

# Theory of inverse electronic relaxation

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In this paper we advance a theory of inverse electronic relaxation (IER) induced by high-order multiphoton excitation of collision-free molecules. The IER process involves spontaneous one-photon radiative decay of molecular eigenstates. These states originate from intramolecular scrambling of vibronic levels corresponding to the ground state electronic manifold with a discrete vibronic level (or a set of such levels) which belong to a low-lying excited electronic state. For a diatomic molecule and for a small polyatomic the molecular eigenstates are excited by a coherent multiphoton excitation process, while for larger polyatomic molecules where the low electronically excited state corresponds to an intermediate level structure or to the statistical limit, incoherent multiphoton excitation of the molecular eigenstates of an "isolated" molecule prevails. Explicit expressions for the rate of IER are derived and the conditions for the observation of this novel phenomenon are established.

## I. INTRODUCTORY REMARKS

There is currently intensive experimental and theoretical effort aimed towards the elucidation of the photo-physical and chemical processes in high-energy vibrational states of polyatomic molecules which are reached by collisionless multiphoton excitation<sup>1</sup> (CME). While statistical models<sup>2-5</sup> have been successful in understanding the kinetics of photofragmentation above the dissociation threshold, little is known concerning the mechanism of the CME of a congested bound molecular level structure below the threshold. Unimolecular models<sup>2-5</sup> predict that in most cases multiphoton photofragmentation results in the production of ground-state fragments, as is the case for thermal reaction, although the CME of tetramethyl dioxetane<sup>6</sup> provides a notable exception to this rule. Some (though by no means conclusive) experimental evidence for the production of electronically excited radicals by CME was reported<sup>7</sup> and it was noted<sup>8</sup> that a random radiative coupling model<sup>8-10</sup> for the excitation of the intramolecular quasicontinuum can account for the accessibility of electronically excited configuration via CME.

Very recently, Karny *et al.*<sup>11</sup> have reported the observation of fluorescence from the first electronically excited state of chromyl chloride resulting from CME. Karny *et al.*<sup>11</sup> interpreted their observations in terms of infrared transitions between high vibrational levels of the ground state and the low vibrational levels of an electronically excited configuration. The effects of interstate radiative coupling, considered by Karny *et al.*,<sup>11</sup> as well as the consequences of intrastate radiative coupling within the high vibration levels of the ground state should be considered for a complete description of fluorescence of the parent molecule resulting from CME. The consequences of intrastate radiative coupling bear a close analogy to the intramolecular  $V-E$  process. In this paper, we advance a theory of excitation of an electronically excited molecular state by CME, considering both intrastate ( $V-E$ ) and interstate (radiative) coupling. We shall refer to the phenomenon of CME of an electronic state of the parent molecule as inverse electronic relaxation (IER). We address ourselves to the following questions:

(1) To what extent is the notion of IER compatible with the idea of practical irreversibility inherent in the conventional theory of electronic relaxation?<sup>12</sup>

(2) How do the characteristics of the IER depend on the intramolecular coupling and intramolecular level structure in the statistical limit, in the intermediate level structure, and for the small molecule case?

(3) How do the features of the IER depend on the nature of the CME process? When the molecular level structure is sparse, multiphoton excitation preserves phase coherence,<sup>13</sup> while multiphoton excitation of a congested, dense, level structure of an "isolated" molecule results in intramolecular erosion of phase coherence effects due to random radiative coupling.<sup>8-10</sup>

A preliminary version of the theory of IER, demonstrating that the notion of IER is consistent with the conceptual framework of the theory of intramolecular radiationless transitions, was reported by us.<sup>14</sup> The present theory of IER in "isolated" small molecules and for molecules whose level structure corresponds to the intermediate case considers the coupling between a (zero-order) molecular quasicontinuum of the ground electronic state with a single (zero-order) discrete level, which corresponds to an electronically excited configuration, and which in turn is coupled to a radiative continuum originating from spontaneous one-photon decay to the ground electronic-vibrational state [Fig. 1(a)]. This physical picture bears a close analogy to inverse predissociation.<sup>15,16</sup> In the statistical limit,<sup>12</sup> we consider [Fig. 1(b)] coupling between the ground-state molecular quasicontinuum excited by CME and another intramolecular quasicontinuum of vibronic levels corresponding to an electronically excited configuration, which in turn is coupled to a final radiative one-photon continuum. This physical picture bears a close analogy to the features of delayed fluorescence of a guest molecule in a medium,<sup>17</sup> except that, in the latter case, incoherent thermal excitation prevails. From the point of view of general methodology, it should be emphasized that the presence of the radiative continuum on the final decay channel insures the irreversibility of the IER process.

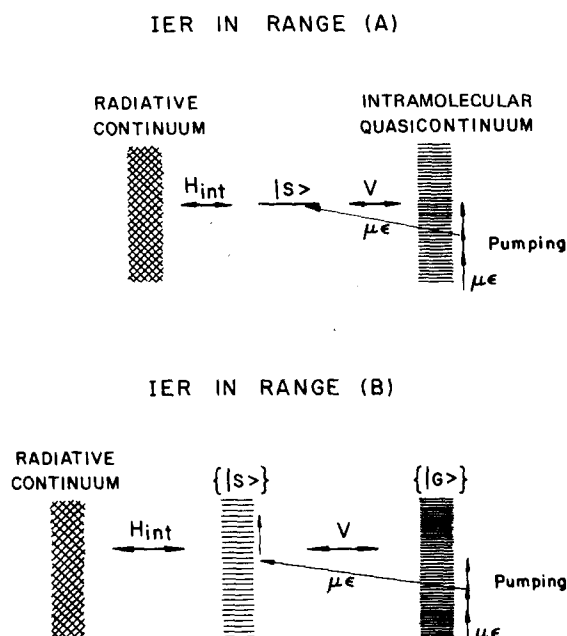


FIG. 1. Schematic representation of inverse diatomic relaxation. (a) IER in range *A* is characterized by IR radiative coupling in the ground state manifold to levels which are coupled to a level  $|S\rangle$ , as well as by direct IR radiative coupling between high lying  $|G\alpha\rangle$  levels and  $|S\rangle$ , where  $|S\rangle$  belongs to an excited electronic state. Radiative emission from  $|S\rangle$  then follows. (b) IER in range *B*. Here, the level  $|S\rangle$  is replaced by a statistical manifold of such levels.

