

References and Notes

- (1) Address correspondence to Laboratory of Molecular Biology, University of Wisconsin, Madison, Wis. 53706.
- (2) For a discussion, see P. J. Kuntz in "Dynamics of Molecular Collisions," Part B, W. H. Miller, Ed., Plenum Press, New York, N.Y., 1976, Chapter 2; in particular, see pp 103 ff.
- (3) (a) J. C. Polanyi and W. H. Wong, *J. Chem. Phys.*, **51**, 1439-1450 (1969); (b) N. H. Hijazi and K. J. Laidler, *ibid.*, **58**, 349-353 (1973).
- (4) D. C. Wigfield and B. Lem, *Tetrahedron*, **31**, 9-11 (1975).
- (5) (a) J. E. Leffler, *Science*, **117**, 340-341 (1953); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, pp 156-161.
- (6) (a) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Am. Chem. Soc.*, **94**, 1364-1365 (1972); (b) J. Bron, *Can. J. Chem.*, **52**, 903-909 (1974).
- (7) (a) N. Jonathan, S. Okuda, and D. Timlin, *Mol. Phys.*, **24**, 1143-1164 (1972); (b) R. L. Wilkins, *J. Chem. Phys.*, **58**, 2326-2332 (1973).
- (8) J. T. Muckerman, *J. Chem. Phys.*, **56**, 2997-3006 (1972).
- (9) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334-338 (1955).
- (10) (a) For a discussion, see J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions," Part I, 3rd ed., E. S. Lewis, Ed., Wiley, New York, N.Y., 1974, pp 466-468; (b) for a review of the use and *misuse* of the Hammond postulate, see D. Fărcasiu, *J. Chem. Educ.*, **52**, 76-79 (1975).
- (11) J. C. Polanyi, *J. Chem. Phys.*, **31**, 1338-1351 (1959).
- (12) R. A. Marcus, *J. Phys. Chem.*, **72**, 891-899 (1968).
- (13) M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **51**, 1451-1469 (1969).
- (14) To derive eq 1, consider constructing any array of m particles. For $m = 3$, obviously $n = 3$. After three particles, for each one successively added to an array, three additional interparticle distances will completely specify the particle's relative position and therefore the configuration of the enlarged array. Hence, $n = 3 + 3j$, where j is the number of particles added after the first three. Since $j = m - 3$, $n = 3 + 3(m - 3) = 3m - 6$.
- (15) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544-2551 (1963).
- (16) D. G. Truhlar, *J. Am. Chem. Soc.*, **94**, 7584-7586 (1972).
- (17) An MO calculation for the F-atom transfer HF + H predicts an activated-complex HF bond length of 1.14 Å; see C. F. Bender, B. J. Garrison, and H. F. Schaefer III, *J. Chem. Phys.*, **62**, 1188-1190 (1975). Pauling's relation (see text) with the assumption that bond order is conserved, and therefore $b = 0.5$, predicts in good agreement a value of 1.10 Å. Free-radical abstractions and S_N2 displacements are condensed-phase reactions possibly exhibiting conservation of bond order.
- (18) See almost any reference cited in Table I.
- (19) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542-553 (1947). The relation is essentially eq 6 with x changed to b .
- (20) The first derivative of the Morse function as a function of x is ${}^1E'_2(x) = 2D\alpha\beta_2(x^{2\alpha\beta_2-1} - x^{\alpha\beta_2-1})$; hence, ${}^1E'_2(0) = {}^1E'_2(1) = 0$. A similar expression can be written for the AB bond. For the meaning of the symbols, see text below.
- (21) Naturally the absolutely shortest potential curve would consist of straight line segments; however, it is assumed, as expressed in eq 11-16, that there are additional constraints on the chemical system which preclude this. It should be noted that arc-length minimization of a coordinate function does not in general similarly minimize the vector function (\mathbf{R}) of which it is a component.
- (22) A. R. Miller, "An Arc Length Minimization Theorem for General Double-Knot Spline Functions", manuscript to be submitted to *Appl. Math. Optim.*
- (23) See C. B. Boyer, "A History of Mathematics", Wiley, New York, N.Y., 1968, p 192.
- (24) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, N.Y., 1966, pp 82, 179-183, 209-214, 339-345.
- (25) The reaction parameters used for both the BEBO and LEPS simulations were as follows: $D_1 = 90$ kcal/mol, $D_3 = 85$ kcal/mol, $r_1 = r_2 = 1.09$ Å, $r_3 = 1.54$ Å. For the BEBO simulation, the noble-gas parameters were those given by Johnston and Parr¹⁵ and Johnston.²⁴
- (26) S. Sato, *J. Chem. Phys.*, **23**, 592-593 (1955).
- (27) For further discussion of the method, see (a) ref 24, pp 58-62, 171-173, and 177-179, and (b) ref 7a.
- (28) S. Sato, *J. Chem. Phys.*, **23**, 2465-2466 (1955).
- (29) See, for example, G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, New York, N.Y., 1950, p 101.
- (30) G. W. Koeppel and A. J. Kresge, *Chem. Commun.*, 371-373 (1973).
- (31) I thank Professor R. Claude Woods, University of Wisconsin, Madison, for suggesting the complete correction.
- (32) (a) For the normal vibrations of CH_4 and CH_3 , see G. Herzberg, ref 29, Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules", 1945, pp 100 and 179. (b) For the corresponding frequencies for CH_4 , see G. Herzberg, ref 29, Vol. III, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", 1967, p 619. (c) For the corresponding frequencies for CH_3 , see A. Snelson, *J. Phys. Chem.*, **74**, 537-544 (1970). (d) The zero-point energy z is given by $z = 1.4299 \times 10^{-3} \nu$ kcal/mol, where ν is in cm^{-1} . (e) Application of the formula in *d* to each vibration (some degenerate) gives a zero-point energy of 27.2 kcal/mol for CH_4 and 18.3 kcal/mol for CH_3 , or a net correction of 8.9 kcal/mol. (f) The zeroth-level dissociation energy for CH_4 is 104.2 kcal/mol: J. C. Amplett and E. Whittle, *Trans. Faraday Soc.*, **64**, 2130-2142 (1968).
- (33) I thank Professor L. M. Raff, Oklahoma State University, Stillwater, for suggesting the appropriateness of this vibration.
- (34) A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, **97**, 2757-2763 (1975).
- (35) I thank Professor A. A. Zavitsas, Long Island University, Brooklyn, for sending me a listing of his Program ZAV/3.
- (36) NOTE ADDED IN PROOF. While this paper was in press, it was brought to my attention that a similar paper was in press elsewhere; see N. Agmon, *J. Chem. Soc., Faraday Trans. 2*, in press. In the latter, a rearranged form of eq 24 is derived and its physical realism corroborated; use of the relation is based on a symmetry principle (related to arc length minimization).

