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New Approach to Nonradiative Intramolecular Transitions

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A unified and *completely* time-independent approach based on Feshbach's formalism for nuclear reactions, in which radiative and nonradiative processes are treated on an equal basis, is used to describe the behavior of isolated molecules in a radiation field. The expressions developed are complete and link excited states of measurable lifetime to resonances arising from the action of Green functions. Approximations in the form of the assumption that the ground and excited states can be described as Born–Oppenheimer states are finally introduced only to show how matrix elements could be estimated and to relate our results to those of previous studies. An important feature of the present formulation is that, except for particular models as the ones used by Jortner and co-workers, it demonstrates that the radiative and nonradiative decay modes for large molecules are independent of each other to a high degree of approximation. Without substantial modification, the present model yields no information about transitions between excited states.

INTRODUCTION

Nonradiative intramolecular transitions have been the subject of numerous recent studies, both theoretical and experimental.[1] It has been established that radiationless processes occur in isolated molecules and that, to a good approximation, the medium (e.g., the solvent) merely provides a sink for the dissipation of vibrational energy.

The theory developed by Robinson and Frosch[2,3] is illustrative of the approach based on the time-dependent transitions between zero-order states which are taken to be Born–Oppenheimer states. This leads to an expression for the nonradiative lifetime,

$$\tau_{nr}=\hbar/2\pi\rho\beta_{el}^2F^2, \tag{1}$$

where β_{el} is the matrix element of the perturbing Hamiltonian which couples the initial and final electronic states, ρ is the density of final states, and F is the Franck–Condon vibrational overlap factor. The expression emphasizes the importance of vibrational modes in radiationless processes.

The time-dependent approach has recently been criticized,[1] and several authors have treated the problem of nonradiative decay from the point of view of the breakdown of the Born–Oppenheimer approximation.[4–9] Here, the excited states of the molecule are considered to be stationary states, i.e., eigenstates of the total molecular Hamiltonian, and the occurrence of radiationless transitions as time-dependent processes is linked to the adequacy of the description in terms of Born–Oppenheimer states. While broad in concept, the detailed analyses based on the stationary-state formulation lack generality since they are based on specific simplified molecular models and expansion methods. In this connection it should be noted that the representation chosen to describe the decaying state is, essentially, a matter of convenience and does not reflect on the physical observables.

In this paper we present a unified, completely time-independent approach to the behavior of isolated molecules in a radiation field in which radiative and nonradiative processes are treated on an equal basis. The method, which is based on Feshbach's treatment of nuclear reactions,[10–12] utilizes projection operators to select the levels involved in the transitions and the resolvents (Green functions) of pertinent Hamiltonian operators to generate the complete eigenvalue problem for nuclear wavefunctions and expressions for the transition matrix elements and their associated linewidths. In close analogy to the situation with nuclear reactions, the transition probabilities are shown to consist of contributions from direct processes which are not associated with a time delay, and from resonances which correspond to excited states of finite lifetime. Of particular interest is that this formulation reveals, in contrast with the conclusions reached by Jortner and co-workers,[5,6] that for large molecules radiative and intramolecular perturbations are separable except for very restrictive models.

DEVELOPMENT OF THE MODEL

The system we are considering consists of an isolated molecule in a radiation field. With respect to the prop-

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[1] B. R. Henry and M. Kasha, Ann. Rev. Phys. Chem. **18**, 161 (1968).

[2] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **37**, 1962 (1962).

[3] G. W. Robinson and P. R. Frosch, J. Chem. Phys. **38**, 1187 (1963).

[4] M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).

[5] J. Jortner and R. S. Berry, J. Chem. Phys. **48**, 2757 (1968).

[6] D. P. Chock, J. Jortner, and S. A. Rice, J. Chem. Phys. **49**, 610 (1968).

