise for clusters: How rapidly is the energy transferred between the solute and the solvent molecules in the cluster? Outside the threshold region a reduction in $k_{\text{rate}}(E)$ with increasing cluster size was observed experimentally [1]. A principal question is whether this reduction is due to the increase, with increased cluster size, in the number of coordinates which can share the excess energy or whether it is due to increased frictional effects by the solvent molecules, or both. If the solvent molecules outside the first solvent layer in the cluster have little effect on the frictional forces, then this question can be addressed by comparing the reaction rates with those clusters that contain more than one solvent layer. Again, if instead of using stilbene one replaces one of the phenyl groups attached to the C=C double bond, the solvent viscosity effects should be less and the energy-sharing role of the extra coordinates more readily discerned. Yet again, microcanonical studies with molecules deliberately chosen, as in the solution case, to favor a one-coordinate approach would also be of particular interest.

It is clear that the study of solvent dynamics in solution has proved to be a rich field. A number of questions remain to be resolved, and the study of clusters can open new avenues.

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DISCUSSION ON THE REPORT BY R. A. MARCUS

Chairman: E. Pollak

J. Troe: In our own work measuring energy-specific excited stilbene lifetimes in stilbene–hexane clusters, we found for larger clusters that there is no isomerization. We interpreted this as evidence for "boiling off" of the cluster partners, removing energy from stilbene and thus suppressing the isomerization. This is an alternative to increasing the effective size of the reacting molecule. Which interpretation do you favor? We also clearly showed that the barrier for isomerization is decreased by the first cluster partners, as evidenced in our studies of the thermal reaction between gas and liquid phases.

R. A. Marcus: I understand that the observed effect of a decrease in rate constant $k(E)$ with increasing cluster size at a fixed E was not due to a boiling off of the hexane molecules (and hence to a reduced E), but I refer to my colleague, Ahmed Zewail, for an answer to your question.

A. H. Zewail: My answer to Prof. Troe is that, in our experiment, already the cluster with one solvent shows the shift in E_0. As for the boiling off of solvent molecules in larger clusters this is a nontrivial problem that we have considered in our paper. Based on the analysis of the translational energy and the kinetics, we concluded that the exponential decays (rates) are determined by the isomerization [see *Chem. Phys. Lett.* **242,** 380 (1995)]. In any event, only one solvent molecule (at most) can be evaporated for the available energy studied experimentally; recall that the binding energy of hexane is relatively large.

H. Hamaguchi: I would like to comment on the stilbene photoisomerization in solution. We recently found an interesting linear relationship between the dephasing time of the central double-bond stretch vibration of S_1 *trans*-stilbene, which was measured by time-resolved Raman spectroscopy, and the rate of isomerization in various solutions. Although the linear relationship has not been established in an extensive range of the isomerization rate, I can point out that the vibrational dephasing time measured by Raman spectroscopy is an important source of information on the solvent-induced vibrational dynamics relevant to the reaction dynamics in solution.

R. A. Marcus: It is good to hear about that; certainly one needs all types of information to be incorporated.

D. M. Neumark: Prof. Marcus, your theoretical treatment was motivated by experimental studies of isomerization in clusters with very few solvent molecules ($n = 1, 2$). How appropriate is your theory to these small clusters? In particular, can one discuss concepts such as viscosity and solvent friction in small clusters?

R. A. Marcus: The experiments involved hexane rather than argon and went from $n = 0$ to $n = 5$ hexane molecules. In *Chem. Phys. Lett.* **244,** 10 (1995), I considered two limiting cases for the energy sharing of the *trans*-stilbene with the modes of the solvent molecules. Experiments comparing results for one and two shells of solvent molecules in the cluster may provide information on which limiting model might be the more appropriate. Previous experiments on *trans*-stilbene in solvents suggest a rapid energy sharing. In the above article I also gave a rough expression relating the "viscosity" or friction for the cluster to molecular properties, but I am sure it can be improved upon.

B. Hess: The structure and function of solvent components constituting the active site of enzymic reactions represent an exciting puzzle in protein chemistry. In an active pocket, a restricted cluster number is given by the small set of amino acid residues, mostly hydrophobic, in the nearest neighborhood to the ligand and its reaction partners. As Prof. Marcus pointed out, Frauenfelder and his collaborators studied experimentally the effect of solvent viscosity on protein dynamics. In case of CO myoglobin they could show that over a wide range in viscosity the transition rates in heme-CO are inversely proportional to the solvent viscosity and can consequently be described by the Kramers equation [1]. A complementary study was carried out to explore the effect of viscosity on the photocycle of bacteriorhodopsin. Here again the Kramers equation in a modified form was found to be useful [2]. Most recently, the photodissociation of carbon monoxide myoglobin was studied in crystals at liquid helium temperatures by two different groups [3]. Schlichting et al. [4] could show that CO dissociation leads to tilting of the proximal histidine and a decompression and motion of the F-helix toward its junction with the E-helix. These conformational changes are linked to an increase of the enthalpic barrier decreasing the association rate coefficient. It was speculated that the energy stored in this conformation of the residue and its neighbors is released during structural fluctuations associated with ligand escape. These and other observations (see also Ref. 5) illustrate the necessity to extend the theoretical approach of Prof. Marcus's theory to the domain of intramolecular interactions in protein dynamics. I would be glad if he could comment on this development.