Reactive Complex Theory of Photochemical Reactions. A Nonequilibrium Approach to Chemical Rate Processes in Condensed Media

Dennis J. Diestler* and Francis K. Fong

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received March 1, 1977

Abstract: A description of photochemical reactions in dense media is formulated in terms of the quantum statistical mechanical theory of molecular relaxation. The present formulation represents a fundamental departure from equilibrium rate theories derived from Eyring's transition-state theory. A central feature of the model is the photoactivation of a "reactive complex", which may undergo either deactivation to the ground state or reaction to yield the primary photochemical products. The theoretical description is specialized to photofragmentation reactions in solvent media. The rate constants for both deactivation and primary reaction are calculated by invoking the Born-Oppenheimer adiabatic approximation. Deactivation results from a coupling of the reaction coordinate to the center-of-mass motion of the reactive complex. Reaction, on the other hand, arises from coupling of the states of the reactive complex with those of solvent-separated fragments along the reaction coordinate itself. The theory is in qualitative accord with the results of recent picosecond time-resolved laser studies of the geminate recombination of iodine atoms in organic liquid solvents.

I. Introduction

In recent years there have been a number of developments in the quantum statistical mechanical (QSM) theory of rate

processes in condensed media.¹⁻⁹ These efforts depart from conventional equilibrium rate theories derived from Eyring's transition-state theory (TST).¹⁰⁻¹² The principal goal of the new approach is to derive explicit expressions for the rate

constant in terms of the molecular properties of the equilibrium configurations of the reactant and product systems.⁸ The theoretical treatment has been applied to a variety of thermally activated rate processes: dielectric relaxation of polar molecules in nonpolar solvents,¹ interstitial migration in ionic crystals,^{1,3} carbocation rearrangement,⁴ and bimolecular reactions in liquid solvent media.⁹ The purpose of this paper is to present a QSM model for photochemical reactions in dense media.

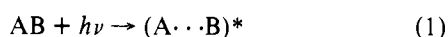
A thermally activated process may be described as a nuclear rearrangement of a system from one local equilibrium configuration (reactants) to another (products). It is common to partition the multidimensional configuration space of the system into a reaction coordinate R and the remaining degrees of freedom (d.f.) "normal" to R . From a classical viewpoint, the rearrangement takes place as the system traverses R from reactants to products. From a quantum-dynamical point of view, the rearrangement is induced by a coupling between the zero-order states of reactant and product. In the QSM model which we have developed,^{1,3,4,7,8} the rate constant, calculated by perturbation theory, depends explicitly upon the displacement ΔR between the equilibrium configurations of reactant and product, the activation barriers E_a between reactant and product configurations, i.e., the maximum in the potential-energy profile along R , and the effective mass m_r and frequency ω_r of vibration of the "reactive complex" along R at the local minimum of the reactants.⁸ The concept of the reactive complex, which we shall delineate fully below, should not be confused with that of "activated complex" in the TST.