[7] W. Rhodes, B. R. Henry, and M. Kasha, "Radiationless Transitions in Molecules," Bulletin No. 37, Pt. A, Institute of Molecular Biophysics, Florida State University, Tallahassee, Fla., September 1968.

[8] W. Rhodes, J. Chem. Phys. **50**, 2885 (1969).

[9] J. H. Young, in Ref. 7.

[10] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962); **43**, 410 (1967); L. Estrada and H. Feshbach, *ibid.* **23**, 123 (1963).

[11] R. H. Lemmer, Rept. Progr. Phys. **29**, 131 (1966).

[12] A previous adaptation of Feshbach's approach to the decay of unstable states, using a time-dependent formalism, has been described by L. Mower, Phys. Rev. **142**, 799 (1966); **165**, 145 (1968).

erties of this field, it is only necessary to specify that the frequency of the radiation correspond to a transition between accessible states of the molecule. Moreover, only single photon excitation and decay processes are considered. It does not detract from the generality of the final conclusions to assume that before interaction the radiation is monochromatic. The history of the system is considered traceable from the infinitely distant past, when the photons and the molecule were independent, to a period of interaction and, ultimately, to the final states in the infinitely distant future. Care has to be exercised in defining the final states. We stipulate that all processes (excitation and decay) involve transitions between *iso*-energetic states, and for this purpose define (*vide infra*) composite electronic-radiation-field wavefunctions which are eigenfunctions of a zero-order Hamiltonian. Since they are considered to be states of the total system, the initial state at $t=-\infty$, the excited states generated by photon absorption, and the final states have identical energy contents with this definition. Furthermore, the final states clearly fall into two distinct categories: those which result from the radiative decay of an excited state and, consequently, in the Born–Oppenheimer sense, possess relatively little internal vibrational energy, and those which arise from nonradiative decay and incorporate a substantial amount of internal vibrational energy. It is assumed that the final states defined in this manner are stable.[13] In a dense medium the excess vibrational energy would, of course, be dissipated in collisions with other molecules, and it is presumed that this external relaxation is fast relative to the relaxation of the excited states.[2,3]

We now wish to develop expressions for the rates of the various decay processes which can occur in this quite general model system, and to accomplish this we will follow Lemmer's[11] formalism of Feshbach's treatment. We start by defining the stationary-state wavefunctions Ψ of the system which satisfy the eigenvalue problem

$$(E-\mathcal{H})\Psi=0, \tag{2}$$

where $\mathcal{H}$ is the total nonrelativistic Hamiltonian. The latter is displayed as the sum of Hamiltonians for the molecule $\mathcal{H}_m$, the radiation field $\mathcal{H}_f$, and their interaction $(\mathcal{V}_{fm})$, i.e.,

$$\mathcal{H}=\mathcal{H}_m+\mathcal{H}_f+\mathcal{V}_{fm}. \tag{3}$$

Now consider the molecular Hamiltonian $\mathcal{H}_m$ in more detail. We specify it in terms of the sum of the nuclear kinetic-energy operator

$$\mathcal{T}_N=-\hbar\sum_K \nabla_K^2/2M_K,$$

the electronic kinetic-energy operator

$$\mathcal{T}_E=-\hbar^2\sum_k \nabla_k^2/2m,$$

and the Coulombic energy term

$$\mathcal{U}(r,R)=-\sum_k\sum_K(Z_K/r_{kK})+\sum_{K<L}(Z_KZ_L/r_{KL})+\sum_{k<l}r_{kl}^{-1}$$

as:

$$\mathcal{H}_m=\mathcal{T}_N+\mathcal{T}^E+\mathcal{U}(r,R). \tag{4}$$

It is now assumed that the kinetic-energy operator $\mathcal{T}_N$ is the perturbation responsible for nonradiative processes,[4–8,14] and if a zero-order Hamiltonian is specified in the manner discussed by Messiah[15] we may set $\mathcal{H}_0=\mathcal{T}_E+\mathcal{U}(r,R)+\mathcal{H}_f$ and recast Eq. (3) in the form

