

Multiphonon Processes in the Nonradiative Decay of Large Molecules

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Radiationless transition rates for polyatomic molecules are investigated in the simplest case of the statistical limit, i.e., large energy gaps between the two electronic states. By analogy with the theory of optical line shapes in solids, the "golden rule" rate expression for the nonradiative decay, which is usually written as a double sum over initial and final vibronic states, is equivalently represented in closed form as a single Fourier integral. For the case in which the vibrations are assumed to be harmonic, but may have different frequencies and equilibrium positions in the two electronic states, general closed-form analytic expressions, which include all of the vibrational modes, are obtained for the transition rates. The energy gap law is again obtained in the weak coupling statistical limit along with a proper description of the propensity rules for the promoting mode. For the case of the aromatic hydrocarbons, the effective energy gap is found to be in agreement with Siebrand's analysis, and explicit account is taken of the competition between the C-H modes and the C-C skeletal modes (which have large oscillator displacements) or the out-of-plane modes (which have large frequency changes) for the electronic energy which is involved in the relaxation process. The deuterium isotope effect is again found to be dominated by the modes of highest frequency (C-H or C-D), but corrections due to the C-C modes, which may be measurable, are explicitly included. The theory is also extended to include the role of the host medium as an inert heat bath by considering the intermolecular phonons as potential accepting modes. The approximations employed are compared with those usually made in Boltzmann statistical mechanics, thereby providing greater understanding as to the role of the Franck-Condon principle in the determination of the nonradiative decay rates.

I. INTRODUCTION

Recently considerable theoretical effort has been devoted to the elucidation of the nature of radiationless transitions in the excited electronic states of large molecules.¹ When we consider those relaxation phenomena which do not involve changes in molecular composition or molecular charge, two classes of radiationless processes may be identified:

- (a) relaxation between different electronic states, e.g., internal conversion and intersystem crossing²⁻²²;
- (b) photochemical rearrangement reactions in excited electronic states of large molecules, such as *cis-trans* isomerization and electrocyclic reactions.²³⁻²⁵

Much of the previous theoretical work^{2,9,10,14-20} on electronic relaxation processes in large molecules focused attention on the nature of the intramolecular dissipative process in the case of a dense manifold of (zero-order) vibronic levels, the nature of irreversibility in the electronic relaxation process, and the consequences of coupling of radiative and nonradiative decay channels, but paid little attention to photochemical rearrangement reactions. The theory was mainly concerned with providing a general understanding of all of the diverse phenomena which are classified as involving radiationless transitions, and therefore did not deal with specific details^{11-13,21} which are peculiar to a given molecule, or class of molecules. Thus, being equipped with a general qualitative understanding of the "mechanisms" leading to the different manifestations of radiationless transitions, we now investigate the quantitative factors which affect the experimentally observed nonradiative decay rates in specific classes of molecules. The simplest case, namely electronic

relaxation in molecules in the statistical limit,¹⁶ is the only one which is discussed in this paper.

The gross features of both electronic relaxation and some photochemical rearrangement processes in a large molecule (statistical limit) can be described in terms of a simplified model which is based on the following assumptions:

- (a) A two-manifold electronic system is considered, consisting of a small number of (zero-order) vibronic states $\phi_{s1}, \phi_{s2}, \dots$, etc., for one manifold and a dissipative quasicontinuum of levels $\{\phi_{lj}\}$ for the second manifold. The first index labels the electronic manifold, while the second index corresponds to the vibronic level within a given electronic manifold. The general form of the zero-order Born-Oppenheimer functions is

$$\phi_{si}(\mathbf{q}, \mathbf{Q}^{(s)}) = \phi_s(\mathbf{q}, \mathbf{Q}^{(s)}) \chi_{si}(\mathbf{Q}^{(s)}), \quad (\text{I.1a})$$

$$\phi_{lj}(\mathbf{q}, \mathbf{Q}^{(l)}) = \phi_l(\mathbf{q}, \mathbf{Q}^{(l)}) \chi_{lj}(\mathbf{Q}^{(l)}), \quad (\text{I.1b})$$

where \mathbf{q} represents the electronic coordinates, $\mathbf{Q}^{(\alpha)}$ labels the nuclear coordinates in the electronic state $\alpha \equiv s, l$, while ϕ and χ correspond to electronic and vibrational wavefunctions.

- (b) The radiationless process involves intramolecular relaxation. We shall limit ourselves to consideration of an inert medium as discussed in Sec. IX which does not modify the molecular energy levels or the spin-orbit coupling in the molecule under study.

- (c) Interference effects between resonances may be neglected. It is thus assumed that the spacings between consecutive resonances (centered about the energies E_{si} , of the zero-order states ϕ_{si}) considerably exceed the widths of these resonances.²⁶

Given (b) and (c), the nonradiative decay prob-

ability of the sparse manifold $\{\phi_{si}\}$ is given by the conventional "golden rule" expression²⁷

$$W = (2\pi/\hbar) \sum_i \sum_j p(si) |V_{si,lj}|^2 \delta(E_{si} - E_{lj}), \quad (I.2)$$

where the off-diagonal matrix elements of the electronic Hamiltonian are

$$V_{si,lj} = \langle \phi_{si} | V | \phi_{lj} \rangle, \quad (I.3)$$

with

$$V = H - H_{BO}, \quad (I.3')$$

and $p(si)$ is the probability that the system be initially in the zero-order state ϕ_{si} , so that $\sum_i p(si) = 1$. Provided that the vibrational relaxation (and excitation) rates considerably exceed the nonradiative decay probability, thermal equilibrium prevails and

$$p(si) = Z^{-1} \exp(-\beta E_{si}), \quad (I.4)$$

where $Z = \sum_i \exp(-\beta E_{si})$ is the partition function and $\beta = (k_B T)^{-1}$.

Equation (I.2) has been reduced, in the past, by crude factorization methods which separate it into a product of coupling matrix elements of the form $|V_{si}|^2$ and a density of states $\rho = \sum_j \delta(E_{si} - E_{lj})$. Furthermore, the McCoy-Ross-Robinson-Frosch recipe, in which the coupling matrix elements (I.3) are approximated in terms of a product of an electronic term and a Franck-Condon vibrational overlap factor, has become popular.

Equation (I.2) in the harmonic approximation is completely analogous to the formal expressions for the probability of nuclear recoil in Mossbauer spectroscopy in solids,²⁸⁻³⁰ and to the transition probabilities in the theory of line shapes and zero phonon lines in the optical spectra of solids.³¹⁻³⁶ In an extensive study of radiative and nonradiative processes in solid-state theory, Kubo and Toyozawa^{34,37} have demonstrated that the full "golden rule" expression (I.2), containing the double sum over initial and final states, and involving any arbitrary operator, can be written exactly as a single definite (Fourier or Laplace) integral. In the context of nonradiative phenomena, the theory has been applied to multiphonon ionization processes in solids.^{34,36} Since a solid is just a large molecule, Lin and Bersohn,^{9,10} and later Englman and Jortner,²² proposed that molecular nonradiative decay processes in the statistical limit be considered to be (intra-molecular) multiphonon processes in a large molecule. Lin and Bersohn have discussed some of the implications of the "golden rule" rate as to the nature of the promoting and accepting modes and the temperature dependence and isotope effects in radiationless transitions. Lin⁹ had also demonstrated how the inclusion of the nuclear momentum operator gives rise to the propensity rule for the promoting modes. Englman and Jortner²² have recently used the many-phonon approach to the full rate expression (I.2) to derive approximate expressions for the nonradiative decay probability

(I.3) which could be reduced to simple analytic forms for two limiting cases which are determined by the magnitude of a reduced vibrational coupling strength function (not to be confused with the electronic coupling strength!). The strong coupling limit (which corresponds to the existence of substantial horizontal displacement of the multidimensional potential-energy surfaces of the two electronic states) may be appropriate to some photochemical rearrangement processes²⁵ and some radiationless transitions between charge-transfer states (e.g., $A^+B^- \rightarrow AB$ type),³⁸ while the weak coupling limit (for which the relative horizontal displacement of the two potential-energy surfaces is small) is appropriate to the description of electronic relaxation processes in aromatic hydrocarbons and possibly some heteroaromatics. Thus, Englman and Jortner were able to show that the full rate expression (I.2) does in fact imply both the experimentally observed energy gap law for radiationless transition rates in aromatic hydrocarbons and the nature of the accepting modes. The studies of Lin and Bersohn^{9,10} and of Englman and Jortner²² involved several approximations which were introduced to simplify the rather cumbersome theoretical expressions for the nonradiative decay probability in the harmonic approximation. Lin's formal expression recast the nonradiative decay rate in terms of a Fourier integral, and even these expressions involve some approximations concerning the role of frequency changes between the two electronic states. The equations of Englman and Jortner are physically transparent, but only a simple model system (involving just shifted identical potential surfaces) was studied. These authors also neglected the dependence of the rate (I.2) on the nuclear kinetic-energy operator. In view of current experimental and theoretical interest in electronic relaxation processes and organic photochemical rearrangement reactions we felt that a more complete study of the nonradiative decay of the harmonic molecule would be of value.

In the present work we utilize the generating function method to derive general expressions for the nonradiative rate in the harmonic approximation. These expressions can be considerably simplified for the simple displaced potentials model and also for a more general case of physical interest, which involves both displacement of potential surfaces and moderate changes in the vibrational frequencies between the two electronic states. The weak and strong coupling limits are discussed in more detail than in previous work. In the strong coupling case the decay probability can be recast in terms of a traditional rate equation which involves a generalization of the Eyring pre-exponential factor. In the weak coupling limit we have been able to elucidate the role of the promoting modes in the energy gap law. We also assess the role of different intramolecular vibrational modes (characterized either by displacement of the origin or modification of the force

constants for the potential surfaces) on the non-radiative decay probability. It is demonstrated how the effects of an external inert medium on the non-radiative decay can be included in the theoretical scheme by considering simultaneously intramolecular and intermolecular multiphonon processes. Finally, a discussion is given of the possible extension of the theory to bypass some of the restrictions imposed by the Harmonic approximation.

II. GENERATING FUNCTIONS AND GREEN'S FUNCTIONS

The generating function method³⁴ is designed to compute the generalized density-of-states function of the form (I.2) (e.g., the density of states weighted by the matrix elements of an arbitrary operator). Thus, this technique can be used to calculate the line shape of optically allowed or forbidden transitions in large molecules, where the operator V is then a constant or proportional to one of the oscillator displacements, respectively. Although we focus attention on the non-radiative decay probability, it should be borne in mind that these methods are quite general. We shall give a brief summary of the method so as to introduce the notation used and to specify the approximations employed, separating those approximations which are necessary from those which are merely convenient. We have attempted to keep the number of cumbersome equations to a minimum, so some of the details are summarized in the appendices.

We consider the generalized line-shape function

$$F(E) = Z^{-1} \sum_i \sum_j |V_{si,lj}|^2 \exp(-\beta E_{si}) \times \delta(\Delta E + E_{lj} - E_{si} - E), \quad (\text{II.1})$$

where the energies of the vibronic levels in each electronic manifold are measured from the zeroth level of that manifold, so that ΔE corresponds to the energy gap between the lowest vibronic components of the two electronic states

$$\Delta E = E_{s0} - E_{l0}. \quad (\text{II.2})$$

The transition probability (I.2) is obviously

$$W = (2\pi/\hbar) F(0). \quad (\text{II.3})$$

Rather than use (II.1), we consider its Fourier transform

$$f(t) = \int_{-\infty}^{\infty} \exp\left(\frac{i(E - \Delta E)t}{\hbar}\right) F(E) dE, \quad (\text{II.4})$$

which can be expressed in the form

$$f(t) = Z^{-1} \sum_i \sum_j V_{si,lj} \exp(iE_{lj}t/\hbar) V_{lj,si} \times \exp(-iE_{si}\tau/\hbar), \quad (\text{II.5})$$

where

$$\tau = t - i\hbar\beta. \quad (\text{II.5}')$$

It is considerably easier to evaluate $f(t)$ than $F(E)$. From $f(t)$ the line-shape function is obtained by the inverse transformation

$$F(E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} f(t) \exp\left(-\frac{i(E - \Delta E)t}{\hbar}\right) dt. \quad (\text{II.6})$$

Thus the transition probability is

$$W = (\hbar^2)^{-1} \int_{-\infty}^{\infty} f(t) \exp\left(-\frac{i\Delta Et}{\hbar}\right) dt. \quad (\text{II.7})$$

The expression for the generating function [Eq. (II.5)] can be recast in terms of the operators

$$V_{sl}(\mathbf{Q}) = \int d\mathbf{q} \phi_s(\mathbf{q}, \mathbf{Q}) V \phi_l(\mathbf{q}, \mathbf{Q}) \quad (\text{II.8})$$

(where \mathbf{Q} implies *all the nuclear coordinates*) and the Green's functions for nuclear motion in the electronic states s and l , which are

$$G_s(\mathbf{Q}^{(s)}, \tau; \mathbf{Q}^{(s)'}, 0) = \sum_i \chi_{si}(\mathbf{Q}^{(s)}) \chi_{si}^*(\mathbf{Q}^{(s)'}) \times \exp(-iE_{si}\tau/\hbar), \quad (\text{II.9a})$$

$$G_l(\mathbf{Q}^{(l)'}, -t; \mathbf{Q}^{(l)}, 0) \equiv G_l^*(\mathbf{Q}^{(l)}, t; \mathbf{Q}^{(l)'}, 0) = \sum_j \chi_{lj}(\mathbf{Q}^{(l)'}) \chi_{lj}^*(\mathbf{Q}^{(l)}) \exp(iE_{lj}t/\hbar). \quad (\text{II.9b})$$

Then Eq. (II.4) can be displayed in a transparent form in terms of the trace over total vibrational states of the matrix (operator) product,

$$f(t) = Z^{-1} \text{Tr}(V_{sl} G_l V_{ls} G_s), \quad (\text{II.10})$$

or in the explicit form

$$f(t) = Z^{-1} \iint d\mathbf{Q} d\mathbf{Q}' [V_{sl}(\mathbf{Q}) G_l(\mathbf{Q}^{(l)'}, -t; \mathbf{Q}^{(l)}, 0)] \times [V_{ls}(\mathbf{Q}') G_s(\mathbf{Q}^{(s)}, \tau; \mathbf{Q}^{(s)'}, 0)]. \quad (\text{II.11})$$

The formal result (II.11) is greatly simplified in the case that the vibrational motion in both electronic states can be expressed in terms of independent oscillators; *these need not be harmonic, or have the same frequencies in both states*. In this case the vibrational wavefunctions and energies of (II.9) are separable into products and sums, respectively, of the modes, so that the Green's functions for each of the vibronic states are separable into products of Green's functions g_j^α for each of the vibrational modes j in both of the electronic states $\alpha = l$ or s :

$$G_\alpha(\mathbf{Q}^{(\alpha)}, T; \bar{\mathbf{Q}}^{(\alpha)}, 0) = \prod_{j=1}^N g_j^\alpha(Q_j^{(\alpha)}, T; \bar{Q}_j^{(\alpha)}, 0). \quad (\text{II.12})$$

To our knowledge, the only useful case for which an oscillator Green's function is known in closed form is the case of the harmonic oscillator. It would be of great interest in understanding the effects of anharmonicity to obtain the g_j^α for other than harmonic oscillators. This could be accomplished using perturbation theory if the anharmonicities are considered to be small. Although anharmonicities do affect true Franck-

Condon factors and matrix elements of $\partial/\partial Q$, the harmonic approximation does lead to values of the FC factors which are semiquantitatively valid, and we expect that the harmonic approximation will give useful information about the optical line shape and nonradiative decay probability.