A proper consideration of photochemical reactions extends beyond the discussion of thermally activated rate processes. It is necessary to take into account the various competitive processes consequent to the photoactivation of the reactive system. A molecule absorbs a photon and undergoes transition to a chemically active state, a reactive complex that may undergo the following competitive processes: (a) photophysical relaxation via radiative or radiationless pathways that return the molecule to its ground state (the "back reaction") and (b) chemical reaction that results in ionization, isomerization, or fragmentation of the reactant molecule. Of primary interest to the photochemist is the quantum efficiency of the photochemical pathway, which may be expressed in terms of the rate constants for the various competing processes.¹³

A great deal of attention has been devoted to the treatment of *photophysical* processes in isolated molecules^{7a,14} and molecular systems in condensed phases.^{7,15} While photoisomerization^{16,17} and photofragmentation¹⁸ of *isolated* molecules have been examined by several authors, no effort thus far has been made to develop a model for photochemical processes in dense media. In the following section we describe such a model that explicitly invokes the role of solvent. We have specialized this description to photofragmentation reactions, although with suitable modifications it can be extended to other types of photochemical processes. In section III, we develop explicit expressions for the rate constants for deactivation and primary reaction. Section IV is then devoted to application of the model to the geminate recombination of iodine atoms in solution. We close in the last section with a summary of the principal features of our model, some possible extensions, and a brief comparison with "activated complex" theory.

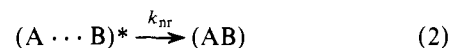
II. The Physical Model

Consider a dilute solution of molecules AB in solvent S. We assume the existence of electronically excited states accessible by absorption of a photon according to

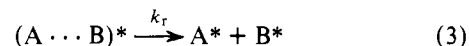


where the asterisk denotes an excited state. The photoexcita-

tion of a vapor-phase molecule into the state $(AB)^*$ normally leads quickly to dissociation. In solution, however, the entity $(A \cdots B)^*$ is quasi-bound, i.e., it is held together by the solvent cage at appropriately small values of R_{AB} (the separation of the centers of mass of the fragments A and B). The state $(A \cdots B)^*$, which we term the "reactive complex", may be deactivated via photophysical relaxation with rate constant k_{nr}



The deactivation competes with dissociation



having a rate constant k_r . Process 3 is generically known as the primary photochemical reaction. The resulting solvent-separated fragments A^* and B^* may recombine and deactivate to give AB, or they may diffuse away from each other, eventually encountering other species with which they can undergo *secondary* reactions.

Processes 2 and 3 both involve the relaxation of $(A \cdots B)^*$ from some initial distribution of vibronic levels. The energy given up (or absorbed) in transitions between initial and final vibronic levels must be absorbed (or given up) by modes of motion (i.e., d.f.) other than R_{AB} (i.e., the reaction, or dissociation, coordinate). The efficiency with which a given mode can mediate the vibronic transitions depends upon the strength of its coupling to R_{AB} . Thus, in developing a theory of the relaxation processes 2 and 3, we must consider the possible dynamical participation of the following additional d.f.: (1) localized oscillatory motions of centers of mass of $(A \cdots B)^*$ itself or neighboring S molecules; (2) orientational (i.e., rotational or librational) motions of AB or S; (3) internal (i.e., vibrational) modes of AB or S; (4) radiation-field modes.

As an illustrative example, and in the calculation of k_{nr} to follow, we assume that A, B, and S are structureless, i.e., they possess no internal d.f. Further, we neglect orientational motions. We adopt as d.f. "relevant" to the relaxation process the dissociation (reaction) coordinate R_{AB} and the center-of-mass (COM) coordinate r of the reactive complex. In the spirit of the Lennard-Jones-Devonshire cell model,¹⁹ we smear the Z nearest-neighbor S's over the surface of a sphere to give a cell potential which effectively confines the reactive complex to a solvent cage. Fixing r , we sketch a profile (along R_{AB}) in Figure 1 of the Born-Oppenheimer adiabatic potential-energy surfaces for the ground state and a typical photoactive excited state. At small values of R_{AB} the potential curves are determined mostly by *intramolecular* (chemical bonding) forces, and differ little from those for the isolated AB. As R_{AB} increases, the *intermolecular* interactions between AB and S become increasingly important. The potential energy rises until the fragments pass over the "solvent" barrier, beyond which they become a solvent-separated pair, each fragment occupying its own cell.