$$\mathcal{H}=\mathcal{H}_0+\mathcal{V}, \tag{5}$$

where $\mathcal{V}=\mathcal{T}_N+\mathcal{V}_{fm}$. It is clear that $\mathcal{H}_0$ is essentially the Born–Oppenheimer Hamiltonian for which

$$[E_i(R)-\mathcal{H}_0]\phi_i(r,R)=0. \tag{6}$$

Here the index i specifies both the molecular electronic state and the radiation field state so that $E_i(R)$ represents a particular electronic energy surface plus free photon energy. The total wavefunction Ψ may now be expanded in a *complete* set of Born–Oppenheimer states defined in this manner, and we write

$$\Psi=\sum_i\phi_i(r,R)\chi_i(R), \tag{7}$$

where $\chi_i(R)$ represents the nuclear wavefunction and the sum symbolically includes an integration over the continuum states. This expansion may be justified by the realization that the structured absorption and emission spectra often shown by even rather complex molecular systems indicates Born–Oppenheimer wavefunctions to furnish good descriptions of the terminal states involved.

It is clear that for the radiation–molecule interaction model we are considering the system ultimately returns to the same *molecular* electronic state in which it started. Since the radiative decay processes will involve photons of different energy, the wavefunctions defined by Eq. (6) must be labeled accordingly. We therefore set $\phi_i\equiv\phi_{i\nu}$, where i labels the molecular electronic state and ν the photon state. In this notation the final states are $\phi_{0\nu}$, and the two types of final states correspond to a zero-photon state (ϕ_{00}) arising from nonradiative decay and a collection of one-photon states $(\phi_{0\nu};\ \nu=1,2,\cdots,n)$ resulting from radiative decay. The latter are chosen to comprise only states resulting from electronic transitions. Consequently, the $\phi_{0\nu}$ specify the "open channels"[10,11] available to the system, which may be selected from the total wavefunction by the projection operator[16]

$$\mathcal{O}=\sum_\nu|\phi_{0\nu})(\phi_{0\nu}|=|\boldsymbol{\phi}_0)(\boldsymbol{\phi}_0|.$$

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[13] This is a reasonable assumption since the rates of decay processes involving the emission of infrared photons are intrinsically slow; cf. P. Seybold and M. Gouterman, Chem. Rev. **65**, 413 (1965).

[14] If transitions between states of different multiplicity are to be included, this operator must be augmented by another operator which couples these states; cf. Ref. 4.

[15] A. Messiah, *Quantum Mechanics*, (North-Holland Publ. Co. Amsterdam, 1962), Vol. 2, Chap. 21.

[16] We employ Dirac notation with the convention[11] that round brackets $|\cdots)$ refer to electronic coordinates and angular brackets $|\cdots\rangle$ refer to both electronic and nuclear coordinates.

The complimentary space then corresponds to "closed channels,"[10,11] which are projected by the operator $\mathcal{P}=1-\mathcal{O}$. These operators have the well-known properties $\mathcal{O}^2=\mathcal{O}$, $\mathcal{P}^2=\mathcal{P}$, and $\mathcal{O}\mathcal{P}=\mathcal{P}\mathcal{O}=0$. Clearly,

$$\mathcal{O}\Psi=\sum_{\nu}^{n}\phi_{0\nu}(r,R)\chi_{0\nu},$$

and

$$\mathcal{P}\Psi=\sum_{\nu=n+1}\phi_{0\nu}(r,R)\chi_{0\nu}+\sum_{i\neq 0,\nu}\phi_{i\nu}(r,R)\chi_{i\nu}.$$

The meaning of the index ν for the nuclear wavefunction $\chi_{0\nu}$ in the range $\nu=0, 1, 2, \cdots, n$ is as follows: When $\nu=0$ it refers to the nuclear function associated with a vibrationally highly excited molecule in its electronic ground state, and when $\nu=1, 2, \cdots, n$ it refers to a vibrational level in the vicinity of the corresponding zero-point level.