To reduce the formal result into a useful and tractable theoretical expression, the following approximations are made:

(a) The harmonic approximation is invoked for the potential-energy surfaces of the electronic states s and l . The adiabatic harmonic potential surfaces for the two states are then given in the form

$$U_s = \frac{1}{2} \sum_i \sum_{i'} \alpha_{ii'} (\tilde{Q}_i - \tilde{Q}_i^{0(s)}) (\tilde{Q}_{i'} - \tilde{Q}_{i'}^{0(s)}),$$

$$U_l = \frac{1}{2} \sum_j \sum_{j'} \beta_{jj'} (\tilde{Q}_j - \tilde{Q}_j^{0(l)}) (\tilde{Q}_{j'} - \tilde{Q}_{j'}^{0(l)}) - \Delta E. \quad (\text{II.13})$$

The $\tilde{Q}^{(l)}$ and $\tilde{Q}^{(s)}$ terms in Eq. (II.11) represent general nuclear displacements, while $\{\tilde{Q}_i^{0(s)}\}$ and $\{\tilde{Q}_j^{0(l)}\}$ correspond to the equilibrium configurations of the two electronic states. The individual oscillator Green's functions g_j^α are displayed in Eq. (A1).

(b) The directions of the principle axis for the normal coordinates are identical in the two electronic states. This is not a necessary approximation. It is straightforward but tedious to consider the case where the modes in the two states are linear combinations of each other, resulting from changes in molecular symmetry, etc. The different equilibrium configurations of the two electronic states are $\{Q_j^{0(s)}\}$ and $\{Q_j^{0(l)}\}$ ($j=1 \cdots N$). N is the total number of vibrational modes. Thus the normal coordinates can be labeled as $Q_j^{(s)} = Q_j - Q_j^{0(s)}$ and $Q_j^{(l)} = Q_j - Q_j^{0(l)}$ ($j=1 \cdots N$). Let $\omega_j^{(s)}$ and $\omega_j^{(l)}$ represent the frequencies of the j th normal mode in the states s and l , respectively, both characterized by the effective mass M_j . It is convenient to define reduced normal coordinates and displacements:

$$q_j^{(s)} = (M_j \omega_j^{(s)} / \hbar)^{1/2} \quad Q_j^{(s)} = \beta_j^{1/2} (q_j^{(l)} + \Delta_j^{(l)}) \quad (\text{II.14a})$$

$$q_j^{(l)} = (M_j \omega_j^{(l)} / \hbar)^{1/2} \quad Q_j^{(l)} = \alpha_j^{1/2} (q_j^{(s)} - \Delta_j^{(s)}), \quad (\text{II.14b})$$

where

$$\Delta_j^{(s)} = (M_j \omega_j^{(s)} / \hbar)^{1/2} (Q_j^{0(l)} - Q_j^{0(s)}), \quad (\text{II.15a})$$

$$\Delta_j^{(l)} = (M_j \omega_j^{(l)} / \hbar)^{1/2} (Q_j^{0(l)} - Q_j^{0(s)}) \equiv \Delta_j, \quad (\text{II.15b})$$

and

$$\alpha_j = \omega_j^{(l)} / \omega_j^{(s)}; \quad \beta_j = \omega_j^{(s)} / \omega_j^{(l)}. \quad (\text{II.16})$$

Equation (II.13) can be now reduced to the form

$$U_s = \frac{1}{2} \sum_j \hbar \omega_j^{(l)} \beta_j (q_j + \Delta_j)^2, \\ U_l = \frac{1}{2} \sum_j \hbar \omega_j^{(l)} q_j^2 - \Delta E. \quad (\text{II.17})$$

We assume that the electronic matrix elements in the operator $V_{sl}(\mathbf{Q})$ [Eq. (II.6)] are slowly varying functions of the nuclear coordinates. This assumption is reasonable except near an intersection point of the two potential surfaces, whereupon a new representation of the vibronic wavefunctions has to be found in a manner analogous to the treatment of the Jahn-Teller problem. Such a situation probably occurs in some photochemical processes, and merits further theoretical studies.

Utilizing the results of the work of Lin⁹ and of Bixon and Jortner,¹⁵ the operators V_{sl} can be written in the form

$$V_{sl}(\mathbf{Q}) = \sum_{k=1}^p C_{sl}^k [i\hbar / (M_k)^{1/2}] (\partial / \partial Q_k^{(l)}), \quad (\text{II.18})$$

where for internal conversion

$$C_{sl}^k \equiv J_{sl}^k = [\hbar / (M_k)^{1/2}] \\ \times \langle \phi_s(\mathbf{q}, \mathbf{Q}^{(s)}) | i(\partial / \partial Q_k^{(l)}) | \phi_l(\mathbf{q}, \mathbf{Q}^{(l)}) \rangle, \quad (\text{II.19})$$

while for the case of intersystem crossing

$$C_{sl}^k = \sum_{\gamma \neq l, s} \left(\frac{\langle \phi_s | H_{so} | \phi_\gamma \rangle J_{\gamma l}^k}{E_{so} - E_{\gamma 0}} + \frac{J_{s\gamma}^k \langle \phi_\gamma | H_{so} | \phi_l \rangle}{E_{\gamma 0} - E_{l0}} \right), \quad (\text{II.20})$$

where H_{so} is the spin-orbit coupling operator and $E_{so} - E_{\gamma 0}$ or $E_{l0} - E_{\gamma 0}$, is the energy gap between the spin-orbit coupled states.⁹ The summation over k in Eq. (II.17) is taken over the small number of promoting modes ($p \ll N$), for which the J^k terms are appreciable.

The generating function (II.10) can be expressed in the form

$$f(t) = Z^{-1} \sum_k \sum_{k'} [\hbar^2 / (M_k M_{k'})^{1/2}] C_{sl}^k C_{sl}^{*k'} \\ \times \iint d\mathbf{Q} d\mathbf{Q}' [i(\partial / \partial Q_k^{(l)}) G_l(\mathbf{Q}^{(l)'}, -t; \mathbf{Q}^{(l)}, 0)] \\ \times [i(\partial / \partial Q_{k'}^{(s)}) G_s(\mathbf{Q}^{(s)}, \tau; \mathbf{Q}^{(s)'}, 0)]. \quad (\text{II.21})$$

Using the factorization (II.12) in (II.21), the generating function for the nonradiative process is given by

$$f(t) = \sum_{k=1}^p |C_{sl}^k|^2 \tilde{f}_k(t) \prod_{j \neq k} f_j(t) \\ + \sum_{k \neq k'} C_{sl}^k C_{sl}^{*k'} \tilde{h}_k(t) \tilde{h}_{k'}^*(t) \prod_{j \neq k, k'} f_j(t), \quad (\text{II.22})$$

where the $f_j(t)$ terms correspond to the single-mode generating functions for optical absorption. These terms, which arise from Franck-Condon vibrational overlap factors, are given by

$$f_j(t) = Z_j^{-1} \iint dQ_j d\tilde{Q}_j g_j^s(Q_j^{(s)}; \tilde{Q}_j^{(s)}, 0) \\ \times g_j^l(\tilde{Q}_j^{(l)}, -t; Q_j^{(l)}, 0), \quad (\text{II.23})$$

where

$$Z_j = \sum_{v_j} \exp[-\beta \hbar \omega_j^{(s)} (v_j + \frac{1}{2})] \\ = 1/2 \sinh(\frac{1}{2} \beta \hbar \omega_j^{(s)}),$$

is the partition function. The $\tilde{f}_k(t)$ correspond to single-mode generating functions which involve the nuclear momentum operator for the promoting mode Q_k :

$$\begin{aligned}\tilde{f}_k(t) = Z_k^{-1}(\hbar^2/M_k) \iint dQ_k d\tilde{Q}_k \\ \times [i(\partial/\partial Q_k) g_k^s(Q_k^{(s)}, \tau; \tilde{Q}_k^{(s)}, 0)] \\ \times [i(\partial/\partial \tilde{Q}_k) g_k^l(\tilde{Q}_k^{(l)}, -t; Q_k^{(l)}, 0)]. \quad (\text{II.24})\end{aligned}$$

Finally, some mixed-type single mode generating functions appear in Eq. (II.23): These are given by

$$\begin{aligned}\tilde{h}_k(t) = [\hbar/(M_k)^{1/2}] \iint dQ_k d\tilde{Q}_k \\ \times [i(\partial/\partial \tilde{Q}_k) g_k^l(\tilde{Q}_k^{(l)}, -t; Q_k^{(l)}, 0)] \\ \times g_k^s(Q_k^{(s)}, \tau; \tilde{Q}_k^{(s)}, 0). \quad (\text{II.25})\end{aligned}$$

It should be noted at this point that Eq. (II.22) contains a direct contribution from each promoting mode and an interference term between pairs of promoting modes. As discussed below, in the harmonic approximation, when $\Delta_k=0$, the latter term vanishes.

We have completed the formal representation of the nonradiative transition probability in the harmonic approximation by expressing it as the Fourier transform of a product of generating functions. Making use of Eqs. (II.23)–(II.25) and the explicit form (II.12) of the Green's function, then, the calculation of the generating function is reduced to a straightforward although somewhat cumbersome evaluation of elementary integrals. The result (II.22) is still completely general for independent oscillator modes in the two electronic states, and reduces to the expression given by Lin⁹ in the harmonic approximation when $\Delta_k=0$.

III. SINGLE-MODE GENERATING FUNCTIONS FOR THE NONRADIATIVE DECAY PROBABILITY

Following the consideration of Lin and Bersohn,¹⁰ the N molecular normal modes include a small number p ($p \ll N$) of promoting modes and a large number ($\approx N$) of accepting modes. The classification is based on the magnitude of the electronic terms C_{si}^k [Eqs. (II.18)–(II.20)], the reduced displacements of origins [Eq. (II.15)] and the α terms [Eq. (II.16)]. For the promoting modes one can assert that

$$C_{si}^k \neq 0; \quad \Delta_k = 0; \quad \alpha_k \neq 1 \quad (\text{or } \alpha_k = 1). \quad (\text{III.1})$$

The accepting modes are characterized by

$$\begin{aligned}C_{si}^j \approx 0; \quad \Delta_j \neq 0; \quad \alpha_j \neq 1 \quad (\text{or } \Delta_j \neq 0; \alpha_j = 1); \\ (\text{or } \Delta_j = 0; \alpha_j \neq 1). \quad (\text{III.2})\end{aligned}$$

An analysis of the Δ values for $\pi \rightarrow \pi^*$ excited states of aromatic hydrocarbons from spectroscopic data was provided by Byrne, McCoy, and Ross, who conclude the $\Delta_j \neq 0$ only for carbon-hydrogen stretches and skeletal stretches. It should be noted that:

(a) A promoting mode can simultaneously act as an accepting mode (providing that $\alpha \neq 1$) and

(b) A number of modes can be completely inactive (i.e., $C_{si}^i = 0$; $\alpha_i = 1$ and $\Delta_i = 0$). Although such a mode will be included in the class of accepting modes, its contribution to $f(t)$ will be unity, and it will not affect the nonradiative decay probability.