III. Expressions for the Rate Constants

The rate constant k_r for the primary reaction 3 may be calculated roughly within the framework of the simple QSM theory developed in ref 8. We explicitly consider only motion along R_{AB} and approximate the potential-energy curves of the reactive complex and the solvent-separated pair by two horizontally displaced harmonic wells (see Figure 1). The dissociation of $(A \cdots B)^*$ results from a coupling between the harmonic zero-order states of $(A \cdots B)^*$ and $A^* + B^*$. Following Freed and Fong,³ we take this coupling to be simply the difference between the "true" adiabatic surface (solid line in Figure 1) and the harmonic fit (dashed line in Figure 1)

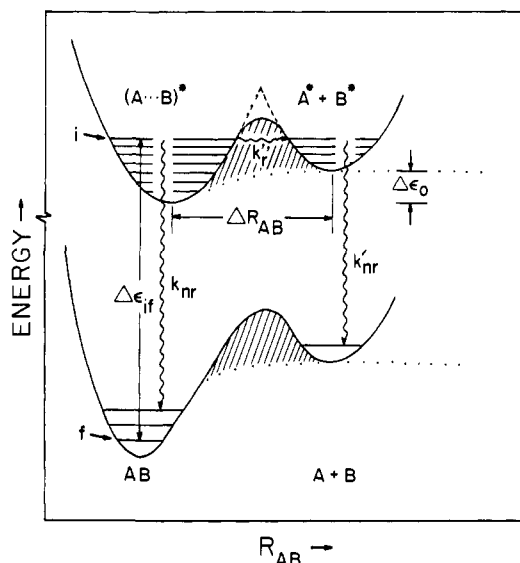


Figure 1. Schematic diagram of the potential-energy curves for the ground-state molecule AB and the excited reactive complex (A...B)*. The dotted (---) portions of the curves refer to the isolated molecule and the solid (—) ones to the molecule contained in the solvent cage. The shaded area represents the effect of the solvent, which is assumed to be the same in both states. The dashed (---) curves are harmonic approximations to the potential wells of the quasi-bound (A...B)* and solvent-separated pair A* + B*. For the sake of simplicity, it is assumed here and in the text that the harmonic potentials have the same force constants, i.e., frequencies of vibration, and are displaced from one another horizontally (along the reaction coordinate) by ΔR_{AB} and vertically by $\Delta\epsilon_0$. The i and f denote two specific vibronic levels of (A...B)* and AB, respectively.

thereto. By previously described³ procedures we get

$$k_r = |V'|^2 \hbar^{-2} [m_r \omega_r^2 (\Delta R_{AB})^2 k_B T \hbar^{-2} / 2\pi]^{-1/2} \times \exp\{-[\Delta\epsilon_0 - m_r \omega_r^2 (\Delta R_{AB})^2] / [2m_r \omega_r^2 (\Delta R_{AB})^2 k_B T]\} \quad (4)$$

where \hbar is Planck's constant, k_B is Boltzmann's constant, T is the absolute temperature, m_r and ω_r are the effective mass and frequency, respectively, of the vibration of (A...B)* along R_{AB} ; and ΔR_{AB} and $\Delta\epsilon_0$ are respectively the horizontal and vertical displacements of the (assumed) harmonic potentials. In arriving at eq 4, we have invoked the following approximation. The coupling potential $V'(R_{AB})$ is peaked at the point of intersection (cusp) of the harmonic curves (see Figure 1). Since the overlap of the zero-order states is greatest in the vicinity of this cusp, we can replace the full $V'(R_{AB})$ in the integrand of the coupling matrix elements by its value at the cusp. Thus, in eq 4 V' is just the difference between the cusp and the corresponding point on the "true" curve.

The calculation of the rate constant k_{nr} for the "back reaction" 2 can be accomplished by the following scheme. We assume, as discussed in section II, that the COM coordinate (r) of AB plays an explicit dynamical role in the deactivation process. Hence, we take as the strongly coupled "relevant" modes of motion R_{AB} and r , i.e., the stretching motion of (A...B)* and the wall-to-wall bouncing of (A...B)* in its solvent cage. For the zero-order states, we assume products of vibronic levels (i of (A...B)* or f of ground-state AB) and the localized translation-like states of the COM motion in the effective potential due to AB in the corresponding vibronic level (i or f). We further assume that the effective COM potentials are harmonic, with the force constant (frequency) depending upon the vibronic level. The reactive complex is deactivated via transitions $i \rightarrow f$ induced by vibronic non-Born-Oppenheimer coupling (H'_{NBO}); the excess energy is accepted by the COM mode and subsequently dissipated into the solvent modes.