Manipulation of Eq. (2) by means of the partitioning technique in operator form[17] furnishes the relation

$$[E-\mathcal{O}\mathcal{H}\mathcal{O}-\mathcal{O}\mathcal{H}\mathcal{P}(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}\mathcal{H}\mathcal{O}]\mathcal{O}\Psi=0, \quad (8)$$

which, by utilizing the definitions of $\mathcal{H}$ and $\mathcal{O}\Psi$, becomes

$$\sum_{\nu}\{[E-E_{0\beta}]\delta_{\beta\nu}-(\phi_{0\beta}\mid\mathcal{V}\mid\phi_{0\nu})$$
$$-(\phi_{0\beta}\mid\mathcal{V}\mathcal{P}(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}\mathcal{V}\mid\phi_{0\nu})\}\chi_{0\nu}(R)=0, \quad (9a)$$

or, in matrix notation,

$$\{E\cdot\mathbf{1}-\mathbf{E}_0-(\boldsymbol{\phi}_0\mid\mathcal{V}\mid\boldsymbol{\phi}_0)$$
$$-(\boldsymbol{\phi}_0\mid\mathcal{V}\mathcal{P}(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}\mathcal{V}\mid\boldsymbol{\phi}_0)\}\boldsymbol{\chi}_0=0, \quad (9b)$$

where $\mathbf{E}_0$ is diagonal.

Equation (9) represents the complete eigenvalue problem for the nuclear states $\chi_{0\nu}$. The operator $\mathcal{P}$ appears only in the last term, where it provides a means of exciting the molecule. Consequently, just as in the case of nuclear reactions,[10,11] this term may be considered responsible for the generation of excited states.

Equation (8) provides a particularly elegant means of displaying the adiabatic approximation.[18] For this purpose we consider the molecule in its ground state in the absence of the radiation field so that $\mathcal{H}_0=\mathcal{T}_E+\mathcal{U}(r,R)$, $\mathcal{V}=\mathcal{T}_N$, and $\phi_{0\nu}\equiv\phi_0$. Moreover, $\mathcal{O}=|\phi_0)(\phi_0|$. The adiabatic approximation excludes coupling involving excited states, so the resolvent term of Eq. (8) is dropped, and instead of Eq. (9) we have

$$[E-E_0(R)-(\phi_0\mid\mathcal{T}_N\mid\phi_0)]\chi_0(R)=0. \quad (10)$$

Recognizing that $\mathcal{T}_N$ operates on the product $\phi_0\chi_0$, we find that[18]

$$[E-E_0(R)-(\phi_0\mid\mathcal{T}_N\mid\phi_0)-\mathcal{T}_N]\chi_0(R)=0. \quad (11)$$

The usual way of obtaining this result is by means of the expansion (7), which furnishes a series of coupled equations for the nuclear wavefunctions χ_i from which the coupling terms are dropped. This has the disadvantage of explicitly circumventing display of the resolvent term of Eq. (8), which is responsible for the time-delayed or resonance processes and which, ultimately, yields expressions for the lifetimes.

When E is close to an eigenvalue of the operator $\mathcal{P}\mathcal{H}\mathcal{P}$, the resolvent term in Eq. (9) becomes singular and varies very rapidly with the energy E. Thus, if we define the eigenvalue problem

$$(\epsilon_s-\mathcal{P}\mathcal{H}\mathcal{P})\Phi_s=0 \quad (12)$$

and specify a complete set of states Φ_s (these are states of the whole system), we can partition the reduced resolvent into

$$\mathcal{P}(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}=\mathcal{P}'(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}'$$
$$+\mathcal{P}''(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}'', \quad (13)$$