## II. MODEL SYSTEM

We consider a two electronic level system described by the molecular Hamiltonian  $H_M = H_{BO} + V$ . The eigenstates of the Born–Oppenheimer Hamiltonian  $H_{BO}$  are  $\{|G\alpha\rangle$  and  $\{|S\beta\rangle\}$ , where  $|G\rangle$  and  $|S\rangle$  denote the ground electronic state and the electronically excited state, respectively, while  $|\alpha\rangle$  and  $|\beta\rangle$  label the vibronic levels in the two electronic configurations, respectively. The vibronic states  $\{|G\alpha\rangle$  and  $\{|S\beta\rangle\}$  constitute proper nuclear eigenstates within each electronic manifold. The

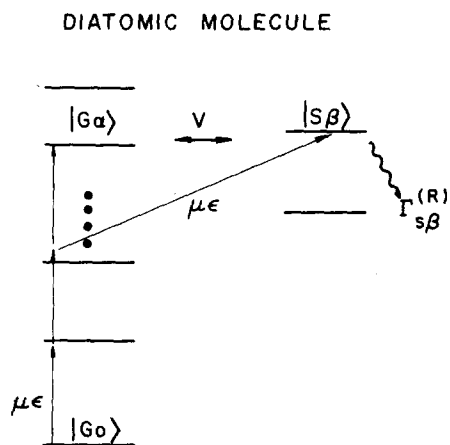


FIG. 2. IER in a diatomic molecule. In the isolated molecule case, a close encounter between two vibrational levels ( $|G\alpha\rangle$ ,  $|S\beta\rangle$ ) belonging to the two electronic manifolds is necessary.

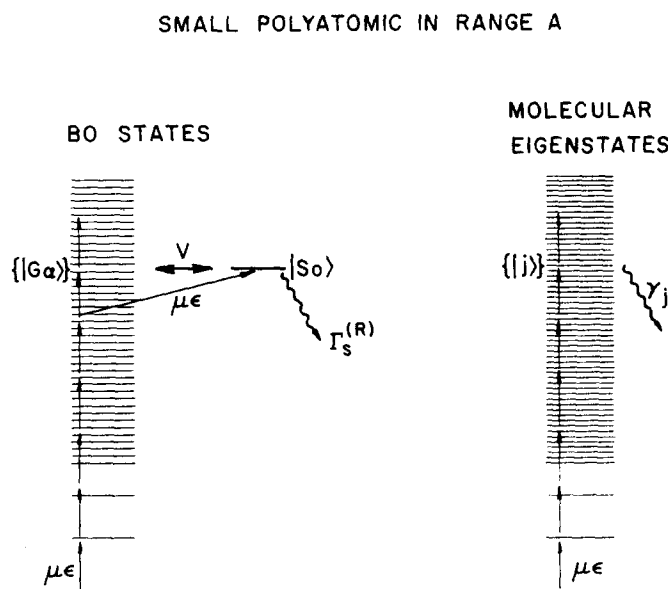


FIG. 3. IER in a small polyatomic molecule. The ground state manifold is dense but not necessarily statistical. The excited state manifold is discrete in the interesting energy region. Alternatively, the molecular eigenstates basis may be utilized. The same picture applies for range *A* of large molecules.

only nonvanishing off-diagonal intramolecular coupling terms are  $V_{G\alpha,S\beta} = \langle G\alpha | V | S\beta \rangle$ , which combine different electronic configurations. Next, we consider radiative damping of the zero-order states. Each  $|S\beta\rangle$  state decays via spontaneous one-photon emission to low-lying vibronic levels of the ground electronic state in the vicinity of  $|G0\rangle$  (Figs. 2 and 3). This radiative decay can be adequately described by assigning radiative widths  $\Gamma_{S\beta}^{(R)}$  to each of the states in the  $\{|S\beta\rangle\}$  manifold. Each  $|S\beta\rangle$  state can be considered to decay into its own set of ground state vibronic levels, so that interference effects in the radiative decay can be disregarded. For a symmetry-allowed one-photon transition, we can safely assume that the radiative decay widths are independent of the initial state, setting  $\Gamma_{S\beta}^{(R)} = \Gamma_S^{(R)}$  for all  $\beta$ .

Finally, we have to consider some of the details of the multiphoton excitation process. The molecule is driven by an intense infrared (IR) radiation field which is characterized by an amplitude  $\epsilon$  of the electric field, by a frequency  $\omega$  and by a pulse duration  $\tau_p$ . Three simplifying assumptions will be subsequently involved: Firstly, we assume that IR radiative coupling prevails only between states or groups of states which are separated by energy  $\sim \hbar\omega$ . Each group of molecular states may be denoted by  $\{|G\alpha, n\rangle\}$ , which corresponds to the molecular levels  $\{|G\alpha\rangle$  excited by the absorption of  $n$  infrared (IR) photons, and located at  $E \approx n\hbar\omega$  above the ground  $|G0\rangle$  level. The only appreciable radiative coupling combines sequential manifolds and is denoted by  $\mu_{G\alpha, G\alpha'}^{n, n+1} \epsilon$ , where  $\mu$  is the dipole moment operator. To describe the radiative coupling at energies  $E$  in the vicinity of the electronic origin of the *S* electronic state (corresponding to the  $|S0\rangle$  vibronic level which is located at  $E_{S0}$ ), let us denote by  $\{|g\alpha, k-1\rangle\}$  the state or manifold of states located at  $E \approx E_{S0} - \hbar\omega$  [ $k$  is defined

by  $k \approx (E_{S0} - E_{G0})/\hbar\omega$ . The transition moments for excitation are  $\mu_{G\alpha, G\alpha'}^{k-1, k}$  and  $\mu_{G\alpha, S0}^{k-1, k}$ , denoting intrastate and interstate IR excitation, respectively. We are not aware of numerical calculations of these transition moments, so that for the time being both types of coupling terms will be retained in our theoretical scheme. Secondly, we assert that the IRCME process can be handled within the framework of the rotating wave approximation (RWA), disregarding high frequency contribution to the equations of motion. Third, spontaneous IR decay process will be disregarded.

The first assumption of sequential radiative coupling is reasonable; to relax this assumption will require to go beyond the RWA. The applicability of the RWA inherent in the first and second assumptions is justified as long as the characteristic Rabi frequencies are considerably smaller than the incident frequency. The third assumption is justified as the pulse duration  $\tau_p$  is usually considerably shorter than the decay time for spontaneous IR decay.