The deactivation rate constant may be expressed formally

as

$$k_{nr} = 2\pi\hbar^{-1} \sum_i \sum_{\nu_i} p_{i\nu_i} \sum_f \sum_{\nu_f} |\langle i\nu_i | H'_{NBO} | f\nu_f \rangle|^2 \times \delta(E_{i\nu_i} - E_{f\nu_f}) \quad (5)$$

where i labels vibronic levels of (A...B)* and f those of AB, ν_i and ν_f denote, respectively, the corresponding COM states, $p_{i\nu_i}$ is the probability that (A...B)* is initially in vibronic level i and COM state ν_i , having total energy

$$E_{i\nu_i} = \epsilon_i + \epsilon_{\nu_i}$$

The coupling matrix element is given more explicitly by

$$\langle i\nu_i | H'_{NBO} | f\nu_f \rangle = \int d\tau_e \int dR_{AB} \int dr \times \phi_{ex}^*(\tau_e; R_{AB}) \chi_i^*(R_{AB}) \Psi_{\nu_i}^*(r) H'_{NBO} \times \phi_g(\tau_e; R_{AB}) \chi_f(R_{AB}) \Psi_{\nu_f}(r)$$

where ϕ_{ex} and ϕ_g are the Born-Oppenheimer electronic wave functions for (A...B)* and AB, respectively, χ_i and χ_f are the vibrational wavefunctions associated with initial and final vibronic levels, and Ψ_{ν_i} and Ψ_{ν_f} are the initial and final COM localized, translation-like wave functions. In general, the operator H'_{NBO} acts upon both electronic (τ_e) and nuclear (R_{AB} , r) coordinates. However, assuming for simplicity that H'_{NBO} operates only upon ϕ_g and also invoking the Franck-Condon approximation for both the vibrational (R_{AB}) and COM(r) modes, we have

$$\langle i\nu_i | H'_{NBO} | f\nu_f \rangle = V_{elec} \langle \chi_i | \chi_f \rangle \langle \nu_i | \nu_f \rangle \quad (6)$$

where

$$V_{elec} = \int d\tau_e \phi_{ex}^* H'_{NBO} \phi_g$$

is evaluated at the minimum of the adiabatic curve for (A...B)* (see Figure 1).

Substituting eq 6 into eq 5, we can evaluate the average over ν_f and sum over ν_i by standard procedures.^{20,21} Assuming that only the frequency of the COM mode shifts, we get

$$k_{nr} = \hbar^{-2} (2\pi)^{1/2} e |V_{elec}|^2 \sum_i p_i \sum_f |\langle \chi_i | \chi_f \rangle|^2 (\Delta\omega_{fi})^{-1} \times [1 - \exp(-\hbar\omega_i/k_B T)] \exp[-\Delta\epsilon_{if}\omega_i/(\Delta\omega_{fi}k_B T)] \quad (7)$$

where e is the base of the natural logarithm, p_i is now the probability that (A...B)* is initially in vibronic level i (irrespective of the state of the COM mode), ω_i and ω_f are the frequencies of the harmonic COM modes with (A...B)* in level i and AB in level f , $\Delta\epsilon_{if}$ is the energy difference between levels i and f , and $\Delta\omega_{fi} (= \omega_f - \omega_i)$ is the shift in the frequency of the COM mode associated with the vibronic transition $i \rightarrow f$.

In reaching eq 7 we have assumed

$$\omega_f > \omega_i$$

which is physically reasonable. The effective cell potential "seen" by the COM mode is overall quite anharmonic. However, in the initial state, the COM mode is not highly excited and hence the amplitude of the COM motion is relatively small, i.e., it "sees" only the region near the minimum of the cell potential, which can be well approximated by a harmonic potential of low frequency (ω_i). In the final state the COM mode is relatively more excited, having accepted energy $\Delta\epsilon_{if}$ from the internal mode (R_{AB}) of (A...B)*. Hence, the COM executes relatively large-amplitude oscillations within the cell and thus "sees" the steeper portions of the cell walls most of the time. These steeper portions of the cell potential are effectively represented by a harmonic potential of greater frequency (ω_f).