The general expressions for the integrals (II.23)–(II.25) in the harmonic approximation are only needed in certain asymptotic limits (e.g., high or low temperature, moderate frequency changes, etc.), where these cumbersome expressions may be greatly simplified. For convenience the results are summarized in the Appendices, and the simpler limiting forms are quoted when necessary. However, it should be noted at this point that when the origin of the accepting mode is not shifted between the two electronic states (i.e., $\Delta_j = 0$) the exponential term in Eq. (A2) is unity, and the contribution of this mode to the generating function arises from the pre-exponential term (provided of course that $\beta_j \neq 1$). This conclusion was previously reached by Kubo, who explicitly considered the case $\Delta_j = 0$, $\beta_j \neq 1$.³⁷ In the general case ($\Delta_j \neq 0$, $\beta_j \neq 1$) somewhat less elaborate calculations than those presented herein lead to the conclusion that the β_j terms give rise to a temperature-dependent shift of the band maximum. Finally, the “mixed-type” single-mode generating function [Eq. (II.28)] must be considered. Inspection of Eqs. (II.25) and (II.21) immediately implies that for $\Delta_k = 0$ the terms h_k involve integration over odd functions so that in the harmonic approximation, assuming $\Delta_k = 0$, as is appropriate for aromatic hydrocarbons⁸ (the case of $\Delta_k \neq 0$ is straightforward to handle)

$$\tilde{h}_k(t) = 0. \quad (\text{III.3})$$

Thus the generating function becomes

$$f(t) = \sum_{k=1}^p |C_{si}^k|^2 \tilde{f}_k(t) \prod_{j \neq k} f_j(t). \quad (\text{III.4})$$

The general expressions obtained herein are rather complicated even for the simple case of the harmonic molecule with different frequencies and different origins of the normal modes in the two electronic states. To get further physical insight into the nature of nonradiative decay some simple applications are now considered.

IV. DISPLACED POTENTIAL SURFACES

We first invoke the simplifying assumption that the normal modes and their frequencies are the same in the two electronic states except for displacements in the origins of the normal coordinates.⁴⁰ Thus we can set $\alpha_j = \beta_j = 1$ or $\omega_j^{(s)} = \omega_j^{(l)} = \omega_j$ for all the normal modes j , and the single-mode generating functions now take the simple form for $\Delta_k = 0$ [y_j is defined in (A5)],

$$f_j(t) = \exp\{-\frac{1}{2}\Delta_j^2 [\coth y_j (1 - \cos \omega_j t) - i \sin \omega_j t]\}, \quad (\text{IV.1})$$

$$\tilde{f}_k(t) = \frac{1}{2} \hbar \omega_k [\cos(\omega_k t) \coth y_k + i \sin(\omega_k t)]. \quad (\text{IV.2})$$

The transition probability is then obtained by writing (III.4) as products of terms from (IV.1) and (IV.2) and then substituting this into the Fourier integral (II.7). The resulting equation for the transition probability is the appropriate generalization of the formula for the optical line shape, where the transition moment is now the nuclear momentum operator.

In order to introduce the weak and strong coupling limits it is convenient to collect the positive and negative exponentials that come from products of $f_j(t)$. We define

$$G_+(t) = \frac{1}{2} \sum_j \Delta_j^2 (\bar{n}_j + 1) \exp(i\omega_j t), \quad (\text{IV.3a})$$

$$G_-(t) = \frac{1}{2} \sum_j \Delta_j^2 \bar{n}_j \exp(-i\omega_j t), \quad (\text{IV.3b})$$

where \bar{n}_j corresponds to the number of excited vibrations with frequency ω_j at thermal equilibrium,

$$\bar{n}_j = [\exp(\beta \hbar \omega_j) - 1]^{-1}, \quad (\text{IV.4})$$

and G_{\pm} are often called phonon-generating functions. The dimensionless quantity

$$G = G_+(0) + G_-(0) = \frac{1}{2} \sum_j \Delta_j^2 (2\bar{n}_j + 1) \quad (\text{IV.5})$$

is often referred to as the phonon-coupling strength. The final expression for the nonradiative decay rate in the simple displaced potential surface model is then

$$\begin{aligned} W = \sum_k |(C_{st})^k|^2 \omega_k / 4\hbar \exp(-G) \\ \times \left\{ (\coth y_k + 1) \int_{-\infty}^{\infty} dt \right. \\ \times \exp \left[-i \left(\frac{\Delta E}{\hbar} - \omega_k \right) t + G_+(t) + G_-(t) \right] \\ \left. + (\coth y_k - 1) \int_{-\infty}^{\infty} dt \right. \\ \times \exp \left[-i \left(\frac{\Delta E}{\hbar} + \omega_k \right) t + G_+(t) + G_-(t) \right] \Big\}, \quad (\text{IV.6}) \end{aligned}$$

where we see that the net effect of the promoting mode is to decrease or increase the effective energy gap to $\Delta E \pm \hbar \omega_k$ with the temperature dependence of $\coth y_k \pm 1$. This propensity rule for the promoting mode follows naturally from the assumption that $\Delta_k = 0$.

In the limit of zero temperature (e.g., $\beta \hbar \omega_j \gg 1$ for all j) this result is reduced to the much simpler form

$$\begin{aligned} W(\beta \rightarrow \infty) = \sum_k |(C_{st})^k|^2 \omega_k / 2\hbar \exp(-\frac{1}{2} \sum_j \Delta_j^2) \\ \times \int dt \exp[-i(\Delta E/\hbar - \omega_k)t + \frac{1}{2} \sum_j \Delta_j^2 \exp(i\omega_j t)], \quad (\text{IV.7}) \end{aligned}$$

where the effective energy gap is now only $\Delta E - \hbar \omega_k$ since the promoting mode which has no quanta at zero temperature must gain one quantum. Equation

(IV.7) contains only the positive frequency parts $\exp(i\omega_j t)$ since the vibrationless zero-temperature state has no quanta which must be distributed in the electronic relaxation process.

Equations (IV.6) and (IV.7) involve an extension of the previous treatment of Englman and Jortner²² since the effect of the promoting modes is now explicitly included in conformity with the work of Lin.⁹

In order to get some further insight into the nature of the different features of electronic relaxation processes and possibly some photochemical rearrangement reactions, it is useful to consider some limiting cases which are determined by the magnitude of the coupling strength [Eq. (IV.5)]. Define the molecular rearrangement energy in the excited state,

$$E_M = \frac{1}{2} \sum_{j=1}^N \hbar \omega_j \Delta_j^2, \quad (\text{IV.8})$$

which corresponds just to half of the Stokes shift for the two electronic states under consideration. For the model which just involves displaced potential surfaces the various coupling limits can be defined as follows²²:

(a) In the strong coupling limit,

$$G \gg 1, \quad (\text{IV.9})$$

and therefore the displacements of the origins between the two electronic states considerably exceed the root mean square vibrational displacements, $(\hbar/M_j \omega_j)^{1/2}$, for at least some of the normal modes. In other words, in this case $E_M \gg \hbar \langle \omega \rangle$ (where $\langle \omega \rangle$ is the mean vibrational frequency), so that the molecular rearrangement energy considerably exceeds the mean vibrational energy and the relative displacement of the potential-energy surfaces is large.

(b) The weak coupling limit, which is generally found for internal conversion and intersystem crossing in aromatic hydrocarbons, is encountered when $G \leq 1$ or $E_M \approx \hbar \langle \omega \rangle$, so that the relative displacement for each normal mode is small.

In the next two sections, we examine the simplifications of the rate expressions (IV.6) and (IV.7) in these two limits. For simplicity appropriately chosen mean frequencies are used. In Sec. VII the general case is treated.

V. THE WEAK COUPLING LIMIT FOR DISPLACED POTENTIAL SURFACES

We now focus attention on the weak coupling limit and concentrate on the low-temperature case [Eq. (IV.7)]. It should be borne in mind that even within the framework of the harmonic model the present treatment is incomplete, as frequency changes between electronic states have not yet been included. However, the simple model of the displaced potential surfaces is of considerable interest as it enables us to develop some general theoretical methods which are also useful for

the more complicated case of the complete treatment of the "harmonic molecule" which is considered in Sec. VII. Furthermore, this simple model is useful in gaining some insight concerning the pertinent molecular parameters which determine the nonradiative transition probability.

The reduced displacements Δ_j between different $\pi \rightarrow \pi^*$ excited states of aromatic hydrocarbons have been estimated by Byrne *et al.*,⁸ and it is now well established that electronic relaxation processes in these molecules correspond to the weak coupling situation. It is useful to adopt the procedure suggested by Ross *et al.*⁸ and to combine the normal molecular vibrations into several ($i=1 \dots n$) groups which are: (1) C-H (or C-D) stretches, (2) skeletal stretches, (3) skeletal bends, (4) C-H (or C-D) bends, and (5) out-of-plane modes. This classification was recently extended by Burland and Robinson,²¹ who provide extensive spectroscopic data obtained for the first-excited singlet and triplet states and for the ground state of the benzene molecule. The vibrational frequencies within each group are taken to be equal (say ω_i for the i th group). Let d_i be the number of modes within the i th group (i.e., the degeneracy number), so that

$$\sum_{i=1}^n d_i = N.$$

Obviously the reduced displacements within each group can be different, as each contains vibrational normal modes of different symmetry. It will be convenient to define a mean reduced displacement Δ_i for the i th group so that

$$d_i \Delta_i^2 = \sum_{j \in i} \Delta_j^2, \quad (\text{V.1})$$

where the summation of (V.1) is taken over the reduced displacements of the nearly degenerate modes in this group, so that

$$\frac{1}{2} \sum_{j=1}^N \hbar \omega_j \Delta_j^2 = \frac{1}{2} \sum_{i=1}^n d_i \hbar \omega_i \Delta_i^2. \quad (\text{V.2})$$

The integrals appearing in Eq. (IV.7) which determine the transition probability have the form

$$I_k = \int_{-\infty}^{\infty} dt \times \exp \left[- (i \Delta E_k t / \hbar) + \frac{1}{2} \sum_{i=1}^n d_i \Delta_i^2 \exp(i \omega_i t) \right], \quad (\text{V.3})$$

where the effective energy gap is

$$\Delta E_k = \Delta E - \hbar \omega_k. \quad (\text{V.4})$$

The integral I_k can be evaluated for large values of ΔE_k by saddle-point integration.⁴¹ Making use of the procedure suggested by Englman and Jortner,²² the saddle point in the complex t plane is obtained from the

relation

$$-\Delta E_k + \sum_{i=1}^n a_i \exp(i \omega_i t) = 0, \quad (\text{V.5})$$

where we have set

$$a_i = \frac{1}{2} d_i \hbar \omega_i \Delta_i^2.$$

Now let the index M correspond to the group of d_M modes of maximum frequency ω_M (for which $\Delta_M^2 \neq 0$). Defining Y_k by

$$t = - (i / \omega_M) \ln (\Delta E_k Y_k / a_M),$$

we can rewrite (V.5) as

$$1 = Y_k + \sum' \Omega_{m,k} (Y_k)^{\xi_m}, \quad (\text{V.6})$$

where

$$\xi_m = \omega_m / \omega_M < 1, \quad (\text{V.7})$$

the dimensionless (positive) quantities

$$\begin{aligned} \Omega_{m,k} &= (a_m / a_M) (a_M / \Delta E_k)^{1-\xi_m} \\ &\equiv d_M \Delta_M^2 \omega_m / d_M \Delta_M^2 \omega_M (d_M \Delta_M^2 \hbar \omega_M / 2 \Delta E_k)^{1-\omega_m / \omega_M}, \end{aligned} \quad (\text{V.8})$$

and the prime on the summation implies that it is to be taken over all groups of modes $m \neq M$. In general, we expect to have

$$0 \leq \Omega_{m,k} \lesssim 1 \quad \text{for all } m, \quad (\text{V.9})$$

and thus (V.6) is an algebraic equation for the real quantity Y_k . With Y_k defined implicitly as a function of $\{\Omega_{m,k}, \xi_m\}$ via (V.6), the saddle-point approximation to (V.3) is then⁴¹

$$I_k = [2\pi / \hbar \omega_M \Delta E_k Y_k (1 + \sum' \Omega_{m,k} \xi_m Y_k^{\xi_m-1})]^{1/2} \times \exp(-\gamma_k \Delta E_k / \hbar \omega_M), \quad (\text{V.10})$$

where

$$\gamma_k = \ln (\Delta E_k Y_k / a_M) - Y_k (1 + \sum' \Omega_{m,k} Y_k^{\xi_m-1} / \xi_m) \quad (\text{V.11})$$

is a slowly varying function of ΔE_k . Finally, the transition probability in the weak coupling low-temperature limit is obtained from Eqs. (IV.7) and (V.3) as

$$\begin{aligned} W &= \sum_k (|C_{st}^k|^2 \omega_k / 2 \hbar) \exp(-G) I_k \\ &= \sum_k |C_{st}^k|^2 \omega_k \exp(-G) \\ &\quad \times [\pi / 2 \hbar \omega_M \Delta E_k Y_k (1 + \sum' \Omega_{m,k} \xi_m Y_k^{\xi_m-1})]^{1/2} \\ &\quad \times \exp(-\gamma_k \Delta E_k / \hbar \omega_M). \end{aligned} \quad (\text{V.12})$$

As (V.12), (V.11), and (V.6) represent the rate constant as an implicit function of the fundamental molecular parameters $\{d_j, \Delta_j^2, \omega_j, \Delta E_k\}$, in order to obtain a semiquantitative understanding of the dominant factors affecting the nonradiative decay probability, it is desirable to have some limiting cases in which a simple analytic solution to (V.6) is obtainable in a

physically transparent form. Such a limiting case, which is likely to be sufficient in the case of aromatic hydrocarbons in the statistical limit, is given by the condition

$$\Omega_{m,k} \ll 1, \quad \text{all } m, k. \quad (\text{V.13})$$

[In the Appendices we discuss the analytic solutions to (V.6) in the case that condition (V.13) is violated.] When (V.13) is satisfied, we can obtain a solution to (V.6) by expanding in fractional powers of the $\Omega_{m,k}$'s:

$$Y_k = 1 - \sum'_m \Omega_{m,k} + \sum'_{m,m'} \Theta(\Omega_{m',k} \Omega_{m,k}^{\xi_m}). \quad (\text{V.14})$$

Keeping only the leading term gives

$$W = \sum_k |C_{\epsilon k}|^2 \omega_k \exp(-G) \times \{ \pi / 2 \hbar \omega_M \Delta E_k [1 - \sum'_m \Omega_{m,k} (1 - \xi_m)] \}^{1/2} \times \exp(-\gamma_k \Delta E_k / \hbar \omega_M), \quad (\text{V.15})$$

where

$$\begin{aligned} \gamma_k &= \ln(\Delta E_k / a_M) - 1 - \sum'_m (\Omega_{m,k} / \xi_m) \\ &= \ln(2 \Delta E_k / \hbar \omega_M d_M \Delta_M^2) - 1 \\ &\quad - \sum'_m (d_M \Delta_m^2 / d_M \Delta_M^2) (d_M \Delta_M^2 \hbar \omega_M / 2 \Delta E_k)^{1 - \omega_m / \omega_M}. \end{aligned} \quad (\text{V.16})$$

Equation (V.15) [as well as (V.12)] is in the form of the energy gap law. The condition (V.13) is realized provided that:

(a) The effective energy gap greatly exceeds the maximum frequencies, i.e., $\Delta E_k \gg \hbar \omega_M$, a condition for the statistical limit;

(b) the reduced displacements of the high-frequency (C-H or C-D) modes are the same order of magnitude as those of lower frequencies: $\Delta_m \approx \Delta_M$;

(c) the weak coupling limit holds, i.e., $\sum_i \Delta_i^2 \approx 1$; otherwise condition (b) is violated and some of the Δ_m are large. Such a situation may occur for some photochemical rearrangement reactions^{24,25} (see Sec. VI).