### III. LEVEL MIXING IN A DIATOMIC MOLECULE

The simplest physical situation, which is of interest to us, involves accidental near degeneracy between two vibronic levels (or rather two rotational-vibrational levels) which correspond to two distinct electronic states of a diatomic molecule. A characteristic example involves spin-orbit coupling between a pair of vibronic levels which correspond to the  $X^2\Sigma$  ground state configuration and the  $A^2\Pi$  first electronically excited state of the CN molecule.<sup>18</sup> Interstate coupling prevails only between a small number of nearly degenerate vibronic states and, for the sake of simplicity, we shall limit ourselves to a single pair  $|G\bar{\alpha}\rangle$  and  $|S\bar{\beta}\rangle$  of close-lying levels; the relevant nonadiabatic coupling will be denoted by  $V_{\bar{\alpha}, \bar{\beta}}$ . Furthermore, as each level of excitation corresponds to a single molecular level of the ground state manifold, we can suppress the index  $n$ , using  $\alpha$  to denote both the molecular level and the number of photons absorbed. Thus,  $\mu_{G\alpha, G\alpha'}$  may be replaced by the simpler notation  $\mu_{G\alpha, G\alpha'}$ .

In this system, the CME process of the  $|G\alpha\rangle$  manifold is coherent. Accordingly, the excitation and the radiative decay of the diatomic molecule can be described in terms of the effective Hamiltonian formalism. The Hamiltonian for the system is

$$\begin{aligned} H &= H_M + H_{\text{rad}} + H_{\text{int}}, \\ H_M &= H_{\text{BO}} + V, \\ H_{\text{int}} &= \mu \epsilon. \end{aligned} \quad (\text{III. 1})$$

The time dependent wave function is

$$\psi(t) = \sum_{\alpha} C_{G\alpha}(t) |G\alpha\rangle + C_{S\bar{\beta}}(t) |S\bar{\beta}\rangle, \quad (\text{III. 2})$$

where for the sake of simplicity we have incorporated only a single vibronic level in the  $|S\bar{\beta}\rangle$  manifold, which is characterized by the radiative decay width  $\Gamma_S^{(R)}$ . The time evolution of the vector of the amplitudes

$$\mathbf{C}(t) = \begin{pmatrix} C_{G0}(t) \\ C_{G1}(t) \\ \vdots \\ C_{G\bar{\alpha}}(t) \\ \vdots \\ C_{S\bar{\beta}}(t) \end{pmatrix} \quad (\text{III. 3})$$

is governed by

$$i \frac{d\mathbf{C}(t)}{dt} = \mathbf{H}^e \mathbf{C}(t), \quad (\text{III. 4})$$

with the initial condition

$$\mathbf{C}(0) = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}.$$

The effective Hamiltonian  $H^e$  is

$$(H^e)_{G\alpha, G\alpha'} = [E_{G\alpha} + (N - \alpha)\hbar\omega] \delta_{\alpha\alpha'} + \mu_{G\alpha, G(\alpha\pm 1)} \epsilon \delta_{\alpha', \alpha\pm 1}, \quad (\text{III. 5a})$$

$$\begin{aligned} (H^e)_{G\alpha, S\bar{\beta}} &= V_{G\bar{\alpha}, S\bar{\beta}} \delta_{\alpha\bar{\alpha}} \delta_{\beta\bar{\beta}} \\ &+ \mu_G (\bar{\alpha}-1) S\bar{\beta} \delta_{\alpha, \bar{\alpha}-1} \delta_{\beta\bar{\beta}} + \mu_G (\bar{\alpha}+1) S\bar{\beta} \delta_{\alpha, \bar{\alpha}+1} \delta_{\beta\bar{\beta}}, \end{aligned} \quad (\text{III. 5b})$$

$$(H^e)_{S\bar{\beta}, S\bar{\beta}'} = [E_{S\bar{\beta}} + (N - \bar{\alpha})\hbar\omega - \frac{i}{2} \Gamma_S^{(R)}] \delta_{\bar{\beta}\bar{\beta}'} \delta_{\beta'\bar{\beta}}. \quad (\text{III. 5c})$$

Here,  $E_0$  is the energy of the molecular zero-order state  $|\phi\rangle$  and  $N$  represents the initial number of photons.

Equation (III. 4) is solved by diagonalization of the effective Hamiltonian. The probability for IER is defined as the probability for emission from the  $|S\bar{\beta}\rangle$  level. Thus, the total probability for IER during the pulse over the time interval  $t=0 \cdots \tau_p$  is

$$P(\tau_p) = \Gamma_S^{(R)} \int_0^{\tau_p} dt |C_{S\bar{\beta}}(t)|^2, \quad (\text{III. 6})$$

while the decay rate (emission intensity)  $R = dP/dt$  is given by

$$R(t) = \Gamma_S^{(R)} |C_{S\bar{\beta}}(t)|^2, \quad (\text{III. 7})$$

which is, in general, time dependent.

This case for the isolated molecules involves a coherent excitation of a sparse molecular level structure which involves a small number of strongly coupled levels. Collisional or medium perturbations are expected to exhibit a profound effect on the IER process. Two basic medium induced effects should be considered. Firstly, medium induced vibrational relaxation between the states in the  $\{|G\alpha\rangle\}$  manifold will tend to stabilize low-lying  $|G\alpha\rangle$  states below  $|G\bar{\alpha}\rangle$ , reducing the total probability for IER. Secondly,  $T_2$  type processes will enhance the efficiency of multiphoton excitation due to

line broadening. Thus, the time effects of medium perturbation tend to provide opposite contributions and a quantitative treatment of the problem is required. This can be readily formulated in terms of Bloch equations for a multilevel system. In the limit of large medium perturbations, a conventional master equation will be adequate.

It may be possible to enhance the efficiency of multi-photon absorption (via  $T_2$  line broadening) in the absence of an appreciable  $T_1$  relaxation by imbedding the diatomic molecule in low temperature matrices or liquids. Vibrational relaxation of diatomics in such media is relatively slow<sup>19</sup> while proper dephasing (e. g., in liquid nitrogen<sup>20</sup>) is fast. IER following IR multiphoton absorption may therefore be quite efficient.