with

$$\mathcal{P}'=\sum_{t}|\Phi_t\rangle\langle\Phi_t|, \qquad \mathcal{P}''=\sum_{r}|\Phi_r\rangle\langle\Phi_r|,$$

and

$$\mathcal{P}=\mathcal{P}'+\mathcal{P}''.$$

The sum over t includes the resonance terms which lead to time-delayed processes. The sum over r varies only slowly with the energy and leads to the term

$$(\boldsymbol{\phi}_0\mid\mathcal{V}\mathcal{P}''(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}''\mathcal{V}\mid\boldsymbol{\phi}_0)$$

in Eq. (9), which may be added to $(\boldsymbol{\phi}_0\mid\mathcal{V}\mid\boldsymbol{\phi}_0)$ to represent what may be called the direct or prompt processes. These do not make any appreciable contribution to the lifetimes which arise from the resonances. In Eq. (12) no coupling with the open channels appears, so that strictly speaking, the functions Φ_t do not represent the resonant states as they do not decay with time. However, for long-living excited states (we define these, broadly, as states whose decay is measurable), the resonance energy will differ very little from ϵ_t. If we now set $\mathcal{H}'=\mathcal{H}_0+\mathcal{V}+\mathcal{V}\mathcal{P}''(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}''\mathcal{V}$, Eq. (8) can be written as

$$(E-\mathcal{O}\mathcal{H}'\mathcal{O})|\mathcal{O}\Psi\rangle=\mathcal{V}\mathcal{P}'(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}'\mathcal{V}\mid\mathcal{O}\Psi\rangle. \quad (14)$$

In view of the definition of $\mathcal{O}\Psi$, this represents a set of coupled inhomogeneous equations. Their solution consists of the sum of the homogeneous solution with proper boundary conditions and a particular solution, i.e.,

$$|\mathcal{O}\Psi\rangle=\Phi^{+}+(E^{+}-\mathcal{O}\mathcal{H}'\mathcal{O})^{-1}\mathcal{V}\mathcal{P}'(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}'\mathcal{V}\mid\mathcal{O}\Psi\rangle, \quad (15)$$

where

$$(E-\mathcal{O}\mathcal{H}'\mathcal{O})\Phi^{\pm}=0. \quad (16)$$

The incoming state Φ^{+} represents a state which, in the infinitely remote past, coincides with the unperturbed

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[17] P. O. Löwdin, J. Math. Phys. 3, 969 (1962).

[18] Cf., M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954), Appendix 8, pp. 406–407.

incoming wave and which, in the infinitely remote future, is augmented by an outgoing scattered wave.[19] Similarly, the outgoing states Φ^- contain an outgoing unperturbed wave and an incoming scattered wave. The symbol $E^\pm = E \pm i\eta$ is understood to be the limit when $\eta \to 0^+$.

The prompt processes give rise to the direct transition amplitude[19] from an initial state i to a final state f,

$$T_{fi}{}^D = \langle \phi_E{}^0 \phi_{0\nu} \mid \mathcal{Q}(\mathcal{H}' - \mathcal{H}_0)\mathcal{Q} \mid \Phi_i{}^+ \rangle, \tag{17}$$

where $\phi_E{}^0$ is a plane wave of energy $E^0 = E - E_{0\nu}$. Since this term produces no measurable effect, it will not be discussed further. The total transition amplitude for the direct and resonant processes is[20]

$$T_{fi} = T_{fi}{}^D + \langle \Phi_f{}^- \mid \mathcal{V}\mathcal{P}'(E - \mathcal{P}\mathcal{H}\mathcal{P})^{-1}\mathcal{P}'\mathcal{V} \mid \mathcal{Q}\Psi_i \rangle, \tag{18}$$

and we will focus attention on the second term. By multiplying Eq. (15) with $\mathcal{P}'\mathcal{V}$, we obtain for the initial state