Some, necessarily rough, numerical estimates are now in order. For the transitions between the lowest excited singlet state and the ground state in aromatic hydrocarbons, Byrne *et al.*⁸ estimate $0.19 \leq \Delta_M \leq 0.42$ for C-H ($\omega_M \approx 3000 \text{ cm}^{-1}$) and for C-D ($\omega_M \approx 2200 \text{ cm}^{-1}$) stretching modes (while Burland and Robinson²¹ give $\Delta_M = 0.4$ for the first triplet of benzene relative to the ground state), $\Delta_m = 0-2$ for C-C skeletal vibrations⁸ ($\omega_m \approx 1400 \text{ cm}^{-1}$), while $\Delta_i = 0$ for all other modes.^{8,21} Taking a typical value for the energy gap $\Delta E_k \approx 3 \times 10^4 \text{ cm}^{-1}$ and a representative value $\Delta_m = 1$ for the C-C stretching modes, the parameter $\Omega_{m,k}$ for skeletal stretches is expected to lie in the range $0.3 \leq \Omega_{m,k} \leq 0.55$, depending on the value chosen for Δ_M . Alternately, if

we follow Burland and Robinson²¹ and take $\Delta_M = 0.4$, $\Delta_m = 1$ ($\omega_m \approx 1000 \text{ cm}^{-1}$) for only the totally symmetric C-H and C-C modes, $\Omega_{m,k} \approx 1/12$. Although the situation is not entirely satisfactory in this respect, it is hoped that the theoretical expressions derived for the displaced potential surfaces model, which are valid to first order in $\Omega_{m,k}$, do provide a semiquantitative description in the weak coupling limit. In the Appendices, however, we present expressions for the rates which are valid even for $\Omega_{m,k} \sim \Theta(1)$ which may be used when (V.13) is no longer valid.

When Approximation (V.13) is applicable, the simple model calculation [summarized by Eq. (V.15)] leads to the following conclusions [only minor modifications are necessary if $\Omega_{m,k} \sim \Theta(1)$, so (V.13) is not satisfied]:

(a) The rate in the weak coupling limit exhibits the energy gap law; the transition probability is determined by an exponential function of the energy gap modified by the frequency of the promoting mode.

(b) The exponential factors γ_k which determine the transition probability in the weak coupling limit include the corrections from the vibrational modes of lower frequency, which are displayed in (V.15), for convenience, to first order in the parameters $\Omega_{m,k}$.

(c) In the weak coupling case the transition probability is dominated by the maximum frequency ω_M and is thus expected to reveal a substantial isotope effect in the statistical limit of large ΔE_k . The corrections to γ_k from the skeletal modes will therefore affect the quantitative details of this isotope effect.

VI. THE STRONG COUPLING LIMIT FOR THE DISPLACED POTENTIAL SURFACES MODEL

When $G \gg 1$ the functions $G_+(t)$ and $G_-(t)$ in Eq. (IV.3) can be expanded²² in a power series of t retaining only terms up to t^2 :

$$G_+(t) + G_-(t) = G + (itE_M/\hbar) - \frac{1}{2} D^2 t^2 + \Theta(t^3), \quad (\text{VI.1})$$

where

$$D^2 = \frac{1}{2} \sum_j \omega_j^2 \Delta_j^2 (2\bar{n}_j + 1), \quad (\text{VI.2})$$

and obviously $D^2 \approx G \langle \omega \rangle^2$, where $\langle \omega \rangle$ is the mean frequency

$$\langle \omega \rangle = \sum_{j=1}^N (\omega_j / N).$$

Provided that G is large, the generating function $f(t)$ will decay exponentially, roughly as $\exp(-G \langle \omega \rangle^2 t^2 / 2)$, to a small value before the truncated power expansion of $G_{\pm}(t)$ becomes invalid (e.g., when $\langle \omega \rangle t \geq 1$). This power-series expansion in the strong coupling limit is just the cumulant expansion of the transition probability³⁴ where the second moment D^2 dominates the higher moments.

Simple manipulations then lead to the following result

in the strong coupling limit:

$$W = \sum_k \frac{|C_{st}^k|^2 \omega_k (2\pi)^{1/2}}{2\hbar D} \left[(\coth y_k + 1) \times \exp\left(-\frac{(\Delta E - \hbar\omega_k - E_M)^2}{2D^2 \hbar^2}\right) + (\coth y_k - 1) \times \exp\left(-\frac{(\Delta E + \hbar\omega_k - E_M)^2}{2D^2 \hbar^2}\right) \right]. \quad (\text{VI.3})$$

Equation (VI.3) exhibits a Gaussian dependence on the energy parameter $(\Delta E \pm \hbar\omega_k - E_M)$ which is of course analogous to the strong coupling situation in the optical absorption of solids.

To simplify this result, we make use of the approximate relations which involve coarse graining of the vibrational frequencies

$$G \approx (E_M / \hbar \langle \omega \rangle) \coth(\frac{1}{2} \beta \hbar \langle \omega \rangle) \quad (\text{VI.4})$$

and

$$\hbar^2 D^2 \approx E_M \hbar \langle \omega \rangle \coth(\frac{1}{2} \beta \hbar \langle \omega \rangle). \quad (\text{VI.5})$$

Furthermore, we introduce the point intersection of minimum energy E_A for the two potential surfaces (measured from the energy origin $E_{so}=0$). It has been demonstrated²² that the point of minimum energy on the hypercurve of intersection of the two surfaces satisfies the relation

$$E_A = (\Delta E - E_M)^2 / 4E_M. \quad (\text{VI.6})$$

Now provided that $\hbar\omega_k \ll E_A \ll \Delta E \sim E_M$, Eq. (VI.3) can be reduced to the form

$$W = \sum_k \frac{|C_{st}^k|^2 (\omega_k) (2\pi)^{1/2}}{(2E_M k_B T^*)^{1/2}} \times \coth(\frac{1}{2} \beta \hbar \omega_k) \exp(-E_A / k_B T^*), \quad (\text{VI.7})$$

where the effective temperature is defined by

$$T^* = \frac{1}{2} \beta \hbar \langle \omega \rangle \coth(\frac{1}{2} \beta \hbar \langle \omega \rangle). \quad (\text{VI.8})$$

These results imply that

(a) In the low-temperature limit $(\beta \hbar \langle \omega \rangle \gg 1)$ the "tunneling" probability from the lowest vibrational level of the *si* manifold is given by

$$W = \sum_k \frac{|C_{st}^k|^2 (\omega_k) (2\pi)^{1/2}}{(E_M \hbar \langle \omega \rangle)^{1/2}} \exp(-2E_A / \hbar \langle \omega \rangle). \quad (\text{VI.9})$$

(b) For a molecule imbedded in a heat bath at an extremely high temperature $(\beta \hbar \langle \omega \rangle \ll 1)$, the following

limiting form results:

$$W = \frac{kT}{\hbar} \sum_k \frac{(4\pi)^{1/2} |C_{st}^k|^2}{(E_M k_B T)^{1/2}} \exp(-E_A / k_B T). \quad (\text{VI.10})$$

Equation (VI.10) has the appearance of a conventional rate equation, where the energy E_A plays the role of the activation energy. An "entropy-type" term is determined by the electronic coupling terms C_{st}^k and E_M . Finally, it is worth while to notice that the limiting form of the $\coth(y_k)$ function [Eq. (VI.7)] leads to the well-known Eyring pre-exponential form kT/\hbar in the strong coupling high-temperature limit. It is also important to notice that the concept of an "activated complex" does not enter in any way into this description. Clearly the result described is of only academic interest, since extremely high temperatures are required to achieve the limit.

In the strong coupling limit the transition probability is determined by the activation energy E_A as opposed to the energy-gap-type behavior in the weak coupling limit. In the strong coupling limit, the transition probability is determined primarily by the mean molecular frequency $\langle \omega \rangle$ and will exhibit only a moderate isotope effect in contrast with the weak coupling limit.

VII. THE LOW-TEMPERATURE HARMONIC CASE WITH FREQUENCY CHANGES

In the preceding sections we were concerned with the simplest possible model for nonradiative decay processes, where the effects of frequency changes between the two electronic states have been disregarded. There are few experimental data available concerning frequency changes between different electronic states of aromatic molecules. The most complete results pertain to the vibrational analysis of the benzene molecule in its ground and first-excited singlet state.²¹ The frequency changes for the out-of-plane vibrations are of the order of $\approx 50\%$, and at first sight it appears that these low-frequency vibrational modes may be of considerable importance in determining both the gross features of the nonradiative decay and the deuterium isotope effect.

In Lin's treatment⁹ of the harmonic molecule it was assumed that in general only small frequency changes are to be expected, so $\beta_j \approx 1$. This is obviously not the case, and a more complete treatment of the frequency changes is required. Using Eqs. (III.4) and (II.22)–(II.25), the general expressions for the single mode generating functions and for the nonradiative decay probability can be obtained by a straightforward although somewhat lengthy calculation. These general results for the harmonic molecule are displayed in Appendix A [see Eqs. (A.2)–(A.10)]. To simplify these results further consider the low-temperature limit, which is adequate for many practical purposes. Under these circumstances the following general results

are obtained:

$$f_j(t) = A_j \exp\left(-\frac{\beta_j \Delta_j^2 [1 - \exp(i\omega_j^{(l)}t)]}{(\beta_j + 1) + (\beta_j - 1) \exp(i\omega_j^{(l)}t)}\right), \quad (\text{VII.1})$$

$$\tilde{f}_k(t) = \frac{1}{2}(\alpha_k^{1/2} \hbar \omega_k^{(l)}) A_k \exp(i\omega_k^{(l)}t) \{1 + [(1 - \beta_k)^2 / 4\beta_k][1 - \exp(2i\omega_k^{(l)}t)]\}^{-1}, \quad (\text{VII.2})$$

where

$$A_j = \exp(-i\delta_j^{(-)}t) \{\beta_j + \frac{1}{4}(1 - \beta_j)^2[1 - \exp(2i\omega_j^{(l)}t)]\}^{-1/2} \quad (\text{VII.3})$$

and

$$\delta_j^{(-)} = \frac{1}{2}(\omega_j^{(s)} - \omega_j^{(l)}).$$

Now, for the situation which is of physical interest for large aromatic hydrocarbons the relevant frequency changes are in the range $1 \geq \beta_j \geq 0.5$. The coefficients A_j and A_k [Eq. (VII.3)] may be expanded in terms of the parameter $\eta_j = (1 - \beta_j)^2 / 4\beta_j$, while the exponent in Eq. (VII.1) is expanded in terms of the parameter $(\beta_j - 1) / (\beta_j + 1)$, and in both cases only the first term in the expansion is retained (although the inclusion of higher terms is trivial). The transition probability in the low-temperature limit is now given in the form

$$W = \hbar^{-1} \sum_{k=1}^p \frac{1}{2} (|C_{s,l}^k|^2 \omega_k^{(l)} \alpha_k) \exp\left\{-\sum_{j=1}^N \left[\frac{1}{2}\eta_j + \beta_j \Delta_j^2 / (\beta_j + 1)\right]\right\} \left(\prod_{j \neq k} \alpha_j^{1/2}\right) \int dt \exp(-i\Delta \tilde{E}_k t / \hbar) \\ \times \exp\{-\eta_k [1 - \exp(2i\omega_k^{(l)}t)]\} \exp\left\{\sum_{j=1}^N S_j \Delta_j^2 \exp(i\omega_j^{(l)}t) + \sum_j U_j \exp(2i\omega_j^{(l)}t)\right\}, \quad (\text{VII.4})$$

where we have defined

$$S_j = 2\beta_j^2 / (1 + \beta_j)^2, \quad (\text{VII.5})$$

$$U_j = -[\beta_j(\beta_j - 1) / (1 + \beta_j)^2] \Delta_j^2 + \frac{1}{2}\eta_j. \quad (\text{VII.6})$$

Finally, the effective energy gap (see discussion in Sec. VIII) is given in the form

$$\Delta \tilde{E}_k = \Delta E + \sum_{j=1}^N \hbar \delta_j^{(-)} - \hbar \omega_k^{(l)}. \quad (\text{VII.7})$$

The apparent gap [Eq. (VII.7)] is, of course, different for each promoting mode.