**IV. INTERSTATE COUPLING IN SMALL POLYATOMIC MOLECULES**

We shall now consider strong interstate scrambling, due to nuclear momentum or spin-orbit coupling, between two electronic configurations of a small polyatomic molecule (Fig. 3). Notable well-known examples in this category involve the lowest-lying electronically excited states of the same spin multiplicity as the ground state of the triatomic molecules  $SO_2$ ,  $NO_2$ , and  $CS_2$ , where the excited state is strongly coupled to the ground state manifold.<sup>12</sup> Here each  $|S\beta\rangle$  state is strongly coupled to a large number of levels in the  $|G\alpha\rangle$  manifold. It will be sufficient to consider a single, say  $|S0\rangle$ , zero-order state coupled to a  $\{|G\alpha\rangle\}$  manifold. The radiative width of this  $|S0\rangle$  state is  $\Gamma_S^{(R)}$ . The  $\{|G\alpha\rangle\}$  manifold is sparse from  $\alpha=0$  up to and above the range of effective interstate coupling with  $|S0\rangle$  so that coherent excitation prevails all the way. The time evolution of the system can be described either in terms of the zero-order Born-Oppenheimer states or alternatively in terms of molecular eigenstates.

The Born-Oppenheimer description starts from the basis  $\{|G\alpha\rangle, |S0\rangle$ , the time evolution being given again in terms of Eq. (III. 2) and the effective Hamiltonian equation of motion (III. 4). The effective Hamiltonian is now given by

$$\begin{aligned} (H^e)_{G\alpha, G\alpha'}^{nn'} &= [E_{G\alpha} + (N-n)\hbar\omega] \delta_{\alpha\alpha'} \delta_{nn'} \\ &+ \mu_{G\alpha, G\alpha'}^{n, n\pm 1} \epsilon (1 - \delta_{\alpha\alpha'}) \delta_{n', n\pm 1}, \\ (H^e)_{G\alpha, S\beta}^{nn'} &= V_{G\alpha, S\beta}^{K, K} \delta_{\beta 0} \delta_{nK} \delta_{n', K} \\ &+ \mu_{G\alpha, S\beta}^{K-1, K} \epsilon \delta_{\beta 0} \delta_{n, K-1} \delta_{n', K}, \\ (H^e)_{S\beta, S\beta'}^{nn'} &= [E_{S0} + (N-K)\hbar\omega - \frac{i}{2} \Gamma_S^{(R)}] \\ &\times \delta_{\beta 0} \delta_{\beta' 0} \delta_{nK} \delta_{n', K}. \end{aligned} \tag{IV. 1}$$

The solution proceeds along the same lines as in Sec. (II) resulting in the decay rate for IER:

$$R(t) = \Gamma_S^{(R)} |C_{S0}(t)|^2. \tag{IV. 2}$$

An alternative equivalent description rests on the use of the molecular eigenstates  $\{|j\rangle$  which constitute a diagonal representation of the Hamiltonian  $H^e = H_{BO} + V - \frac{i}{2} \Gamma$ , where  $\Gamma$  is the damping matrix. This amounts to partial diagonalization of the effective Hamiltonian

(IV. 1); the only surviving nondiagonal coupling terms are now the radiative interaction  $\mu\epsilon$  and the diagonal energies still have to be modified by addition of the energies of the zero-order states of the radiation field. Far below the electronic origin,  $E_{S0}$  of the excited electronic configuration the  $|G\alpha\rangle$  states are uncontaminated, while in the vicinity of  $E_{S0}$ , level mixing prevails. Accordingly, we have

$$|j\rangle = \begin{cases} a_j |S0\rangle + \sum_{\alpha} b_j^{\alpha} |G\alpha\rangle, & (E_{S0} - \frac{\Delta}{2}) \leq E_j \leq (E_{S0} + \frac{\Delta}{2}), \\ |G\alpha\rangle, & E_j = E_{G\alpha} \geq (E_{S0} + \frac{\Delta}{2}), \\ & E_j = E_{G\alpha} \leq (E_{S0} - \frac{\Delta}{2}). \end{cases} \tag{IV. 3}$$

Each of these molecular eigenstates is characterized by a total decay width

$$\gamma_j \approx \gamma_{G\alpha} + \frac{\gamma_{S0}}{N_A}, \quad (E_{S0} - \Delta/2) \leq E_j \leq (E_{S0} + \Delta/2), \tag{IV. 4}$$

where  $\Delta = 2\pi |V_{S0, G\alpha}|^2 \rho_G$  is a typical spread of the contaminated states and  $N_A \approx \rho_G \Delta$  is a characteristic dilution factor.<sup>21</sup> The radiative width of the molecular eigenstates can be readily obtained by noting that practically  $\gamma_{G\alpha} = 0$  for all  $\alpha$  and the only decay width of  $|S0\rangle$  is radiative  $\gamma_{S0} = \Gamma_S^{(R)}$ . Thus,

$$\gamma_j = \gamma_j^{(R)} \approx \begin{cases} \Gamma_S^{(R)} / N_A, & (E_{S0} - \frac{\Delta}{2}) \leq E_j \leq (E_{S0} + \frac{\Delta}{2}), \\ 0, & \text{otherwise.} \end{cases} \tag{IV. 5}$$

The radiative coupling terms can be conveniently expressed using the molecular eigenstates [Eq. (IV. 3)], representation

$$\begin{aligned} \mu_{jj'}^{nn'} &= \mu_{G\alpha, G\alpha'}^{nn'}, \\ E_j = E_{G\alpha}, \quad E_{j'} = E_{G\alpha'} &\text{ outside } (E_{S0} - \frac{\Delta}{2}) \cdots (E_{S0} + \frac{\Delta}{2}), \end{aligned} \tag{IV. 6a}$$

$$\mu_{jj'}^{K-1, K} = a_j \mu_{G\alpha, S0}^{K-1, K} + \sum_{\alpha'} b_{j'}^{\alpha'} \mu_{G\alpha, G\alpha'}^{K-1, K}, \quad E_j = E_{G\alpha}$$

and

$$E_{j'} \text{ inside } (E_{S0} - \frac{\Delta}{2}) \cdots (E_{S0} + \frac{\Delta}{2}), \tag{IV. 6b}$$

$$\mu_{jj'}^{K, K+1} = a_j \mu_{S0, G\alpha}^{K, K+1} + \sum_{\alpha} b_j^{\alpha} \mu_{G\alpha, G\alpha'}^{K, K+1}, \quad E_j \text{ inside}$$

and

$$E_{j'} = E_{G\alpha'} \text{ outside } (E_{S0} - \frac{\Delta}{2}) \cdots (E_{S0} + \frac{\Delta}{2}). \tag{IV. 6c}$$