We note that each term of the right side of eq 7 exhibits an Arrhenius temperature dependence with an activation energy

$$(E_a)_{if} = \Delta\epsilon_{if}\omega_i/\Delta\omega_{fi}$$

$$= m_{AB}\omega_i(2\omega_i + \Delta\omega_{fi})r_0^2/4 \quad (8)$$

where m_{AB} is the mass of AB and r_0 is the value of r at the intersection of the harmonic COM curves corresponding to levels i and f (see Figure 2). The frequency shift $\Delta\omega_{fi}$ is responsible for this intersection. The activation energy $(E_a)_{if}$ is clearly related to the COM energy of the reactive complex measured from the minimum of the COM potential curve i . It is evident from Figure 2 that $(E_a)_{if}$ increases with increasing $\Delta\epsilon_{if}$ and/or ω_i and that it decreases with increasing ω_f and/or $\Delta\omega_{fi}$ for fixed ω_i .

In order to write eq 7 in closed form, we further assume that ω_i , $\Delta\omega_{fi}$, and $\Delta\epsilon_{if}$ are approximately constant and replace them by their average values $\bar{\omega}$, $\Delta\bar{\omega}$, and $\Delta\bar{\epsilon}$. Invoking the relations

$$\sum_i p_i = 1$$

$$\sum_f |\chi_f\rangle \langle \chi_f| = 1$$

we can perform the sums in eq 7 to obtain

$$k_{nr} = (2\pi)^{1/2} e \hbar^{-2} |V_{elec}|^2 (\Delta\bar{\omega})^{-1} [1 - \exp(-\hbar\omega/k_B T)] \times \exp[-\Delta\bar{\epsilon}\bar{\omega}/(\Delta\bar{\omega}k_B T)] \quad (9)$$

from which we see that the deactivation rate follows predominantly an Arrhenius temperature dependence with an average activation energy

$$\bar{E}_a = \Delta\bar{\epsilon}\bar{\omega}/\Delta\bar{\omega}$$

IV. Application

The rate constant for deactivation k_{nr} is seen from eq 9 to be strongly dependent on the solvent through the exponential factor

$$\exp[-\Delta\bar{\epsilon}\bar{\omega}/(\Delta\bar{\omega}k_B T)]$$

For a given solute AB it is convenient to express the solvent dependence of the rate constant in terms of the ratio

$$k_{nr}(1)/k_{nr}(2) \approx \exp[-\Delta\bar{\epsilon}(\bar{\omega}_1 - \bar{\omega}_2)/(\Delta\bar{\omega}k_B T)] \quad (10)$$

where the indices 1 and 2 denote two different solvents. The electronic coupling matrix element V_{elec} in eq 9 is only weakly dependent on the solvent and is accordingly canceled out in the approximate expression 10. In writing eq 10 we have made the further approximations that

$$\hbar\omega \ll k_B T$$

and that the difference quantities $\Delta\bar{\epsilon}$ and $\Delta\bar{\omega}$ are relatively insensitive to the solvent. In picosecond studies²² of geminate recombination of I atoms in organic liquid solvents it has been established empirically that $k_{nr}(\text{CCl}_4) < k_{nr}(\text{C}_8\text{H}_{18})$. Using eq 10, we may interpret this experimental observation in terms of the inequality

$$\omega(\text{CCl}_4) > \omega(\text{C}_8\text{H}_{18})$$

which is consistent with the expectation that the nearly spherical CCl_4 molecules would form a tighter solvent cage about the $(\text{I}\cdots\text{I})$ than would the irregularly shaped, gangly C_8H_{18} molecules. The tighter cage should result in a higher frequency of COM oscillation.

In order to arrive at a manageable, closed expression for k_{nr} (eq 7) we have introduced several approximations (in addition to perturbation theory, upon which the formal expression for k_{nr} rests from the outset). The Franck-Condon approximation (eq 6), made almost universally in theories of radiationless transitions, is valid if V_{elec} does not depend strongly upon R_{AB}