It should be noted that for the present case we can again distinguish between the weak and strong coupling limits. The strong coupling limit will be realized when some of the displacement parameters Δ_j are large (while still $\beta_j < 2$). In this case we can redefine the molecular rearrangement energy $E_M = \hbar \sum_j (S_j \Delta_j^2 \omega_j^{(l)} + 2U_j \omega_j^{(l)})$ and define the coupling strength in the form $G = D^2 / \langle \omega \rangle$, where $D^2 = \sum_j (S_j \omega_j^{(l)2} \Delta_j^2 + 4U_j \omega_j^{(l)2})$. Now, when $G \gg 1$, we can again follow the treatment presented in Sec. VI, which (apart from a constant numerical factor) will result in a Gaussian dependence of the transition probability on the energy parameter $(\Delta \tilde{E}_k - E_M)$.

In the weak coupling limit we immediately notice the formal analogy between the simple expression obtained for the displaced potential surfaces [Eq. (IV.7)] and the more general result for the harmonic molecule [Eq. (VII.4)]. Adopting the same bookkeeping system as in Sec. V the transition probability is now determined by the integrals

$$\tilde{I}_k = \int dt \exp(-i\Delta \tilde{E}_k t / \hbar) \exp[-\eta_k \exp(2i\omega_k^{(l)}t) + \sum_i (d_i S_i \Delta_i^2 \exp(i\omega_i^{(l)}t) + \sum_i d_i U_i \exp(i\omega_i^{(l)}t))]. \quad (\text{VII.8})$$

Now, for a large effective energy gap $\Delta \tilde{E}_k$, the saddle-point integration method is applicable. Provided that the maximal frequency $\omega_M^{(l)}$ is characterized by small frequency changes ($d_M U_M = 0$), we can immediately adopt the procedure outlined in Sec. V. Let us define the parameters

$$\Omega_{m,k} = (d_m S_m \Delta_m^2 \omega_m^{(l)} / d_M S_M \Delta_M^2 \omega_M^{(l)}) (d_M S_M \Delta_M^2 \hbar \omega_M^{(l)} / \Delta \tilde{E}_k)^{1 - \omega_m^{(l)} / \omega_M^{(l)}}, \quad (\text{VII.9a})$$

equivalent to Eq. (V.8), and

$$\Xi_{m,k} = (2d_m U_m \omega_m^{(l)} / d_M \Delta_M^2 S_M \omega_M^{(l)}) (d_M S_M \Delta_M^2 \hbar \omega_M^{(l)} / \Delta \tilde{E}_k)^{1 - 2\omega_m^{(l)} / \omega_M^{(l)}}, \quad (\text{VII.9b})$$

$$\chi_k = (2\eta_k \omega_k^{(l)} / d_M \Delta_M^2 S_M \omega_M^{(l)}) (d_M S_M \Delta_M^2 \hbar \omega_M^{(l)} / \Delta \tilde{E}_k)^{1 - 2\omega_k^{(l)} / \omega_M^{(l)}}. \quad (\text{VII.9c})$$

Provided that $\Omega_{m,k} \ll 1$ and $\Xi_{m,k} \ll 1$, we now get to first order in these parameters

$$\tilde{I}_k = \left\{ 2\pi / \hbar \omega_M \Delta \tilde{E}_k \left[1 - \sum'_m \Omega_{m,k} \left(1 - \frac{\omega_m^{(l)}}{\omega_M^{(l)}} \right) - \sum'_m \Xi_{m,k} \left(1 - \frac{2\omega_m^{(l)}}{\omega_M^{(l)}} \right) - \chi_k \left(1 - \frac{2\omega_k^{(l)}}{\omega_M^{(l)}} \right) \right] \right\}^{1/2} \exp\left(-\frac{\gamma_k \Delta \tilde{E}_k}{\hbar \omega_M^{(l)}}\right), \quad (\text{VII.10})$$

where

$$\gamma_k = \ln\left(\frac{\Delta \tilde{E}_k}{d_M S_M \Delta_M^2 \hbar \omega_M^{(l)}}\right) - 1 - \sum_{m=1, m \neq k}^n \left(\frac{\omega_m^{(l)}}{\omega_M^{(l)}} \Omega_{m,k} + \frac{\omega_m^{(l)}}{2\omega_M^{(l)}} \Xi_{m,k} \right) - \frac{\omega_M^{(l)}}{2\omega_k^{(l)}} \chi_k. \quad (\text{VII.11})$$

The transition probability can now be explicitly written by inserting Eqs. (VII.10) and (VII.11) into (VII.4). The final result exhibits the energy gap law and the isotope effect in a manner which is similar to the previous treatment (see Sec. V) for the displaced potential surfaces model. We conclude that the effect of the frequency changes of the low-energy out-of-plane vibration on the nonradiative decay probability is relatively small. Using reasonable values for the molecular parameters $\Delta\tilde{E}_k = 3 \times 10^4 \text{ cm}^{-1}$, $\omega_M = 3000 \text{ cm}^{-1}$, $\Delta_M = 0.4$, $\omega_m = 400 \text{ cm}^{-1}$, and $\beta_m = 0.5$, the correction term for the vibrations in γ_k Eq. (VII.11) turns out to be $(\omega_M^{(l)}/2\omega_m^{(l)})\Xi_{m,k} = 0.04$. (Note that in the aromatic hydrocarbons, typical values of γ appear to fall in the range 1–3.^{21,22}) We should also note in passing that the parameter χ_k arising from the contribution of the frequency changes in the promoting mode is negligibly small. It is thus apparent that for a large energy gap, as in the case for the majority of electronic relaxation processes in aromatic hydrocarbons, the gross features of the nonradiative decay process are determined by the high-frequency accepting modes, and the effect of the changes in vibrational frequencies in the low-frequency modes is of minor importance.

VIII. PROPENSITY RULE AND THE EFFECTIVE ENERGY GAP

Using the constraint that the molecular vibrational modes are harmonic, we find that the effective energy gap [Eq. (VII.7)] differs from the electronic energy gap ΔE due to two contributions: one arising from the changes in the vibrational frequencies between the two electronic states and the other originating from the reduction of the energy gap by the vibrational frequency of a promoting mode.

The appearance of the term

$$\hbar \sum_j \delta_j^{(-)} = \frac{1}{2} \hbar \sum_j (\omega_j^{(s)} - \omega_j^{(l)})$$

in the effective electronic energy gap just reflects the change in the zero-point energy between the two electronic states s and l . This term can be significant for nonradiative decay to the ground electronic state. In fact, Siebrand's^{12,13} correlations indicate that for nonradiative decay of the lowest excited triplet state, the effective energy gap should be taken to be $\Delta\tilde{E} \approx (\Delta E - 5000) \text{ cm}^{-1}$, so that the difference between the zero-point energies between the lowest triplet and the ground state for aromatic hydrocarbons is about -4000 cm^{-1} , which is entirely reasonable.

The appearance of the frequency of the promoting mode in the effective energy gap (VII.7) results from the inclusion of the nuclear kinetic-energy operator which induces the nonradiative process, a feature which was disregarded in many studies but has been properly included by Kubo and Toyozawa³⁴ and by Lin.⁹

This result represents a quantitative manifestation of the propensity rule proposed by Berry and Jortner,¹⁶ that is, that the most favorable change in a promoting mode involves a single vibrational quantum. In the harmonic model this propensity rule becomes a selection rule. Obviously, when anharmonic terms are considered, changes in the promoting mode can involve more than a single vibrational quantum. However, for a small degree of anharmonicity, a single quantum change will be more favorable than a two-quantum change, which in turn will be more favorable than a three-quantum change, etc.

The decrease of the effective energy gap (at low temperatures) by $\hbar\omega_k^{(l)}$ has one other important implication. The close analogy between the theory of nonradiative decay and the theory of the line-shape function for optical processes in solids led Englman and Jortner²² to point out that the nonradiative decay can be considered as an optical excitation process in the limit of zero excitation frequency. When we include the nuclear kinetic-energy operator which induces the nonradiative decay process [see Eq. (II.18)] we immediately notice that the operator $i\partial/\partial Q_k$ is characterized by the same selection rules as Q_k , so that the nonradiative decay process is closely related to a symmetry-forbidden electronic transition which is customarily handled by the Herzberg-Teller scheme.⁴² As in the case of the optical symmetry-forbidden transition, the nonradiative process is characterized by a "false origin" at the energy $\hbar\omega_k^{(l)}$. Indeed, provided that the promoting modes are unmodified between the two electronic states (i.e., $\Delta_k = 0$, $\beta_k = 1$ and $\eta_k = 0$), then the transition probability for the nonradiative decay process is determined by the line-shape function [Eq. (II.6)] $F(\hbar\omega_k)$ at the energy corresponding to the promoting mode. Thus the nonradiative decay process can be formally regarded (apart from a constant numerical factor) as a symmetry-forbidden emission process in the limit of zero frequency, where the promoting modes play the role of the nontotally symmetric modes which induce the conventional optical process.

IX. COMMENTS ON MEDIUM EFFECTS ON RADIATIONLESS TRANSITIONS

Recent theoretical studies of electronic relaxation processes describe radiationless transitions as being essentially intramolecular phenomena. It was asserted that radiationless decay processes of molecules which conform to the statistical limit in an "inert" medium are not affected by the host matrix and are determined by the weighted density of states of the isolated molecule. The techniques already discussed can automatically be used to treat radiationless transition rates of statistical limit molecules in an "inert" medium, i.e., to include any intermolecular contributions to the decay rates. The "inert" medium, which is precisely

defined below, corresponds to the most ideal kind of medium, and there are a large number of host media (and hence interesting effects) which do not conform to this limit. However, it is of interest to consider this ideal limit (it requires almost no additional algebra) as a preliminary investigation of medium effects, where a more thorough discussion of the "noninert" medium is deferred until the completion of experimental studies which are now in progress (J. Richards and S. A. Rice). Basically, our model of an "inert" medium is a medium which contributes a large number of low-frequency vibrational modes which can only accept energy, i.e., act as a heat bath, due to changes in oscillator coordinates and/or frequencies. Since these phonon modes are of very low frequencies, the results of Secs. V and VII imply that they will not efficiently compete with the intramolecular modes of highest frequency unless the phonon coupling strength is very large. Thus, we provide the criterion for the efficient competition between the intermolecular and the intramolecular vibrational modes for the electronic energy in radiationless processes, and we discuss the explicit temperature dependence of these criteria.

In more precise terms, a definition of the "inert" medium (and its limitations) is as follows:

(a) The promoting modes correspond only to intramolecular vibrations. It is well known from the theory of vibronic coupling⁴³ that the nontotally symmetric vibrations which lead to interstate mixing in aromatic molecules involve the intramolecular skeleton modes. Furthermore, it appears that the solvent effects on the intensity of the vibronically induced components of an electronic transition (which are built on the fake electronic origin) are small. Thus the vibrational modes of the medium do not contribute to the matrix elements J_{si}^k [Eq. (II.19)] of the nuclear kinetic-energy operator.

(b) The inert medium does not modify the spin-orbit coupling matrix elements. Obviously, when a molecule is imbedded in a solvent which exhibits the external heavy-atom effect⁴⁴ the matrix elements C_{si}^k [Eq. (II.20)] for intersystem crossing will be affected, thus influencing the total nonradiative decay probability.

(c) The inert medium does not enhance the coupling between electronic states of the same multiplicity. Again, some exceptions to this requirement are known. In a pure or mixed molecular crystal, crystal field effects may lead to mixing of electronic states by intermolecular Coulomb interactions.⁴⁵ In crystalline benzene the intensities of the pure electronic components (which are absent in the gas phase spectrum) are comparable with the intensity of the vibronically induced progression.⁴⁶ Thus, under certain circumstances the matrix elements C_{si}^k for internal conversion are enhanced due to the inclusion of second-order terms which involve coupling (via external electro-

static perturbation terms of the medium) between molecular states of the same multiplicity.

(d) The lowest excited electronic state of the medium is located at considerably higher energy than that of the decaying state. Otherwise, electrostatic interactions may mix electronic states of the guest and host molecules modifying the coupling matrix elements. In a similar way, the mixing of guest-host charge-transfer states and the decaying state are assumed to be negligible.

(e) The inert medium does not modify the electronic energy levels. Environmental level shifts can be of considerable importance when the second-excited triplet state is involved in the radiationless decay of the first-excited singlet state. The different lifetimes of the anthracene molecule in the pure crystal and in solution (or in the gas phase) are interpreted in terms of matrix shifts of the lowest vibronic components of the singlet and of the second triplet states. Such situations cannot be handled by the simple two-level model considered by us.

From the foregoing discussion it appears that there are many exceptions which violate the model of an "inert" medium. Restriction (a) seems to be of great generality, while restrictions (b)–(e) are somewhat arbitrary. It was previously assumed that the role of an inert medium is twofold:

(a) The external medium provides a heat bath enhancing the population of the higher vibronic states in the si manifold. In fact the basic "golden rule" relation (I.2) rests on the implicit assumption that vibrational relaxation in the si manifold is more efficient than electronic relaxation.

(b) The medium contributes to the widths of the levels in the $\{\phi_{ij}\}$ dense molecular manifold by vibrational relaxation.^{2,18,19} These vibrational relaxation effect are of considerable importance for electronic relaxation between two electronic states in a large molecule which are separated by a small energy gap. Such molecular states which correspond to an intermediate case in the low-pressure gas phase will reveal irreversible nonradiative decay when embedded in a medium. However, in the statistical limit these effects are of no importance as the intramolecular density of state is sufficiently large.²⁷ Currently there is some experimental evidence indicating that electronic relaxation processes of some large molecules in "inert" host matrices hardly reveal any medium effects.¹⁶ Thus the fluorescence lifetime and the fluorescence quantum yield of the anthracene molecule are practically the same in solution and in the gas phase.⁴⁷ The phosphorescence lifetimes of organic molecules measured at low temperatures are practically independent of the nature of the (inert) solvent.