$$\begin{aligned} \mathcal{P}'\mathcal{V} \mid \mathcal{Q}\Psi_i \rangle &= [1 - \mathcal{P}'\mathcal{V}(E^+ - \mathcal{Q}\mathcal{H}'\mathcal{Q})^{-1}\mathcal{V}\mathcal{P}'(E - \mathcal{P}\mathcal{H}\mathcal{P})^{-1}]^{-1} \\ &\quad \times \mathcal{P}'\mathcal{V} \mid \Phi_i{}^+ \rangle, \end{aligned} \tag{19}$$

which can now be substituted in Eq. (18) to yield an expression for the transition amplitude associated with the resonances,

$$\begin{aligned} T_{fi}{}^{res} = \langle \Phi_f{}^- \mid \mathcal{V}\mathcal{P}'[E - \mathcal{P}\mathcal{H}\mathcal{P} - \mathcal{P}'\mathcal{V}(E^+ - \mathcal{Q}\mathcal{H}'\mathcal{Q})^{-1}\mathcal{V}\mathcal{P}']^{-1} \\ \times \mathcal{P}'\mathcal{V} \mid \Phi_i{}^+ \rangle. \end{aligned} \tag{20}$$

The total width corresponding to the resonances, which is related to the lifetime by the uncertainty principle, is obtained by diagonalizing the operator

$$[\mathcal{P}\mathcal{H}\mathcal{P} + \mathcal{P}'\mathcal{V}(E^+ - \mathcal{Q}\mathcal{H}'\mathcal{Q})^{-1}\mathcal{V}\mathcal{P}']$$

in Eq. (20) and summing over its imaginary parts.[10,11] Since only the operator $\mathcal{P}'\mathcal{V}(E^+ - \mathcal{Q}\mathcal{H}'\mathcal{Q})^{-1}\mathcal{V}\mathcal{P}'$ contributes imaginary components, and the trace remains invariant under the transformation, the total width will be

$$\Gamma = 2 \operatorname{Tr} \operatorname{Im}[\mathcal{P}'\mathcal{V}(E^+ - \mathcal{Q}\mathcal{H}'\mathcal{Q})^{-1}\mathcal{V}\mathcal{P}']. \tag{21}$$

By virtue of the well-known relationship

$$\lim_{\eta \to 0+} (E^+ - F)^{-1} = \text{P.V.}(E - F)^{-1} - i\pi\delta(E - F), \tag{22}$$

for an arbitrary operator F, we find

$$\Gamma = 2\pi \operatorname{Tr}[\langle \mathbf{\Phi} \mid \mathcal{P}'\mathcal{V}\delta(E - \mathcal{Q}\mathcal{H}'\mathcal{Q})\mathcal{V}\mathcal{P}' \mid \mathbf{\Phi} \rangle]. \tag{23}$$

The incoming state function Φ^+ may be expanded in the ϕ basis as

$$\Phi^+ = \sum_\nu \psi_\nu{}^+ \phi_{0\nu}, \tag{24}$$

so that the partial width with respect to a particular resonance t and open (exit) channel ν may be defined as

$$\begin{aligned} \Gamma_t{}^\nu = 2\pi \langle \Phi_t \mid \mathcal{P}'\mathcal{V} \mid \psi_\nu{}^+ \phi_{0\nu} \rangle \langle \phi_{0\nu} \psi_\nu{}^+ \mid \mathcal{V}\mathcal{P}' \mid \Phi_t \rangle \\ \times \delta(E - E_f), \end{aligned} \tag{25}$$

where E_f is the final energy. The singularity introduced by the δ function arises from our assumption of a strictly *iso*-energetic process. Actually we are interested in the transition into a group of close-lying states of density $\rho(E)$ centered at $E = E_f$, i.e.,

$$\begin{aligned} \Gamma_t{}^\nu &= 2\pi \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} |\langle \Phi_t \mid \mathcal{P}'\mathcal{V} \mid \psi_\nu{}^+ \phi_{0\nu} \rangle|^2 \, \delta(E - E_f) \rho(E) \, dE \\ &\simeq 2\pi\rho \, |\langle \Phi_t \mid \mathcal{P}'\mathcal{V} \mid \psi_\nu{}^+ \phi_{0\nu} \rangle|^2, \end{aligned} \tag{26}$$

where we have assumed (*vide infra*) that both $\rho(E)$ and the matrix element vary only very slowly with the energy.