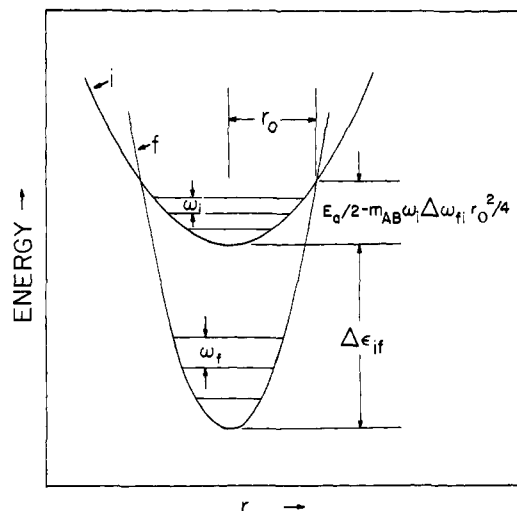


Figure 2. Sketch of the adiabatic potential-energy curves for the center-of-mass (COM) motion. The upper curve represents the effective potential energy "seen" by the COM of the reactive complex $(\text{A}\cdots\text{B})^*$ when it is in vibronic level i ; the lower curve is that "seen" by the AB molecule in level f of its ground state (see Figure 1). The potential curves are approximated by harmonic wells of frequencies ω_i and ω_f , respectively, with $\omega_f > \omega_i$. The reactive complex is deactivated by a transition (arising from coupling of the reaction coordinate and the COM coordinate r) between levels i and f , releasing energy $\Delta\epsilon_{if}$, which is first accepted by the COM mode and then dissipated into the solvent, which functions as a heat bath. The frequency difference $\Delta\omega_{fi}$ has been exaggerated in order to emphasize certain features of the curves. As $\Delta\omega_{fi} \rightarrow 0$ the vertical distance between the intersection of the curves (which occurs at $r = r_0$) and the minimum of the upper curve approaches one-half the activation energy defined by eq 8.

or r . If V_{elec} should vary substantially with R_{AB} or r , it may be expanded in Taylor's series about its minimum and the corrections included in the evaluation of the coupling matrix element $\langle i\nu_i | H'_{NBO} | f\nu_f \rangle$.^{23,24}

We have also assumed that the COM potential curves are harmonic and that the minima coincide, i.e., that only the frequency of the mode shifts, not its equilibrium position. This assumption appears to be appropriate for homonuclear diatomic molecules such as I_2 , however, in the case of reactive systems consisting of dissimilar fragments A and B, it may be necessary to allow for small displacements in the COM potential curves. This can be easily managed by the same techniques used in the so-called weak-coupling limit of radiationless electronic relaxation.^{7b}

Finally, we observe that while it seems reasonable to assume that ω_i , ω_f , and $\Delta\omega_{fi}$ are independent of i and f , $\Delta\epsilon_{if}$ may depend strongly on the initial and final levels. Hence, in general, for greater accuracy one must evaluate each term of the sum in eq 7 individually.

V. Summary and Discussion

We have developed here a model for photochemical reactions in dense media. We have specialized the model to photofragmentation, although it can readily be extended to other photochemical reactions, e.g., photoisomerism. Among the main features of the model is the photoexcitation of a *reactive complex*, which can either be deactivated to the ground state or decompose to yield the primary products. We assume that the vibronic levels of the system can be described in the Born-Oppenheimer adiabatic approximation. The primary reaction, i.e., the decomposition of the reactive complex $(\text{A}\cdots\text{B})^*$, occurs via a nuclear rearrangement along the reaction coordinate R_{AB} and is due to (potential) coupling between the states of $(\text{A}\cdots\text{B})^*$ and the solvent-separated pair A^* and B^* . Only motion along the reaction coordinate is explicitly treated. Our description of the deactivation process, on the other hand, accounts explicitly for the dynamical participation of several

degrees of freedom. In the simple version developed here, we have included only R_{AB} and the center-of-mass coordinate r . The center-of-mass motion accepts the energy released in the deactivating vibronic transitions originating from levels i of $(A\cdots B)^*$.

In general, of course, a variety of modes may strongly participate in the dynamics of either relaxation process (see eq 2 and 3). For example, like the COM mode of AB, the orientational mode of AB or the COM (or orientational) modes of the solvent (S) molecules are of relatively low frequency and could function to accept relatively small amounts of energy. Hence, these modes should efficiently mediate relatively low-energy vibronic transitions. On the other hand, the internal vibrational modes of AB or S are of relatively high frequency and could, by single or few-quantum excitations, with the assistance of the lower frequency COM modes, provide many pathways by which higher energy vibronic transitions could be mediated. The efficiency of these various pathways depends, of course, upon the strength of coupling between R_{AB} and the accepting mode.

It is of interest to note the close analogy that exists between the present view of photodissociation processes and the previously described model for the photosynthetic primary light reaction.²⁵ The photoactivation of $(A\cdots B)^*$ followed by the primary dissociative reaction to yield the A^* and B^* fragments in the present case corresponds formally to the photoexcitation of the charge transfer (CT) state in the reaction-center chlorophyll {Chl a} resulting in the oxidation of {Chl a} and the reduction of the primary electron acceptor A in the photosynthesis problem (compare Figure 1 with Figure 1 of ref 25). In both cases, the quasi-bound state $(A\cdots B)^*$ and the CT state in {Chl a} are envisaged to be electronically excited states of the reactants. Both of these states are photophysically connected with their respective ground-state species through nonreactive pathways with associated rate constants given approximately by eq 9.