It should be pointed out, however, that the qualitative analysis presented above concerning the role of the

inert medium is incomplete as the vibrational modes which involve the solvent molecules have to be incorporated into the theoretical expressions for the nonradiative decay probability. To consider in detail the nonradiative decay of a large molecule in a medium we have to treat the intramolecular phonons and the lattice phonons on the same footing. Consider the guest molecule and the (inert) medium as a supermolecule, which (in the two electronic states s and l) is characterized by vibrational modes involving both the intramolecular vibrations, previously considered, and the intermolecular vibrations of the host molecules with respect to the guest molecule. The latter vibrations correspond to the phonon modes of the pure medium which are perturbed due to the presence of the guest molecule.⁴⁸ This picture of the intermolecular vibrational modes bears a close resemblance to the description of impurity states in ionic crystals by the configuration diagram model.⁴⁹ Thus the supermolecule can be now characterized by N intramolecular vibrational modes and by μ intermolecular phonon modes. The medium modes do not act as promoting modes, so that the p promoting modes still correspond to intramolecular vibrations. To gain physical insight into the effect of the intermolecular modes on the nonradiative decay probability let us consider a generalization of the displaced potential surfaces model (see Sec. IV) where now the $N+\mu$ multidimensional potential surfaces involve both intramolecular modes (characterized by frequencies ω_j and reduced displacement Δ_j where $j=1\cdots N$) and intermolecular modes (characterized by frequencies ω_α at reduced displacements Δ_α where $\alpha=1\cdots\mu$). The phonon-coupling strength now contains a contribution from both intermolecular and intramolecular modes,

$$G = G_N + G_\mu, \quad (\text{IX.1})$$

where

$$G_N = \frac{1}{2} \sum_{j=1}^N \Delta_j^2, \quad (\text{IX.2a})$$

$$G_\mu = \frac{1}{2} \sum_{\alpha=1}^{\mu} \Delta_\alpha^2. \quad (\text{IX.2b})$$

For convenience the low-temperature limit is initially considered. In a similar way the molecular rearrangement energy can be recast in the form

$$E_M = E_M^N + E_M^\mu, \quad (\text{IX.3})$$

where

$$E_M^N = \frac{1}{2} \sum_{j=1}^N \hbar \omega_j \Delta_j^2 \quad (\text{IX.4a})$$

and

$$E_M^\mu = \frac{1}{2} \sum_{\alpha=1}^{\mu} \hbar \omega_\alpha \Delta_\alpha^2. \quad (\text{IX.4b})$$

In the low-temperature limit the nonradiative decay

probability can be written as

$$W = \sum_{k=1}^p (|C_{sl}^k|^2 \omega_k / 2\hbar) \exp[-(G_N + G_\mu)] I_k^{(\mu+N)}, \quad (\text{IX.5})$$

where

$$I_k^{(\mu+N)} = \int_{-\infty}^{\infty} dt \exp[-(i\Delta E_k/\hbar)t + \frac{1}{2} \sum_{j=1}^N \Delta_j^2 \times \exp(i\omega_j t) + \frac{1}{2} \sum_{\alpha=1}^{\mu} \Delta_\alpha^2 \exp(i\omega_\alpha t)], \quad (\text{IX.6})$$

and the effective energy gap ΔE_k is given as before by Eq. (V.4). Thus the effect of the medium phonons is exhibited by the appearance of the medium coupling strength in Eq. (IX.5) and the modification of the Fourier integral (IX.6). Now in principle μ is of the order of Avogadro's number, and to simplify matters it has often been assumed that $\Delta_\alpha^2 \propto (\mu)^{-1}$. Alternatively, we may adopt a coarse graining procedure and assume that the medium frequencies can be characterized by a mean frequency $\langle\omega_\mu\rangle$ (such an approach is equivalent to the Einstein model). Then we can rewrite (IX.6) in a simplified form:

$$I_k^{(\mu+N)} = \int_{-\infty}^{\infty} dt \exp[-(i\Delta E_k/\hbar)t + \frac{1}{2} \sum_{j=1}^N \Delta_j^2 \times \exp(i\omega_j t) + G_\mu \exp(i\langle\omega_\mu\rangle t)]. \quad (\text{IX.6}')$$

It is self evident that the (mean) frequency of the medium modes ($\langle\omega_\mu\rangle \approx 10\text{--}50 \text{ cm}^{-1}$) is considerably lower than that of the intramolecular modes, i.e., $\langle\omega_\mu\rangle \ll \omega_j$ ($j=1\cdots N$) and obviously $\langle\omega_\mu\rangle \ll \omega_M$ (see Sec. V). Now, for a large energy gap and for weak intramolecular coupling (i.e., $G_N \leq 1$) the saddle-point integration method is applicable. We again define a parameter $\Omega_{\mu,k}$ [equivalent to (V.8)] arising from the contribution of the low-frequency medium vibrations

$$\Omega_{\mu,k} = (2G_\mu \langle\omega_\mu\rangle / d_M \Delta_M^2 \omega_M) (d_M \Delta_M^2 \hbar \omega_M / 2\Delta E_k)^{1-(\omega_\mu)/\omega_M}, \quad (\text{IX.7})$$

and as $\langle\omega_\mu\rangle/\omega_M \ll 1$ we have

$$\Omega_{\mu,k} \approx G_\mu \hbar \langle\omega_\mu\rangle / \Delta E_k. \quad (\text{IX.7}')$$

Hence even for large values of G_μ (say $G_\mu \approx 10$) we expect that $\Omega_{\mu,k} \ll 1$. Adopting again the procedure in Sec. V we get

$$I_k^{\mu+N} \approx I_k \exp\{(\Delta E_k/\hbar \omega_M) [(\omega_M/\langle\omega_\mu\rangle) \Omega_{\mu,k}]\} = I_k \exp(G_\mu), \quad (\text{IX.8})$$

where the integral I_k is defined by Eq. (V.10) with $Y_k = 1 - \sum' \Omega_{m,k}$. Combining Eqs. (IX.5) and (IX.6), the over-all factors of $\exp(\pm G_\mu)$ arising from the modes of the medium cancel out. This simple argument can be recast in a more quantitative manner. A straightforward calculation which does not use the approximation (IX.7') leads to the result that in the low-temper-

ature limit the effect of intermolecular phonons is negligible provided that

$$Z_1 = G_\mu (\langle \omega_\mu \rangle / \omega_M) \ln(2\Delta E_k / d_M \hbar \omega_M \Delta M^2) \ll 1. \quad (\text{IX.9})$$

This argument can be extended to finite temperatures taking into account the thermal population of the phonon modes of the medium. The medium effects are of no importance provided that relation (IX.9) is satisfied together with

$$Z_2(T) = G_\mu [(\langle \omega_\mu \rangle / \omega_M) \ln(2\Delta E_k / d_M \hbar \omega_M \Delta M^2)]^2 \times [\exp(\beta \hbar \langle \omega_\mu \rangle / kT) - 1]^{-1} \ll 1. \quad (\text{IX.10})$$

In general the Fourier integral $I_k^{N+\mu}$ [Eq. (IX.8)] can be written

$$I_k^{\mu+N} = I_k \exp[Z_1 + Z_2(T)] \exp(-G_\mu), \quad (\text{IX.11})$$

where I_k is the intramolecular term given in Sec. V. Thus the effects of intramolecular vibrations and intermolecular phonons can be factored out. In the cases that restrictions (IX.9) and (IX.10) are fulfilled, the correction terms are small. It should be borne in mind, however, that experimental methods are currently much more accurate (and perhaps more reliable) than the approximations which were made in the present theoretical treatment and medium effect due to the correction term $\exp[Z_1 + Z_2(T)]$ may be experimentally observable. The most important conclusion arising from the preceding discussion is that the low-frequency vibrational modes of the medium will often exhibit a small effect on the nonradiative decay probability in the statistical limit. Thus provided that the pre-exponential factors C_{st}^k are not appreciably modified by the medium, the nonradiative decay can be indeed considered as equivalent to essentially an added intramolecular process.

Although the intermolecular phonon-coupling function G_μ yields only a minor contribution to the nonradiative decay probability, this parameter plays a central role in determining the optical properties of large molecules in an inert dense medium. In fact, line broadening of the vibronic components of low-lying electronic excitations (where intramolecular coupling is too weak to result in intramolecular line broadening) in low-temperature inert matrices is due to coupling with intermolecular phonons. One can apply the general line-shape function (II.1) for the line shape of an allowed vibronic component of an optical transition provided that the operator V is replaced by the (constant) dipole operator and the vibronic levels correspond just to the intermolecular phonons. If we adopt the simplified displaced potential surfaces model (where now the intermolecular phonon frequencies are the same in the ground and in the excited state) the optical line-shape function can be recast in terms of a Fourier integral and is determined by the phonon-coupling function G_μ . Where $G_\mu \leq 1$, zero-phonon lines will be observed, while when $G_\mu \gg 1$ the optical line

shape will be Gaussian. Systematic studies of medium effects on the optical line shape of guest molecules were partially provided by the study of the Shpol'skii effect.⁵⁰ The zero-phonon line is observed for a large molecule in low-temperature hydrocarbon matrices where the size of the host molecule matches the size of the guest molecule, so in that case $G_\mu \leq 1$. When there is mismatch between the sizes of the guest and the hydrocarbon host molecule, $G_\mu \gg 1$, and a broad band is observed. Thus the intermolecular phonon-coupling strength for a given host molecule can be varied over a wide range using a series of different hydrocarbon glasses. Our theoretical prediction is that over a wide range of G_μ values (say $G_\mu \approx 1$ –10) the nonradiative decay probability (say of the lowest triplet of an aromatic molecule) will be unaffected by the changes in the intermolecular coupling strength and should be invariant in different inert hydrocarbon solvents. When the coupling strength is exceedingly large (say $G_\mu \approx 50$ –100) the nonradiative decay will be somewhat enhanced due to the contribution (IX.11).

X. GOLDEN RULE RATE EXPRESSIONS AND BOLTZMANN STATISTICS

The main theme of the present work is centered around the nature of the energy gap law for nonradiative decay processes. To gain further insight into the nature of the saddle-point integration method, as applied to large energy gaps in the weak coupling limit, moment expansion methods are of interest. The simplest approach involves a moment expansion^{32–34} of the generalized line-shape function [Eq. (II.1)]. This method has been widely applied to the study of optical spectra, but is only of marginal interest for nonradiative decay processes. Another approach involves the expansion of the function $\exp[G_+(t) + G_-(t)]$ [Eq. (IV.6)] in a power series of $\Delta_j^2 \exp(i\omega_j t)$. This approach has been applied to the study of zero-phonon lines in optical spectra,³⁴ and was also adopted by Lin and Bersohn¹⁰ for nonradiative processes. Lin and Bersohn¹⁰ have shown that the general rate expression (I.2) can be written in a rather interesting fashion. For simplicity, we consider the case in which the $\omega_j^{(l)} = \omega_j^{(g)}$, so that the equations are not complicated by the pre-exponential factors in the $f_j(t)$ [Eq. (A2)]. For the zero temperature limit (the general temperature dependence is discussed later), translated into our notation, Eq. (9) of Lin and Bersohn is

$$W = \sum_k \pi \omega_k |C_{st}^k|^2 \exp(-\sum_j \frac{1}{2} \Delta_j^2) \times \prod_j \sum_{n_j=0}^{\infty} [(\frac{1}{2} \Delta_j^2)^{n_j} / n_j!] \delta(\Delta E_k - \sum_j \hbar n_j \omega_j), \quad (\text{X.1})$$

which results from expanding the $\exp[\sum_j \frac{1}{2} \Delta_j^2 \exp(i\omega_j t)]$ in (IV.7) in a power series of $\frac{1}{2} \Delta_j^2 \exp(i\omega_j t)$ and then performing the Fourier integral. We have also

used the fact that Lin and Bersohn's summation

$$\sum_{n=0}^{\infty} \sum_{\{n_j\}}^{\Sigma n_j = n}$$

is equivalent to an unrestricted summation over all of the individual n_j . The last two factors in (X.1) are formally identical to the kinds of expressions encountered in ordinary Boltzmann statistical mechanics: Consider a set of states $\{j\}$ with possible populations n_j , $n_j = 0, 1, 2, \dots, \infty$, with degeneracies $\frac{1}{2}\Delta_j^2$ (not necessarily integral—so we may consider these as probabilities of the states j), and with energies $n_j\hbar\omega_j$. If Boltzmann statistics are used for such a system of “phonons,” the total weight (unnormalized probability) assigned to the configuration $\{n_j\}$ is merely

$$W'\{n_j\} = \prod_j [(\frac{1}{2}\Delta_j^2)^{n_j}/n_j!], \quad (\text{X.2})$$

where our fictitious phonons are considered to be indistinguishable so that there is no over-all factor of $(\sum_j n_j)!$. Equation (X.1) contains a sum over all possible $W'\{n_j\}$ with the delta function which acts as a constraint requiring conservation of energy (with no fluctuations) of the phonons,

$$\sum_j \hbar\omega_j n_j = \Delta E_k. \quad (\text{X.3})$$

Since (X.1) has a sum over all possible sets of $\{n_j\}$ with no restriction as to $N = \sum_j n_j$, this equation is equivalent to the evaluation of the total number of states (i.e., partition function) for a grand canonical ensemble where the number of particles is arbitrary but the energy is fixed. The fact that N is arbitrary is appropriate to the fact that the $\{j\}$ represent oscillators.