For a single resonance t, the total width is clearly the sum of the partial widths, and we see that this sum consists of two parts:

$$2\pi\rho_0 \, |\langle \Phi_t \mid \mathcal{V} \mid \psi_0{}^+ \phi_{00} \rangle|^2,$$

which describes the zero-photon channel and corresponds to the nonradiative process, and

$$2\pi\bar{\rho} \sum_{\nu \neq 0} |\langle \Phi_t \mid \mathcal{V} \mid \psi_\nu{}^+ \phi_{0\nu} \rangle|^2,$$

where $\bar{\rho}$ is an average density of states, which refers to the one-photon channels and corresponds to the radiative processes. We now recall that $\mathcal{V} = \mathcal{J}_N + \mathcal{V}_{fm}$, and note that $\mathcal{V} = \mathcal{J}_N$ for the zero-photon channel and $\mathcal{V} = \mathcal{V}_{fm}$ for the one-photon channels. With rigorous partitioning into final states reached with and without the emission of photons, the coupling terms

$$\langle \Phi_t \mid \mathcal{V}_{fm} \mid \Psi_0{}^+ \phi_{00} \rangle \quad \text{and} \quad \langle \Phi_t \mid \mathcal{J}_N \mid \psi_\nu{}^+ \phi_{0\nu} \rangle$$

are zero. At worst, they are extremely small. We therefore write

$$\Gamma_t{}^{nr} = 2\pi\rho_0 \, |\langle \Phi_t \mid \mathcal{J}_N \mid \psi_0{}^+ \phi_{00} \rangle|^2 \tag{27}$$

for the nonradiative width, and

$$\Gamma_t{}^R = 2\pi\bar{\rho} \sum_{\nu \neq 0} |\langle \Phi_t \mid \mathcal{V}_{fm} \mid \psi_\nu{}^+ \phi_{0\nu} \rangle|^2 \tag{28}$$

for the radiative width. The latter coincides with the expression obtained by perturbation theory.[15]

It is important to recognize that the assumption that $\Gamma_t{}^\nu$ is independent of energy [Eq. (26)], which is essentially equivalent to the high-density coupling case discussed by Rhodes,[8] limits the validity of the separation of the radiative and nonradiative decay modes [Eqs. (27) and (28)] to large molecules. For small molecules these processes are inseparable as determined by the energy dependence of $\Gamma_t{}^\nu$.

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[19] Cf., P. Roman, *Advanced Quantum Theory* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1965), Chap. 4.

[20] M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1958).

As a first approximation we may take Φ_t to be an excited Born–Oppenheimer state, and $|\psi_\nu^+\phi_{0\nu}\rangle$, which represents a particular final state, as $|\phi_{0\nu}\chi_{0\nu}\rangle$. As pointed out earlier, this is a good approximation in view of the Franck–Condon principle. We wish to emphasize, however, that the approximation is introduced in our treatment *after* the development of expressions for the linewidths, and then primarily to indicate a means of evaluating the matrix elements of Eq. (28) and to connect with the results of other studies.[3–7] For several resonances, corresponding to several excited states, we then find

$$\tau_{nr}=\hbar/\left(2\pi\bar{\rho}_0\sum_t|\langle\phi_t\chi_t\,|\,\mathfrak{J}_n\,|\,\phi_{00}\chi_{00}\rangle|^2\right), \tag{29}$$

which has the same general form as Eq. (1).