The time evolution of the pumped molecule can now be expressed in the form

$$\psi(t) = \sum_j d_j(t) |j\rangle. \tag{IV. 7}$$

As in the diatomic molecule case, the set  $\{|j\rangle\}$  is sparse so that only a small number of  $j$  levels contribute appreciably to  $\psi(t)$ . Disregarding the other levels and denoting the remaining set by consecutive integers so that  $E_{j+1} - E_j \approx \hbar\omega$ , we may again suppress the index

denoting the number of photons absorbed, and we obtain the equation of motion for the vector of coefficients  $d(t)$  in the form

$$i\dot{d}(t) = \mathbf{H}^e d(t),$$

$$d(0) = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad (\text{IV. 8})$$

where the effective Hamiltonian in the  $\{|j\rangle\}$  representation is

$$(H^e)_{jj'} = \left( E_j - \frac{i}{2} \gamma_j^{(R)} \right) \delta_{jj'} + \epsilon (\mu_{j,j+1} \delta_{j',j+1} + \mu_{j+1,j} \delta_{j',j-1}), \quad (\text{IV. 9})$$

and where the off-diagonal terms are given by Eq. (IV. 6). Proceeding by conventional methods, we can obtain the time-dependent eigenvectors  $\{d_j(t)\}$  which will result in the decay rate for IER:

$$R = \sum_j \gamma_j^{(R)} |d_j(t)|^2. \quad (\text{IV. 10})$$

It should be noted that Eqs. (IV. 2) and (IV. 10) are equivalent, and the use of either form is merely a matter of convenience.

We conclude this treatment with the following remarks:

(1) The IER in small polyatomics is described in terms of coherent multiphoton excitation of a sparse vibronic manifold until a range of contaminated  $\{|j\rangle\}$  molecular eigenstates is reached. These  $\{|j\rangle\}$  states are active in optical emission which marks the IER process.

(2) The radiative decay rate for the IER is characterized by the "diluted" radiative decay times. As apparent for Eqs. (IV. 2) and (IV. 10),  $R \sim \langle \gamma_j^{(R)} \rangle \approx \Gamma_S^{(R)} / N_A$ .

(3) The CME results in excitation of the molecular eigenstates which are well separated in energy. The resulting IER marks the radiative decay of some of these molecular eigenstates which were coherently excited.

## V. LEVEL STRUCTURE AND IER IN LARGE MOLECULES

We shall now explore the consequences of interstate nonadiabatic coupling between the ground electronic state and an electronically excited configuration of a large molecule.<sup>12</sup> The Born-Oppenheimer states are  $\{|G\alpha\rangle\}$  and  $\{|S\beta\rangle\}$ , being characterized by the (energy dependent) densities of states  $\rho_G$  and  $\rho_S$ , respectively. The molecular eigenstates, i. e., the independently decaying levels,  $\{|j\rangle\}$  are obtained from diagonalization of the Hamiltonian  $\mathbf{H}^e = \mathbf{H}_0 - \frac{1}{2}\Gamma$ , being characterized by the complex eigenvalues  $\lambda_j = E_j - \frac{1}{2}i\gamma_j$ , where  $E_j$  is the energy while  $\gamma_j$  is the decay width. The radiationless decay rate (dephasing width) of each  $|S\beta\rangle$  state is

## POLYATOMIC MOLECULE IN RANGE B

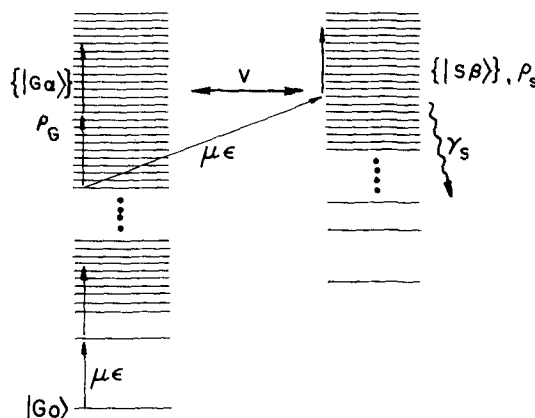


FIG. 4. IER in range B of a polyatomic molecule. Both ground and excited state manifolds are statistical.

$$\Delta_{SB,G} = 2\pi \langle |V_{SB,G\alpha}|^2 \rho_G \rangle,$$

where  $\langle \rangle$  denotes configurational averaging over the  $\{|G\alpha\rangle\}$  manifold. Two energy regions of molecular eigenstates, in the order of increasing energy, can be distinguished:

(A) range A is characterized by a low density of  $|S\beta\rangle$  states, so that

$$\rho_S \Delta_{SB,G} < 1. \quad (\text{V. 1})$$

The level structure in range A consists of a group of  $\{|j\rangle\}$  states, each group having its parentage in a single  $|S\beta\rangle$  level. These groups of contaminated  $\{|j\rangle\}$  states are separated by "black holes" containing pure  $|G\alpha\rangle$  states. The total width of each  $|j\rangle$  state in range A is roughly given by

$$\gamma_j(E_j) \approx \langle \gamma_{G\alpha}(E_j) \rangle + \sum_B \theta(E_j - E_{SB}) \frac{\gamma_S}{N_A(E_{SB})}, \quad (\text{V. 2})$$

$$N_A(E_{SB}) = \rho_G(E_{SB}) \Delta_{SB,G}, \quad (\text{V. 3})$$

where  $\gamma_{G\alpha}$  is the total width of the  $|G\alpha\rangle$  state, which is vanishingly small and can be set equal to zero,  $\gamma_S$  is the total width of each  $|S\alpha\rangle$  state,  $N_A$  is the dilution factor<sup>21</sup> in range A, while  $\theta(X)$  is a step function

$$\theta(X) = \begin{cases} 1, & -\frac{1}{2}\Delta_{SB,G} \leq X \leq \frac{1}{2}\Delta_{SB,G}, \\ 0, & \text{otherwise.} \end{cases} \quad (\text{V. 4})$$

Such intermediate level structure prevails in the small molecule case, discussed in Sec. IV and for large molecules near the electronic origin of the electronically excited state.

(B) range B is characterized by a moderately high density of  $|S\beta\rangle$  states, so that

$$\rho_S \Delta_{SB,G} \geq 1. \quad (\text{V. 5})$$

The black holes disappear and the level structure consists of overlapping  $|j\rangle$  states. The level structure in range B corresponds to two coupled quasicontinua, which are characterized by the densities of states  $\rho_S$  and  $\rho_G$  (Fig. 4). The intramolecular coupling terms

$V_{SB,C\alpha}$  between the quasicontinua are random with respect to magnitude and to sign; consequently, the dilution factor in range  $B$  is given by statistical expression for the ratio of the densities of states

$$N_B(E_j) = \rho_C(E_j) / \rho_S(E_j). \quad (\text{V. 6})$$

We note in passing that when  $\rho_C \Delta_{SB,C} = 1$ , then  $N_A = N_B$ , so there is a smooth transition from the dilution factor in range  $A$  [Eq. (V. 2)] to the dilution factor in range  $B$  [Eq. (V. 6)].