Because of this analogy of (X.1) with Boltzmann statistics, we are tempted to make the approximations which are customary in ordinary statistical mechanics, namely, for large ΔE_k replacing

$$\sum_{\{n_j\}} W'\{n_j\}, \quad (\text{X.4})$$

subject to (X.3), by the maximum term in the summation subject to the constraint (X.3). This is exactly what Ross *et al.*⁸ did without the elaborate formal analogy. Since $\Delta E_k/\hbar\langle\omega\rangle$, where $\langle\omega\rangle$ is an average frequency, is never as large as the analogous quantity E/kT in ordinary statistical mechanics, say 10^{23} , the justification for this approximation is much harder to provide. Therefore, we utilize this analogy to include the fluctuations, i.e., the contributions from $W'\{n_j\}$ in the region of $W_{\max}'\{n_j\}$. For this purpose it is convenient to replace the

$$\sum_{n_j} \rightarrow \int_0^{\infty} dn_j,$$

using appropriately $n_j! \rightarrow \Gamma(1+n_j)$ —the gamma function. Such an approximation is valid only for n_j large, but we verify that the final results are also valid for

small n_j (in particular $n_j \rightarrow 0$). The part of (X.1) of interest is then

$$W'(\Delta E_k) = \prod_j \left(\int_0^{\infty} dn_j \frac{(\frac{1}{2}\Delta_j^2)^{n_j}}{\Gamma(1+n_j)} \right) \delta(\Delta E_k - \sum_j n_j \hbar\omega_j), \quad (\text{X.5})$$

which is just the approximate expression obtained by Gelbart *et al.*²⁵ from a steepest-descent evaluation of the I_k . If the δ function in (X.5) is converted to its integral representation, saddle-point integration would give the contribution from W_{\max}' along with the contributions from $W'\{n_j\}$ in the region of W_{\max}' . However, such a treatment is basically equivalent to the saddle-point integration given in Sec. V. We generate a new approximation by taking the δ function in (X.5) to represent a constraint and then find W_{\max}' by the method of Lagrange multipliers. Such an approximation forces $\Delta E_k = \sum_j \langle n_j \rangle \hbar\omega_j$, but allows the energy fluctuations, e.g., $(\Delta E_k)^2 - \sum_j \langle n_j^2 \rangle (\hbar\omega_j)^2$ and higher-order fluctuations, to be nonzero, while the δ function of (X.5) requires all these energy fluctuations to vanish. Such an approximation is valid provided

$$[(\Delta E_k)^2 - \sum_j (\hbar\omega_j)^2 \langle n_j^2 \rangle]^{1/2} \ll \Delta E_k, \quad (\text{X.6})$$

which can of course be checked. Maximizing $W'\{n_j\}$ with respect to variations of the $\{n_j\}$ using the Lagrange multiplier b gives

$$\begin{aligned} \partial[\ln W'\{n_j\} + b \sum_j n_j \hbar\omega_j] / \partial n_j \\ = \log(\frac{1}{2}\Delta_j^2) - \log n_j + b\hbar\omega_j = 0, \end{aligned} \quad (\text{X.7})$$

where Stirling's formula has been used for $\log \Gamma(1+n_j)$. Therefore,

$$n_j^0 = \frac{1}{2}\Delta_j^2 \exp(+b\hbar\omega_j), \quad (\text{X.8})$$

which defines an effective or pseudotemperature $T^* = 1/k_B b$. The constraint (X.3) implies

$$\frac{1}{2} \sum_j \hbar\omega_j \Delta_j^2 \exp(+b\hbar\omega_j) = \Delta E_k \quad (\text{X.9})$$

which is the equation defining b . This equation is identical to the equation (V.5) for the saddle point in the complex t plane which is obtained when evaluating the general Fourier integral (V.3) by the saddle-point method and changing variables $t = -i\hbar b$. (This correspondence indeed implies that b is positive.) Using (X.8) and (X.9), the maximum value of the integrand can be written in the energy gap form as

$$\exp(-\gamma_k \cdot \Delta E_k / \hbar\omega_M) \equiv \exp(-\Delta E_k / k_B T^* + \sum_j n_j^0). \quad (\text{X.10})$$

[Note the similarity of (X.10) to statistical mechanics with “temperature” T^* and a unit chemical potential!] Neglecting the delta function constraint, the fluctuations in n_j about n_j^0 are then given with (unnormalized) probability $\exp[-\frac{1}{2}(n_j - n_j^0)^2/n_j^0]$, implying that these

fluctuations are small for large n_j^0 . The contribution from these fluctuations gives the pre-exponential factors

$$\prod_j (\pi n_j^0/2)^{1/2}.$$

If we consider the possibility that some of the n_j^0 are small, the more exact expression yields

$$W'(\Delta E_k) \rightarrow \prod_j \left[\frac{(\frac{1}{2}\Delta_j^2)^{n_j^0}}{\Gamma(1+n_j^0)} \left(\frac{1}{2\pi} \frac{\partial^2 \log \Gamma(1+n_j^0)}{\partial (n_j^0)^2} \right)^{-1/2} \right], \quad (\text{X.11})$$

where n_j^0 is determined from

$$\partial \log \Gamma(1+n_j^0)/\partial n_j^0 = \log \frac{1}{2}\Delta_j^2 + b\hbar\omega_j, \quad (\text{X.12})$$

with b determined by

$$\sum_j n_j^0 \hbar\omega_j = \Delta E_k. \quad (\text{X.13})$$

For $n_j \rightarrow 0$, we see from (X.1) that its contribution to the product is unity, so that mode can be omitted and the Boltzmann statistics used only for the "larger" n_j^0 , where Stirling's formula for $\log \Gamma(1+n_j^0)$ is valid.

If we include the temperature dependence, the expression for the rate is Lin and Bersohn's Eq. (7), which comes from expanding G_+ and G_- of (IV.3) and then performing the Fourier integration, and is

$$W = \sum_k (\pi\omega_k/2) |C_{sl}^k|^2 \exp(-\sum_j \lambda_j) \times \prod_j \sum_{n_j=0}^{\infty} \sum_{m_j=0}^{\infty} \frac{(\mu_j)^{n_j}}{n_j!} \frac{(\nu_j)^{m_j}}{m_j!} \{ [\coth(\frac{1}{2}\beta\hbar\omega_k) + 1] \times \delta[\Delta E - \hbar\omega_k - \hbar \sum_j (n_j - m_j)\omega_j] + [\coth(\frac{1}{2}\beta\hbar\omega_k) - 1] \times \delta(\Delta E + \hbar\omega_k - \hbar \sum_j (n_j - m_j)\omega_j) \}, \quad (\text{X.14})$$

where

$$\begin{aligned} \lambda_j &= \frac{1}{2}\Delta_j^2 \coth(\frac{1}{2}\beta\hbar\omega_j), \\ \mu_j &= \frac{1}{4}\Delta_j^2 \operatorname{csch}(\frac{1}{2}\beta\hbar\omega_j) \exp(\frac{1}{2}\beta\hbar\omega_j), \\ \nu_j &= \frac{1}{4}\Delta_j^2 \operatorname{csch}(\frac{1}{2}\beta\hbar\omega_j) \exp(-\frac{1}{2}\beta\hbar\omega_j). \end{aligned}$$

Equation (X.14) contains the two sets of "occupation numbers" $\{n_j\}$ and $\{m_j\}$ and two different effective energy gaps arising from the promoting modes as discussed in Sec. VII. The application of "Boltzmann statistics" to (X.14) then follows just as in the zero temperature limit.

Since ΔE_k in practice is not large enough to have very large $\{n_j\}$, the use of Boltzmann statistics to treat the fluctuations is not expected to be as accurate as the development of Sec. V using the saddle-point integration method on the single Fourier integral. The analogy does, however, give added insight into the role of the Franck-Condon principle in radiationless transition rates. Since $0 \leq \frac{1}{2}\Delta_j^2 \lesssim 1$ in the aromatic hydrocarbons, (X.2) and (X.3) tell us that the molecule would like to convert the available energy ΔE_k into the fewest total

number of vibrational quanta (i.e., minimize $\sum_j n_j$) while keeping each of the individual n_j at a minimum—in short, it wants to give the nuclei the minimum possible kinetic energy, and *because* $\frac{1}{2}\Delta_j^2 \lesssim 1$, the Franck-Condon factors still dominate the increase in the density of states.

XI. DISCUSSION

In this paper we have been concerned with the harmonic model for the nonradiative decay of large molecules. The main accomplishments of the present study can be summarized as follows:

(a) General expressions for the nonradiative decay probability in the harmonic approximation have been derived.

(b) These equations are presented in an approximate, but physically transparent, form for the simple displaced potential surfaces model, and for a more general case which has a closer bearing on the real physical situation whereupon frequency changes of the order of 50% are encountered for some of the vibrational modes. In both cases the weak and the strong phonon-coupling limits can be realized.

(c) The analysis of the strong coupling limit for the displaced potential surfaces model results in a generalized activated rate equation.

(d) The energy gap law is theoretically established in the weak coupling limit. The exponential dependence of the nonradiative decay probability on the effective energy gap exhibits an asymptotic behavior which is valid for a large effective energy gap.

(e) The analysis of the general Fourier integral representing the nonradiative decay probability by the mathematical method of saddle-point integration and by the physical approach based on the analogy with Boltzmann statistics makes it possible to assess the role of different accepting modes. In the limit of a large energy gap the most effective accepting modes involve those characterized by the highest-frequency modes as has been pointed out previously by Ross *et al.*,⁸ by Siebrand,^{12,13} and by Burland and Robinson.²¹ The present treatment provides a theoretical justification for this assumption.

(f) The deuterium isotope effect² in the weak coupling statistical limit in aromatic hydrocarbons is determined by the high-frequency C-H (or C-D) modes, although the corrections to the γ_k from the C-C modes may introduce a measurable effect. Here we concur with the conclusions of Robinson and Frosch, Ross, and Siebrand. On the other hand, in the strong coupling limit the isotope effect is expected to be small.

(g) The low-frequency out-of-plane modes lead only to a minor contribution to the over-all nonradiative decay probability and the isotope effect in the weak coupling large energy gap situation in aromatic hydrocarbons.

(h) The many-phonon theory of nonradiative decay

can be extended to incorporate intramolecular phonons as accepting modes. As these medium modes are characterized by low frequency, their effect on the decay probability is small provided their effective number is not too large. This treatment of the effects of an inert medium provides a theoretical justification for considering the nonradiative decay as an intramolecular phenomena. The major effect of the medium as a heat bath at moderate temperatures ($kT \ll \omega_\mu$) leads in the weak coupling statistical limit to a modification of the nonradiative decay probability by the factor $\coth(\beta\hbar\omega_k/2)$ which involves the thermal population the promoting modes. This result is known from Lin's work.

We may conclude that the theoretical treatment of the weak coupling large energy gap case within the framework of the harmonic approximation result in predictions which are in qualitative agreement with the bulk of experimental data on electronic relaxation in aromatic molecules. Indeed, the analysis of Ross *et al.* has established that electronic relaxation between low-lying excited electronic states of large molecules correspond to the weak coupling limit. Examples which violate this rule, in which electronic relaxation corresponds to the strong coupling case, are as yet unknown. Possible examples which may correspond to the strong coupling case involve electronic relaxation in charge-transfer complexes,³⁸ where large configuration changes are encountered along the intermolecular coordinate. Another example which may involve large configurational changes between the lowest-excited singlet state and the ground state involves the biphenylene molecule.^{51,52} This molecule is the only known aromatic hydrocarbon which does not exhibit observable fluorescence or phosphorescence decay. It is possible that a large configuration change in the excited state which involves "folding" of the rings is responsible for the efficient nonradiative decay which will now correspond to the strong coupling case. It will be extremely interesting to study the temperature dependence and the deuterium isotope effect on this nonradiative process.

Ross *et al.*⁸ have also concluded that the weak coupling limit does not appear to be valid for heterocyclic molecules. As these molecules might exhibit large frequency and/or geometry changes, they merit further study.

Up to this point we have been concerned with the harmonic model for a polyatomic molecule, so that the vibrational modes are considered to be treated independently on an equal basis. In many cases of physical interest which involve both electronic relaxation and photochemical unimolecular processes a single vibrational mode has to be singled out because of physical considerations or in view of the breakdown of the harmonic approximation for that particular mode. Circumstances in which the harmonic model has to be

extended are:

(a) Partial inclusion of anharmonicity effects.^{11-13,21} The complete treatment of the anharmonicity problem is very complex as in this case the independent-modes approximation can break down. A first step towards the inclusion of anharmonicity effects will involve retaining the independent-modes approximation and including deviations from the harmonic potential within one mode. It was suggested by Siebrand and Henry⁵³ that the C-H stretching modes may involve a substantial contribution from anharmonicity effects. The present approach based on the generating functions method obviously extends previous treatments as an arbitrary number of modes may be included in addition to the single "anharmonic" mode.

(b) A proper treatment of some large configurational changes. It was recently pointed out by Gelbart *et al.*²⁵ that some photochemical reactions such as *cis-trans* isomerization are not amenable to treatment within the framework of the harmonic model, as the torsional mode cannot be regarded to be harmonic. It was thus proposed by Gelbart *et al.*²⁵ that the torsional mode be factored out in the general expression for the nonradiative decay probability, while the harmonic nature of the other modes is retained. In some cases the harmonic model can be still retained; however, it may be useful to separate two different type of modes.

(c) Optical selection studies in an "isolated" molecule. Electronic relaxation in different excited vibronic levels can be studied in the low-pressure gas phase by monitoring the fluorescence which results from narrow band excitation. In the theoretical study of these effects one has to separate the optically active modes from other intermolecular modes. Such an experiment was recently performed by Schlag and Weyssenhoff,⁵⁴ who have monitored the energy dependence of the nonradiative decay probability of the β -naphthylamine molecule from different optically selected vibronic levels in low-pressure gas phase.