DISCUSSION

The model we have described provides a simple picture of the decay of excited states and leads to expressions for the lifetimes similar to those found by others. The lifetime is linked to resonances, which might be viewed as the propagation of excitation energy within the molecule by the resolvent $(E-\mathcal{P}\mathcal{H}\mathcal{P})^{-1}$. The development is based on exact relationships, and thus affords a clear view of the interactions leading to decay. Previous treatments of the problem have invariably employed linear expansions at an early stage, and have consequently obscured the physical origin of the lifetimes.

Jortner and co-workers[5,6] have reached the conclusion that, for molecules possessing high densities of molecular eigenstates, radiative and nonradiative decay modes affect each other. Their analysis is based on a specific configuration interaction model involving zero-order states which are formulated as superpositions of Born–Oppenheimer states, and the assumption thst each molecular eigenstates is associated with an independent lifetime. The nonradiative transitions are considered to arise from the interference between coherently excited states within the line broadened by intramolecular effects. We believe these conclusions to be intimately linked with the model employed. To illustrate this, we suppose like Jortner *et al.*[5,6] that Φ_t is more adequately represented by a superposition of Born–Oppenheimer states than by the single term $\phi_t\chi_t$ as we have assumed above. Thus,

$$\Phi_t=a_{\alpha t}\phi_\alpha\chi_\alpha+\sum_{\beta\neq\alpha}a_{\beta t}\phi_\beta\chi_\beta, \tag{30}$$

where the major contribution comes from $\phi_\alpha\chi_\alpha(a_{\alpha t}\gg a_{\beta t})$. The radiative width [Eq. (28)] then becomes

$$\begin{aligned}\Gamma_t^R=2\pi\bar{\rho}\sum_{\nu=0}\Big\{&a_{\alpha t}^2|\langle\phi_\alpha\chi_\alpha\,|\,\mathcal{V}_{fm}\,|\,\psi_\nu^+\phi_{0\nu}\rangle|^2\\&+\sum_{\beta\neq\alpha}a_{\alpha t}^2|\langle\phi_\alpha\chi_\beta\,|\,\mathcal{V}_{fm}\,|\,\psi_\nu^+\phi_{0\nu}\rangle|^2\\&+2\sum_{\beta<\gamma}a_{\beta t}a_{\gamma t}\langle\phi_\beta\chi_\beta\,|\,\mathcal{V}_{fm}\,|\,\psi_\nu^+\phi_{0\nu}\rangle\\&\times\langle\phi_{0\nu}\psi_\nu^+\,|\,\mathcal{V}_{fm}\,|\,\phi_\gamma\chi_\gamma\rangle\Big\}.\end{aligned} \tag{31}$$

The third sum in Eq. (31) represents interference terms similar to those described by Jortner *et al.*[5,6]

Finally, we might ask what our model tells us about transitions between excited states. The answer is, unfortunately, very little without some rather basic modifications. Thus, the off-diagonal elements of the matrix $\mathbf{\Gamma}^\nu$ in the Φ representation are not defined. Cases where more than one excited state is involved correspond to overlapping resonances, and the model implies that these are essentially generated simultaneously. Since for a particular final state (exit channel) $\Gamma^\nu=\sum_t\Gamma_t^\nu$, we see that degeneracy in the excited-state manifold leads to further line broadening and decrease of the lifetime.

After submission of this manuscript for publication, Freed and Jortner[21] have described the application of the Green function formalism to the problem of the radiative decay of polyatomic molecules. Utilizing the techniques developed by Mower[12] and Goldberger and Watson,[22] these authors also conclude that intramolecular interactions and coupling with the radiation field must be treated simultaneously, and that decaying excited states are best described in terms of resonant states in the sense implied by Eq. (9). Further, the conditions under which the radiative and nonradiative decay processes make independent contributions to the experimental lifetime, and the implications of a nondiagonal damping matrix have been examined by Bixon and Jortner.[23]

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