We close by emphasizing that our concept of the reactive complex differs fundamentally from that of the activated

complex in transition-state theory. Unlike the activated complex, a transient species located at the top of the barrier to chemical reaction, the reactive complex in our theory is a stable molecular entity (in the zeroth order of time-dependent perturbation theory). Aside from this conceptual difference, the present formulation provides explicit expressions for the rate constant, eq 4 and 9, in terms of molecular parameters and thermodynamic state variables (e.g., temperature). Numerical fits of rate data using eq 4 and 9 should therefore furnish useful information about the microscopic properties of the system which are most influential in determining its dynamical behavior.

References and Notes

- (1) F. K. Fong and D. J. Diestler, *J. Chem. Phys.*, **57**, 4953 (1972).
- (2) S. H. Lin and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3192 (1972).
- (3) K. F. Freed and F. K. Fong, *J. Chem. Phys.*, **63**, 2890 (1975).
- (4) F. K. Fong, *J. Am. Chem. Soc.*, **96**, 7638 (1974).
- (5) V. M. Fain, *J. Chem. Phys.*, **65**, 1854 (1976).
- (6) S. H. Lin, K. P. Li, and H. Eyring, *Phys. Chem.*, **7**, 1 (1975).
- (7) F. K. Fong, "Theory of Molecular Relaxation", Wiley-Interscience, New York, N.Y., 1975: (a) Section 5.4; (b) Chapter 6.
- (8) F. K. Fong, *Acc. Chem. Res.*, **9**, 433 (1976).
- (9) F. K. Fong, *J. Am. Chem. Soc.*, submitted.
- (10) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).
- (11) W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).
- (12) K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, N.Y., 1969.
- (13) G. Porter, V. Balzani, and L. Moggi, *Adv. Photochem.*, **9**, 147 (1974).
- (14) K. F. Freed in "Topics in Applied Physics", Vol. 15, F. K. Fong, Ed., Springer-Verlag, Heidelberg, 1976, Chapter 2.
- (15) D. J. Diestler in ref 14, Chapter 3.
- (16) W. M. Gelbart, K. F. Freed, and S. A. Rice, *J. Chem. Phys.*, **52**, 2460 (1970).
- (17) A. Warshel and M. Karplus, *Chem. Phys. Lett.*, **32**, 11 (1975).
- (18) S. Mukamel and J. Jortner, *J. Chem. Phys.*, **65**, 3735 (1976).
- (19) See, for example, D. A. McQuarrie, "Statistical Thermodynamics", Harper and Row, New York, N.Y., 1973, Chapter 12.
- (20) K. F. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).
- (21) S. F. Fischer, *J. Chem. Phys.*, **53**, 3195 (1970).
- (22) T. J. Chung, G. W. Hoffman, and K. B. Eisenthal, *Chem. Phys. Lett.*, **25**, 201 (1974).
- (23) A. Nitzan and J. Jortner, *J. Chem. Phys.*, **58**, 2412 (1973).
- (24) W. A. Wassam and F. K. Fong, *J. Chem. Phys.*, **65**, 3102 (1976).
- (25) F. K. Fong, *J. Am. Chem. Soc.*, **98**, 7840 (1976).

Strengths of A–A Single Bonds in Symmetric A_2B_{2n} Molecules and Ions¹

Benjamin M. Gimarc,*² Shakil A. Khan, and Michael C. Kohn

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received March 14, 1977

Abstract: In symmetric A_2B_4 molecules and ions with 34 and 38 valence electrons, two AB_2 monomers are joined by an A–A single bond. In 50-electron ethanelike A_2B_6 structures, two AB_3 monomers are also linked by an A–A single bond. Symmetric BAAB systems with 18 and 26 electrons have A–A single bonds. A qualitative MO model of the electronic structures of these systems is developed and then used to explain observed trends of increasing A–A bond strength with increasing electronegativity difference ΔX between central atoms A and substituents B. An increase in ΔX tends to strengthen the A–A bond in the A_2B_4 and A_2B_6 classes. For example, the central bond in F_2B-BF_2 is much stronger than that in O_2N-NO_2 . Larger ΔX increases the weighting and extent of hybridization of the central atom AOs in the orbitals responsible for net bonding in these systems. While the same rule holds for the 26-electron BAAB series, the reverse is true for the 18-electron examples. For instance, the central C–C bond in PCCP is stronger than that in NCCN for which ΔX is larger. The same principles apply in these cases but the rule reverses because of different properties of the MO that provides net bonding. The electronegativity rule is used to rationalize the nonexistence of certain compounds or to explain their preference for less symmetric structures.

We develop here a qualitative MO model³ of the electronic structures of certain molecules and ions with the general formulas A_2B_{2n} . The model is based on extended Hückel cal-

culations⁴ for a number of different A_2B_2 , A_2B_4 , and A_2B_6 systems. The calculations and the qualitative model assume that MOs are formed from a basis set consisting of a single s