The total widths of each of the molecular eigenstates in range  $B$  are given by

$$\gamma_j(E_j) = \langle \gamma_{C\alpha}(E_j) \rangle + \frac{\gamma_S}{N_B}, \quad (\text{V. 7})$$

where we can again safely get  $\gamma_{C\alpha} = 0$ . For our model system which involves the interstate coupling between the ground state manifold and an electronically excited manifold, the only width is the radiative decay width of the  $\{|S\beta\rangle\}$  states  $\gamma_S = \Gamma_S^{(R)}$ . We can thus identify the total widths of the  $|j\rangle$  states with the corresponding radiative widths

$$\gamma_j^{(R)}(E_j) = \sum_B \theta(E_j - E_{SB}) \Gamma_S^{(R)} / N_A \quad (\text{V. 8a})$$

in range  $A$  and

$$\gamma_j^{(R)}(E_j) = \Gamma_S^{(R)} / N_B \quad (\text{V. 8b})$$

for range  $B$ .

The characteristics of the IER are determined by the features of the CME process of the molecular level structure. The  $\{|G\alpha\rangle\}$  manifold is pumped by multiphoton excitation to the energy range in the vicinity of and above  $E_{S0}$ , which marks the electronic origin of the electronically excited configuration. The total density of  $|G\alpha\rangle$  states (or of  $|j\rangle$  states) in the vicinity of  $S0$  is high for a large molecule. For a typical interesting molecule such as  $\text{CrO}_2\text{Cl}_2$ ,<sup>11</sup>  $\rho_G(E_{S0}) \sim 10^6 - 10^7$  cm for the total density of  $\{|G\alpha\rangle\}$  states.<sup>22</sup> It is now apparent that CME of a congested level structure of the ground electronic configuration of a large molecule cannot be described in terms of a coherent process, such as proposed in Sec. IV for a small polyatomic molecule. It was recently suggested that the irregular radiative coupling between groups of states on the ground potential surface, which are separated by  $\hbar\omega$ , results in intramolecular erosion of coherence effects in the CME of large molecules.<sup>8-10</sup> Consequently, the multiphoton excitation process of the congested level structure in the vicinity of  $E_{S0}$  can be well described in terms of a master equation for the populations. The condition for erosion of coherence effects in the vicinity of  $E_{S0}$  implies strong radiative coupling with the IR field in that energy range

$$\langle (\mu_{jj}^{K-1,K})^2 \rangle \epsilon^2 \rho_j^2 \approx \langle (\mu_{G\alpha,C\alpha}^{K-1,K})^2 \rangle \epsilon^2 \rho_G^2. \quad (\text{V. 9})$$

Condition (V. 9) for incoherent multiphoton excitation of a single molecule implies that the effective average Rabi frequencies exceed the mean level spacing. This condition will be satisfied for CME of medium-sized polyatomics such as  $\text{CrO}_2\text{Cl}_2$  near  $E_{S0}$ .

The incoherent excitation of a single molecule implies that an incoherent superposition of  $|j\rangle$  states will be active in emission. To gain some insight into the nature of the IER, let us consider a hypothetical experiment where  $\tau_p$  is considerably shorter than all the radiative decay times  $(\gamma_j^{(R)})^{-1}$  [Eq. (V. 8)]. We start at  $t=0$  (following the pulse) from an incoherent superposition

$$\psi(t=0) = \sum_j C_j |j\rangle, \quad (\text{V. 10})$$

where the coefficient  $C_j$  are determined by the initial (incoherent) excitation condition and are characterized by random phases. The radiative decay rate in range  $A$  for a group of molecular eigenstates originating from a state  $S0$  is

$$R(t) = \Gamma_S^{(R)} P_S(t), \quad (\text{V. 11})$$

$$P_S(t) = \langle |S0| \psi(t) \rangle^2.$$

It can be readily shown that the occupation probability of the radiative state  $S0$  is

$$P_S(t) = \sum_j \sum_{j'} C_j C_{j'}^* a_j a_{j'} \times \exp[-i(E_j - E_{j'})t] \exp[-\frac{1}{2}(\gamma_j^{(R)} + \gamma_{j'}^{(R)})t], \quad (\text{V. 12})$$

where  $a_j = \langle S0|j\rangle$ . The random character of the  $C_j$  coefficients implies that the cross terms in Eq. (V. 12) are negligible so that we are left with

$$P_S(t) = \sum_j |C_j|^2 |a_j|^2 \exp(-\gamma_j^{(R)} t). \quad (\text{V. 13})$$

Taking  $|a_j|^2 \sim 1/N_A$ , we obtain from Eqs. (V. 11) and (V. 13)

$$R \approx \frac{\Gamma_S^{(R)}}{N_A} \sum_j |C_j|^2 \exp(-\gamma_j^{(R)} t), \quad (\text{V. 14})$$

which, in general, exhibits a nonexponential decay rate. The typical decay rate, which we identify with the IER rate, is essentially determined by the diluted radiative decay time  $\Gamma_S^{(R)}/N_A$ .

Summarizing, the IER process in range  $A$  of a large molecule is characterized by the following features:

(1) The multiphoton excitation in the ground electronic state is determined by random radiative coupling between groups of molecular levels and results in the excitation of an incoherent superposition of  $\{|j\rangle\}$  states whose subsequent radiative decay is amenable to experimental observation. The IER process is nothing but the radiative decay of incoherently excited molecular eigenstates.

(2) The emission rate associated with the IER process is given by

$$\gamma_j^{(R)} \approx \frac{\Gamma_S^{(R)}}{N_A} \approx \rho_G^{-1} \frac{\Gamma_S^{(R)}}{\langle \Delta_{S\alpha,C} \rangle}, \quad (\text{V. 15})$$

which is determined by (a) the inverse level spacing in the background  $\{|G\alpha\rangle\}$  manifold and (b) the ratio  $r$  between the radiative width of a zero-order "doorway state" and the dephasing width of this state. Since usually  $r = (\Gamma_S^{(R)}) / \langle \Delta_{S\alpha,C} \rangle \lesssim 1$ , we expect that the mean level

spacing  $\rho_G^{-1}$  of the background Born–Oppenheimer states constitutes an upper limit for this radiative decay rate.