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R. A. Marcus: Concerning the issue raised by Prof. Benno Hess, a number of treatments of the "solvent dynamics" of chemical reactions in proteins or liquid solvents assume one slow (X) and one or more fast coordinates. The theories then differ in the nature of how a rate constant $k(X)$ depends on X. Agmon and Hopfield, for example, used a $k(X)$ specific for the ligand–heme dissociation process they were considering. Sumi and I used a $k(X)$ specific for the electron transfer reactions we were considering [1]. In today's talk, which concerns an isomerization, I used for $k(X)$ the analog of an RRKM rate constant appropriate to it. These various treatments have in common the same differential equation for the probability distribution $P(X)$ along X. They differ in the process considered and in the nature of solution. There is still much to be done, particularly for systems that deviate from single time-exponential behavior, to use some of the existing numerical solutions, to test various analytical approximations, and to develop new analytical approximations. It was interesting to hear from Prof. Hess about the new and detailed structural information becoming available for the protein systems, and extending the theory will be an interesting problem.

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W. Hebel: I have a rather general question for Prof. Marcus. You are discussing the complicated solvent dynamics of molecular clusters. Does this also include large biomolecules such as proteins in aqueous solutions?

Could you perhaps comment on how far research has gone in analyzing and understanding the interaction of biopolymers in aqueous solvents?

R. A. Marcus: Even though solvents and solvent–solute interactions or interactions with a protein can be very complicated and the resulting motion can be highly anharmonic, under a particular condition there can be a great simplification because of the many coordinates (perhaps analogous to the central-limit theorem in probability theory).

The condition is that of linear response of the solvent or protein, for example, that the change in dielectric polarization of the solvent be proportional to the change in charge of a solute. With this condition fluctuations give rise to a quadratic expression for free-energy changes. This simplification ultimately led, in the case of electron transfer reactions in appropriate atoms or group transfer, to new predicted relationships among rate constants of different reactions. The linear response approximation for the electron transfer systems was subsequently also tested by various investigators by computer simulations of solvent and of proteins.

J. Troe: Professor Marcus, you were mentioning the 2D Sumi-Marcus model with two coordinates, an intra- and an intermolecular coordinate, which can provide "saddle-point avoidance." I would like to mention that we have proposed multidimensional intramolecular Kramers–Smoluchowski approaches that operate with highly non-parabolic saddles of potential-energy surface [Ch. Gehrke, J. Schroeder, D. Schwarzer, J. Troe, and F. Voss, *J. Chem. Phys.* **92,** 4805 (1990)]; these models also produce saddle-point avoidances, but of an intramolecular nature; the consequence of this behavior is strongly non-Arrhenius temperature dependences of isomerization rates such as we have observed in the photoisomerization of diphenyl butadiene.

R. A. Marcus: I used the words *saddle-point avoidance*, incidentally, to conform with current terminology in the literature. More generally, one could have said, instead, avoidance of the usual (quasi-equilibrium) transition-state region (i.e., the most probable region if viscosity effects were absent).

E. Pollak: In relation to the point discussed by Profs. Troe and Marcus, we have shown that those cases considered as saddle-point avoidance are consistent with variational transition-state theory (VTST). If one includes solvent modes in the VTST, one finds that the variational transition state moves away from the saddle point; the bottleneck is simply no longer at the saddle point.

A. H. Zewail: I have a question for Prof. Marcus concerning the fact that, in the bulk solvation problem, there are two regimes for the description of solvation, the continuum model and the detailed molecular dynamics. Do you expect that in clusters the friction model will change as the number of solvent molecules changes from small to large?

R. A. Marcus: In *Chem. Phys. Lett.* **244,** 10 (1995), a very rough approximate hard-sphere model used for liquids was mentioned to relate the *frictional coefficient* to the pair distribution function in the cluster.

D. J. Tannor: One would think that as one adds more and more layers of solvent one is introducing irreversible decay of the correlation function of the solute–solvent coupling. The main physical content of the Grote–Hynes expression for the rate constant is that contributions from this correlation function that are slow compared with the time scale for reaction do not really contribute to the reaction rate. This suggests that by starting with a description of only the first solvent shell and introducing shorter and shorter solvent memory, one will see a transition that resembles that of adding more and more solvent shells.

R. A. Marcus: About the problem raised by Prof. Tannor, there are a number of questions to be resolved, such as energy migration to the solvent in the cluster, the detailed dynamical effect of successive layers of solvent in larger clusters, and comparing with cluster experiments of other suitably chosen reactants, for example, $R_1R_2C = CR_3R_4$, where R_3 and R_4 are so small that the molecule has no frictional effect in solution. Such an isomerization has previously been studied in liquids. In the present chapter several experiments are suggested to disentangle the various factors influencing the energy-dependent rate contants.

H. Hamaguchi: What information do you have concerning the structure and dynamics of the hexane-dressed stilbene molecule? How flexible or how rigid is the structure?

R. A. Marcus: I personally do not have the information.

A. H. Zewail: To provide a partial answer to the question of Prof. Hamaguchi, the structure of the 1:1 stilbene–hexane species was determined with the help of rotational coherence spectroscopy. For higher clusters we used atom–atom model potentials and deduced structures.