The theoretical expressions presented in this paper can be used to handle the mode factorization problem. To treat the breakdown of the harmonic approximation for a given mode (promoting or accepting) the general golden-rule expression can be recast in terms of a convolution integral involving the partition of energy between the "nonharmonic" part and the "harmonic" part of the molecule which now involves $N-1$ modes. Adopting the Fourier transform techniques for these two components, the latter part can be evaluated again in the harmonic approximation while the nonharmonic part involves a sum over Franck-Condon overlap integrals. To handle the optical selection problem theoretically we have to consider a modified form of a single mode generating function, which corresponds to the optically active mode. These problems deserve further theoretical study.

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APPENDIX A: SINGLE-MODE GENERATING FUNCTION FOR THE HARMONIC MOLECULE

For a one-dimensional harmonic oscillator,

$$g_j^\alpha(Q_j^{(\alpha)}, T; \tilde{Q}_j^{(\alpha)}, 0) = [M_j \omega_j^{(\alpha)} / 2\pi i \hbar \sin(\omega_j^{(\alpha)} T)]^{1/2} \exp\{ (iM_j \omega_j^{(\alpha)} / 4\hbar) [(\tilde{Q}_j^{(\alpha)} - Q_j^{(\alpha)})^2 \cot(\frac{1}{2}\omega_j^{(\alpha)} T) - (\tilde{Q}_j^{(\alpha)} + Q_j^{(\alpha)})^2 \tan(\frac{1}{2}\omega_j^{(\alpha)} T)] \}. \quad (\text{A1})$$

$$f_j(t) = \exp\left(\frac{-\beta_j \Delta_j^2}{2P_j(1+Y_j)}\right) / V_j X_j, \quad (\text{A2})$$

where

$$P_j = [\exp(i\delta_j^{(-)}t) \coth y_j + (1 - \coth y_j) \cos \delta_j^{(-)}t] [\exp(i\delta_j^{(-)}t) - \exp(i\delta_j^{(+)}t) + (\coth y_j - 1) \times (\cos \delta_j^{(-)}t - \cos \delta_j^{(+)}t)]^{-1}, \quad (\text{A3})$$

$$\delta_j^{(-)} = \frac{1}{2}(\omega_j^{(s)} - \omega_j^{(l)}); \quad \delta_j^{(+)} = \frac{1}{2}(\omega_j^{(s)} + \omega_j^{(l)}), \quad (\text{A4})$$

$$y_j = \beta \hbar \omega_j^{(s)} / 2, \quad (\text{A5})$$

$$Y_j = i(\beta_j - 1) \cot(\frac{1}{2}\omega_j^{(l)}t) / 2P_j, \quad (\text{A6})$$

$$X_j = [\beta_j - \frac{1}{2}(1 - \beta_j)^2 \coth y_j (W_j / V_j^2)]^{1/2}, \quad (\text{A7})$$

$$V_j = (1 - \coth y_j) \cos(\delta_j^{(-)}t) + \coth y_j \exp(i\delta_j^{(-)}t), \quad (\text{A8})$$

and

$$W_j = \sin(\omega_j^{(l)}t) [\exp(i\omega_j^{(s)}t) \coth(2y_j) + (1 - \coth 2y_j) \cos(\omega_j^{(s)}t)]. \quad (\text{A9})$$

$$\tilde{f}_k(t) = (S_k / X_k V_k) [\hbar(\omega_k^{(s)} \omega_k^{(l)})^{1/2} / 2\beta_k] \{1 - \frac{1}{2}i[(1 - \beta_k)^2 / \beta_k] (\coth y_k) (W_k / V_k^2)\}^{-1}, \quad (\text{A10})$$

where

$$S_k = [\exp(i\delta_k^{(+)}t) + (\coth y_k - 1) \cos \delta_k^{(+)}t] [\exp(i\delta_k^{(-)}t) \coth y_k + (1 - \coth y_k) \cos(\delta_k^{(-)}t)]^{-1}. \quad (\text{A11})$$

APPENDIX B: DETERMINATION OF THE SADDLE POINT

The general saddle-point equation for the real variable Y from (V.6) (dropping the subscript k) is

$$1 = Y + \sum' \Omega_m(Y) \xi_m, \quad (\text{B1})$$

where $0 \leq \Omega_m$, $0 < \xi_m < 1$. In the case of frequency changes, there are also terms of the form $\Xi_m(Y)^{2\xi_m}$ for which $2\xi_m$ may be > 1 , but basically similar kinds of considerations apply. The most likely situation in which (V.13) is violated in aromatic hydrocarbons occurs in the case of C-C skeletal vibrations for which $\Omega_{C-C} \lesssim \Theta(1)$. Thus, for simplicity, considering the case in which only $\Omega_{C-C} \equiv \Omega \neq 0$ (the other modes are added afterwards) (B1) becomes ($\xi_m \rightarrow \xi$),

$$1 = Y + \Omega Y^\xi. \quad (\text{B2})$$

For $\omega_{C-H} \approx 3000 \text{ cm}^{-1}$ and $\omega_{C-C} \approx 1400 \text{ cm}^{-1}$, $\xi \approx 7/15$. Because $\frac{1}{2} - \xi \approx 1/30 \ll 1$, we would expect that the solution to the saddle point in (B2) is close to that of

$$1 = Y_0 + \Omega Y_0^{1/2} \quad (\text{B3})$$

or

$$Y_0 = \frac{1}{4}[-\Omega + (\Omega^2 + 4)^{1/2}]. \quad (\text{B4})$$

Writing

$$Y = Y_0 + \epsilon, \quad (\text{B5})$$

the saddle-point equation (B2) can be expanded to first order (or even second, if necessary) in ϵ . Using

$$Y_0^\xi = Y_0^{1/2} \exp[(\xi - \frac{1}{2}) \ln Y_0] \approx Y_0^{1/2} [1 + (\xi - \frac{1}{2}) \ln Y_0], \quad (\text{B6})$$

we get

$$\epsilon_1 = \frac{-\Omega Y_0^{1/2} (\xi - \frac{1}{2}) \ln Y_0}{1 + \Omega \xi / Y_0^{1/2}}, \quad (\text{B7})$$

which seems to work well even for Ω as large as unity.

In the perdeutero-aromatic hydrocarbons, since $\omega_{C-D} \approx 2200 \text{ cm}^{-1}$, ξ_{C-D} falls to about $7/11$, so $\xi - \frac{1}{2} \approx 3/22$ and terms to $\Theta(\epsilon^2)$ may then be necessary. Alternately, as $\frac{2}{3} - \xi = 1/33 \ll 1$, the more cumbersome but tractable cubic equation (from $Y \equiv X^3$) may be used as the starting approximation.

In order to add on the other modes, we merely have

to include the Ω_m for the other modes. For $\Omega_m \ll 1$, all $m \neq \text{C-C skeletal}$, we can consider $\Omega_m \approx \mathcal{O}(\epsilon)$, and then to first order

$$\epsilon = \epsilon_1 - \sum_m'' \Omega_m Y_0 \xi_m (1 + \Omega \xi / Y_0^{1/2})^{-1}, \quad (\text{B8})$$

where the double prime on the summation implies that the C-C and C-H stretching modes are to be omitted.

In the more general case in which it is of interest to consider the case of two $\Omega's \approx \mathcal{O}(1)$ for different $\xi's$, it is then necessary to find other simple analytic solutions to the basic saddle-point equations. Because of our imprecise knowledge of the explicit values of the $\xi's$ and $\Omega's$, etc., it is highly desirable to have explicit analytic solutions so that it is possible, hopefully, to make semiquantitative statements of general trends which are independent of the exact values of these fundamental molecular quantities, but basically reflect their approximate magnitudes.

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nances will be encountered in the regions of interest where the ϕ_{ij} are not densely distributed.

²⁷ Because the $\{\phi_{ij}\}$ represent a discrete manifold, mathematically irreversibility is not inherent in (I.2) for an isolated molecule. However, when account is taken of the physical situation in which there is a natural time scale for any real experiment, the Dirac delta functions in (I.2) should be replaced by functions with finite width; so provided the $\{\phi_{ij}\}$ are sufficiently dense, physical irreversibility ensues.²⁸ As we only consider smooth approximations to (I.2) which can be expressed as ordinary functions, not generalized (delta) functions, it is simplest to keep (I.2) in its present form rather than introducing the physical width of each state $\{\phi_{ij}\}$.

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$$H = H_{\text{CBO}} + V_{\text{HT}} + V_{\text{BO}}, \quad (1)$$

where H_{CBO} is the Hamiltonian in the crude BO approximation and V_{HT} are the Herzberg-Teller interactions such that our

$$H_{\text{BO}} = H_{\text{CBO}} + V_{\text{HT}}. \quad (2)$$

Thus, we assume that the majority of the Herzberg-Teller interactions V_{HT} have already been diagonalized; spin-orbit, which is commonly considered a Herzberg-Teller interaction, is included in V_{BO} , but it is merely semantics as to what spin-orbit is called. In Robinson's language,^{2,14} the energies associated with V_{HT} are often sufficiently large so that no real experiment could follow the time-scale $\hbar/|V_{\text{HT}}|$, and thus V_{HT} is best included in H_0 as is done above in (2) where $H_0 = H_{\text{BO}}$.

⁴⁰ This assumption is common in the treatment of multiphonon processes in the optical absorption in solids.³³

⁴¹ Integrals of the form

$$I = \int_{-\infty}^{\infty} \exp[-A(t)] dt, \quad (1)$$

where the integrand is highly oscillatory and/or is large, can be approximated by saddle-point integration. The saddle point is taken as the point t_0 at which

$$[\partial A(t)/\partial t]_{t_0} = 0, \quad (2)$$

so that the truncated Taylor series expansion

$$A(t) \approx A(t_0) + \frac{1}{2} [\partial^2 A(t)/\partial t^2]_{t_0} (t - t_0)^2 \quad (3)$$

may be used in (1), when $[\partial^2 A(t)/\partial t^2]_{t_0} > 0$, to give

$$I \approx [2\pi/(\partial^2 A/\partial t^2)_{t_0}]^{1/2} \exp[-A(t_0)]. \quad (4)$$

The approximation (4) to (1) obviously breaks down as $(\partial^2 A/\partial t^2)_{t_0} \rightarrow 0$, which is the analog of a classical turning point in WKB approximations, and in this case other approaches must be used. In this paper, the statistical limit is considered, so that the effective energy gaps ΔE_k are taken to be large so that (4) is indeed a valid approximation. Although the saddle-point approximation to the nonradiative decay rates (II.7) is valid in the statistical limit, in practice the analytic determination of the saddle-point may present some difficulties. Although approximation (V.13), which appears to be valid for aromatic hydrocarbons, is

used in the text, in the Appendices we show how to obtain analytic expressions when this condition is violated and some $\Omega \approx \Theta(1)$.

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It is reasonable to assume that in many cases when a large organic molecule is introduced into a mixed organic crystal, a hydrocarbon matrix, or a rare-gas solid, the phonon modes of the host will be sufficiently perturbed to result in localized phonon modes.

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Theoretical Predictions on the Structures of Diimide

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The LCAO MO SCF wavefunctions have been determined for the ground states of the isomeric forms of diimide. Molecular geometries for *trans*(¹A_g), *cis*(¹A₁)-diimide, and 1,1-dihydrodiazine were deduced through the most detailed systematic geometry search to date on the diimide molecule. Contrary to the results from semiempirical calculations where *cis*-diimide has been predicted to be 4.5–8.5 kcal/mole more stable than the *trans* form, this calculation shows that the *trans* form is more stable. Furthermore, contrary to the common assumptions, the bond distances and bond angles are found to be different for different isomeric forms, due to the difference in electronic and nuclear repulsive forces. A discussion is made on the ultraviolet and infrared experimental results and comparison is made between the *trans*-N₂H₂ closed-shell ¹A_g state and the open-shell ³B_g state at the theoretically calculated and the experimentally obtained configurations. The calculated force constants and dipole moment of *cis*-N₂H₂ are reported.

I. INTRODUCTION

In the past decade experimentalists and theoreticians have shown great interest in the diimide molecule. In 1953, Walsh¹ predicted from the number of electrons in the molecule for the then unknown N₂H₂, the planar, bent ground-state structure, in either *cis* or *trans* form. A semiempirical quantum-mechanical calculation for the unknown diimide was also performed by Wheland and Chen² in 1956. From 1955 to present, infrared^{3–10} and mass^{11–14} spectroscopists have claimed the discovery of the presence of yellow solid N₂H₂, stable between 77–120°K as the discharge decomposition product of N₂H₄, NH₃, or hydrazoic acid. Since there were several other possibilities, the experimental identification of N₂H₂ had been a challenge.

In this paper, we wish to report the calculated ground-state structures of *cis*-, *trans*-diimide, and 1,1-dihydrodiazine, their total electronic energies and orbital energies. Our past experience¹⁵ had been such that the

geometries calculated were within 1% of the microwave spectroscopy values. The theoretically calculated frequencies are compared with observed experimental values. A summary analysis is made concerning the conflicting existing spectroscopy data.

We have also found that due to difference in repulsive forces, the equilibrium bond distances and bond angles differ slightly for the different isomeric forms of diimide. Comparison has been made with the other existing calculations (Table I) and with the results of calculations using Hoffman's extended Hückel MO program¹⁶ (Table II).

The diimide molecule is of great chemical and theoretical interest because it is the parent compound of azo chemistry, it has recognized ability as multiple bonds hydrogenation catalyst with both functional and stereo selectivity, and it is also the isoelectronic molecule of ethylene. Therefore, the detailed analysis of the structure of diimide may enhance our knowledge of the low-lying electronic structure of azo compounds