(3) The IER for the intermediate level structure (or near  $E_{S0}$  for the statistical limit) differs from that in the small molecule case (Sec. IV), as in the latter case coherent multiphoton excitation of  $\{|j\rangle\}$  molecular eigenstates prevails, while in the present case incoherent multiphoton excitation occurs within an isolated molecule.

(4) Only a part of the  $\{|G\alpha\rangle\}$  background levels which are quasidegenerate with the low-lying  $\{|S\beta\rangle\}$  states are effectively coupled to each  $|S\beta\rangle$ . This selective inter-state coupling will increase the effective value of  $\rho_G^{-1}$  and enhance the rate of the IER. For the  $\text{CrO}_2\text{Cl}_2$  molecule, provided that all the  $\{|G\alpha\rangle\}$  states which are quasidegenerate with  $|S0\rangle$  are effectively coupled, then  $\gamma_j^{(R)} \sim (10 \mu\text{sec})^{-1}$ , while if 1% of these background states are effectively coupled to  $|S0\rangle$ , then  $\gamma_j^{(R)} \sim (100 \text{nsec})^{-1}$ .

(5) The IER is amenable to experimental observation in a polyatomic molecule provided  $\gamma_j^{(R)}$  is not too small, so that the multiphoton excited  $\{|j\rangle\}$  states will not be damped by IR emission, wall collisions, and conventional collisions on a time scale shorter than  $\gamma_j^{-1}$ . Typical rates for spontaneous IR decay are  $\delta_{\text{IR}} \sim 10^3 \text{sec}^{-1}$  so we require that

$$\gamma_j^{(R)} > 10^3 \text{sec}^{-1} \sim 10^{-8} \text{cm}^{-1}. \quad (\text{V. 16})$$

Thus, IER will be observed in range A provided that the density of effectively coupled background states is

$$\rho_G < 10^8 \text{cm} \quad (\text{V. 17})$$

and since usually  $(\Gamma_S^{(R)}/\langle\Delta_{S\alpha,G}\rangle) \leq 1$ , a conservative estimate for the observability criterion is

$$\rho_G \leq 10^7 - 10^5 \text{cm}. \quad (\text{V. 17a})$$

From these simple order of magnitude estimates, we assert that IER will be observed in range A of a large molecule characterized by an intermediate level structure in the vicinity of  $|S0\rangle$ , so that the number of vibrational degrees of freedom is not excessively large, whereupon  $\rho_G^{-1}$  is not too small in the vicinity of  $E_{S0}$ , and/or the electronic energy gap  $E_{S0}$  is not too large.

Next, we consider the features of IER in range B of a large molecule. In range B, the rate for IER is determined by the radiative widths of the levels in the  $\{|S\beta\rangle\}$  manifold which are now diluted by the  $N_B$  factor [Eq. (V. 6)]. Thus, the rate for IER is

$$\gamma_j^{(R)} \simeq \Gamma_S^{(R)} / (\rho_G / \rho_S) = \rho_G^{-1} \rho_S \Gamma_S^{(R)}. \quad (\text{V. 18})$$

A rough estimate of the ratio of the densities of states which determines the IER rate in range B is given by

$$\frac{\rho_S}{\rho_G} = \left( \frac{E - E_{S0}}{E} \right)^L, \quad (\text{V. 19})$$

where  $E \geq E_{S0}$  is the energy above the electronic origin of the ground state and  $L$  is the number of vibrational degrees of freedom. For large molecules in range B,

$$\frac{\rho_S}{\rho_G} \simeq \exp\left(-L \frac{E_{S0}}{E}\right), \quad (\text{V. 20})$$

so that

$$\gamma_j^{(R)} \simeq \Gamma_S^{(R)} \exp\left(-L \frac{E_{S0}}{E}\right). \quad (\text{V. 21})$$

The following comments regarding range B are in order:

(1) The dilution factor in range B is appreciable. For a medium-sized molecule with  $L = 12$ , taking  $E_{S0}/E = 0.6$ , we obtain  $\gamma_j^{(R)} \sim 10^{-3} \Gamma_S^{(R)} \sim 10^{-5} \text{cm}^{-1} = 10^8 \text{sec}^{-1}$ , which is just on the verge of experimental detection.

(2) In range B,  $\gamma_j^{(R)}$  increases with increasing the excess vibrational energy. This behavior is qualitatively different from that of range A, where experimental data of Kommandeur and Van der Werf<sup>23</sup> indicate the increase of the dilution factor with increasing energy.

(3) Efficient IER characterized by a radiative decay rate  $\gamma_j^{(R)}$  which satisfies restriction (V. 17) may be observed in range B for medium-sized molecules characterized by low  $E_{S0}$  energy gap. In these molecules, increasing excess vibrational energy after range B is reached will enhance the IER, provided that the molecule is still stable with respect to dissociation.

We thus conclude that IER is amenable to experimental observation for medium-sized isolated molecules characterized by low-lying electronically excited configuration. The  $\text{CrO}_2\text{Cl}_2$  molecule, where IER was experimentally demonstrated,<sup>11</sup> just falls into this category. On the basis of the available experimental data,<sup>11</sup> we cannot yet decide whether IER in  $\text{CrO}_2\text{Cl}_2$  originates from range A or from range B, although the former situation is more plausible for such a medium-sized molecule. Detailed studies of the power dependence of the IER as well as the interrogation of the average molecular vibrational excitation energy will be useful to establish this central question.

## VI. MASTER EQUATIONS FOR MULTIPHOTON EXCITATION OF LARGE MOLECULES

The foregoing discussion was useful for the elucidation of the gross features of IER resulting from incoherent CME of the ground state manifold of a large molecule. The final step in our analysis will involve an outline of a complete treatment of IR CME and subsequent IER. We again consider range A in a molecule where the density of  $\{|G\alpha\rangle\}$  levels in the vicinity of  $E_{S0}$  is sufficiently high and the laser is sufficiently intense so that condition (V. 9) for incoherent excitation is satisfied. The populations  $P_{K-1}^{(J)}$  and  $P_K^{(J)}$  of molecular eigenstates located at  $\sim E_{S0} - \hbar\omega$  (absorption of  $K-1$  photons) and at  $E_{S0}$  (absorption of  $K$  photons), respectively, are governed by the simple kinetic equation

$$\frac{dP_K^{(J)}}{dt} = k_{K-1 \rightarrow K}^{(J)} P_{K-1}^{(J)} - k_{K \rightarrow K-1}^{(J)} P_K^{(J)} - \langle\gamma_j^{(R)}\rangle P_K^{(J)}, \quad (\text{VI. 1})$$

where

$$k_{K-1 \rightarrow K}^{(J)} = 2\pi \langle |\mu_{jj}^{K-1, K}|^2 \rho_j^K \rangle \epsilon^2 \quad (\text{VI. 2})$$

and

$$k_{K \rightarrow K-1}^{(J)} = 2\pi \langle |\mu_{jj}^{K, K-1}|^2 \rho_j^{K-1} \rangle \epsilon^2 \quad (\text{VI. 3})$$

are the rates of (incoherent) absorption and stimulated

emission, respectively, and where  $\rho_j^K$  is the density of molecular eigenstates in the energy range corresponding to the absorption of  $K$  photons. At higher fields sequential excitation,  $K \rightleftharpoons K+1 \dots$  can be easily incorporated into Eq. (IV. 1).

When range B is reached, we can describe the IER also in terms of the Born–Oppenheimer basis. We then encounter a familiar physical situation which involves a  $\{|G\alpha\rangle\}$  quasicontinuum coupled to an  $\{|S\beta\rangle\}$  quasicontinuum, which in turn is coupled to a radiative continuum. In the latter process, each  $|S\beta\rangle$  level is coupled to its own radiative channel. The problem becomes analogous to a random coupling model which can be properly described in terms of the kinetic scheme

$$\begin{aligned} \dots, P_{n-1}^G \frac{k_a}{k-a} P_n^G &= P_{n+1}^G \dots, \\ \dots, P_{n-1}^G \frac{k_b}{k-b} P_n^S, P_n^G &= P_{n+1}^S, \dots; \\ \dots, P_n^G \frac{k_c}{k-c} P_n^S, P_n^G &= P_{n+1}^S, \dots; \\ \dots, P_{n-1}^S \frac{k_d}{k-d} P_n^S &= P_{n+1}^S, \dots; \\ P_n^S &\rightarrow P_R, \end{aligned} \quad (\text{VI. 4})$$

where  $P_n^G$  and  $P_n^S$  are, respectively, populations of G and S manifolds corresponding to the absorption of  $n$  photons, and where  $P_R$  is the population of the final one-photon continuum. The incoherent excitation rates are

$$\begin{aligned} k_a &= 2\pi \langle |\mu_{G\alpha, G\alpha'}^{n-1, n}|^2 \rho_G^n \rangle, \\ k_b &= 2\pi \langle |\mu_{G\alpha, S\beta}^{n-1, n}|^2 \rho_S^n \rangle, \\ k_c &= 2\pi \langle |V_{G\alpha, S\beta}^{n, n}|^2 \rho_S^n \rangle, \\ k_d &= 2\pi \langle |\mu_{S\beta, S\beta'}^{n-1, n}|^2 \rho_S^n \rangle, \end{aligned} \quad (\text{VI. 5})$$

and the backward rates are given by the ratios

$$\begin{aligned} k_{-a}/k_a &= \rho_G^{n-1}/\rho_G^n, \quad k_{-b}/k_b = \rho_G^{n-1}/\rho_S^n, \\ k_{-c}/k_c &= \rho_G^n/\rho_S^n, \quad k_{-d}/k_d = \rho_S^{n-1}/\rho_S^n. \end{aligned} \quad (\text{VI. 6})$$

Finally,  $k_e$  represents the rate for spontaneous one-photon emission from the  $\{|S\beta\rangle\}$  manifold. Provided that  $k_e \ll k_a, k_{-c}$ , we encounter a quasiequilibrium condition and

$$\frac{P_n^S}{P_n^G} = \frac{\rho_S^n}{\rho_G^n} \simeq \exp \left[ -L \left( \frac{E_{S0}}{E_{G0} + n\hbar\omega} \right) \right] \quad (\text{VI. 7})$$

at each level  $n$  of the excitation. This kinetic argument demonstrates again that one has to go to quite high energies in range B to observe the IER which concurs with the analysis of Sec. V.

## VII. CONCLUDING REMARKS

The IER process involves one-photon spontaneous radiative decay of molecular eigenstates which are reached by multiphoton excitation. For the “isolated” diatomic molecule and small molecule, the CME is coherent while the CME of molecules characterized by high level densities in the ground state electronic manifold corresponds to incoherent excitation of a collision-free molecule. The presence of the final radiative continuum for spontaneous one-photon decay insures the reversibility of the IER for any molecular level structure,

provided that effective interstate nonadiabatic coupling exists. It is thus legitimate to invoke the concept of IER even for an isolated diatomic, in contrast to the conventional theory of electronic relaxation where the practical irreversible intramolecular relaxation process in an isolated molecule is exhibited only in the statistical limit.

In conclusion, two general comments should be made. First, we address ourselves to the relation between IER and the conventional theory of electronic relaxation. The phenomenon of IER is of general interest within the theoretical framework of intramolecular dynamics and provides a nice demonstration for the characteristics of scrambled molecular eigenstates of a single molecule which can be excited by a novel multiphoton process. It should be emphasized that the present theory is conceptually different from a kinetic picture in which a “reversible internal conversion” takes place between the initially excited  $|S\beta\rangle$  state and the background  $\{|G\alpha\rangle\}$  manifold. The latter may be used as a convenient mathematical analog<sup>24</sup> but in it the nature of the irreversibility is obscure. The present concept of IER rests on the presence of the one-photon radiative continuum which provides a legitimate channel for the decay process. Second, we would like to dwell on the relation between the present theoretical description of the IER induced via CME and the general problem of intramolecular nuclear dynamics and its relevance to multiphoton excitation processes. In the present approach, we did not have to consider the dynamics of intramolecular vibrational relaxation (IVR). This was achieved by conceptually using the exact (anharmonic) nuclear eigenstates for each electronic potential surface. It is assumed, however, that radiative and nonradiative coupling elements are constant in average magnitude over energy widths much larger than the corresponding rates [cf. Eq. (VI. 5)]. This in turn implies that harmonic basis functions which are characterized by strict selection rules have anharmonic widths larger than those rates. It should be stressed however that this is not necessarily equivalent to an RRKM type assumption because large anharmonic widths may result from strong coupling between only a subset of the molecular modes.

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