INVERSE ELECTRONIC RELAXATION

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We explore the possibility of detecting fluorescence emission following high-order infrared multiphoton excitation in the ground electronic manifold of polyatomic molecules and formulate the conditions for the experimental observation of such inverse electronic relaxation process.

The theory of intramolecular electronic relaxation in "isolated", collision-free molecules usually considers the decay of a "doorway" state belonging to an excited electronic configuration to a dense manifold of vibronic levels which correspond to a lower electronic configuration [1]. It is now well established that practical inversibility prevails in the statistical limit. Most of the experiments conducted up to date interrogated electronic relaxation by a one-photon excitation of the doorway state. A different optical excitation mode of "isolated" polyatomic molecules involves a high-order multiphoton excitation on the ground potential surface [2]. Such multiphoton excitation can result in population of an intramolecular quasicontinuum of the ground state manifold which is quasi-degenerate with an electronically excited state. Recently Karny et al. [3] have reported the observation of fluorescence from the first electronically excited state of CrO_2Cl_2 excited by high-order ($N \approx 16$) multiphoton excitation. The observation of prompt fluorescence of the parent molecule provides strong evidence for a collisionless process. Karny et al. [3] interpreted their observations in terms of an intramolecular V–E process, i.e., reverse internal conversion. In this note we present a theory of inverse electronic relaxation (IER) in "isolated" polyatomic molecules, addressing ourselves to the following two questions:

(1) Under what condition may IER be observed?

(2) How can the notion of IER be accommodated with the idea of practical irreversibility inherent in the conventional theory of electronic relaxation?

When an isolated polyatomic molecule is pumped up the vibrational manifold of the ground electronic state, IER may occur in principle by one or both of the following two mechanisms:

(a) In the energy range where the excited electronic manifold is sparse (small molecule, or a narrow energy range in the vicinity of the origin of the electronically excited state of a large molecule) the mechanism is schematically represented by

$$\begin{array}{lcl} \text{ground state} & \overset{V}{\longleftrightarrow} & \text{single} \\ \text{molecular} & & \text{electronically} \\ \text{quasicontinuum} & & \text{excited bound} \\ & & \text{state} \end{array} \quad \begin{array}{c} \overset{H_{\text{int}}}{\longleftrightarrow} \\ \\ \\ \\ \end{array} \quad \begin{array}{l} \text{radiative} \\ \text{continuum} \\ \\ \\ \end{array} \qquad (1)$$

which considers intramolecular nonadiabatic coupling (V) between the (zero-order) molecular quasicontinuum of the ground-state electronic configuration $\{|G\alpha\rangle\}$, and between an electronically excited (zero-order) state $|S\beta\rangle$ quasidegenerate with the ground-state manifold. The state $|S\beta\rangle$ is in turn coupled by the radiative interaction (H_{int}) to a radiative continuum originating from spontaneous one-photon decay to low-lying electronic-vibrational levels of the ground state. This physical picture bears a close analogy to inverse predissociation (fig. 1), except that the nature of the initial state is different in the two cases. In the inverse predissociation process the initial state is a coherent superposition (wavepacket) of states of the dissociative continuum while in the IER the molecular eigenstates contribute incoherently to the initial state as discussed below.

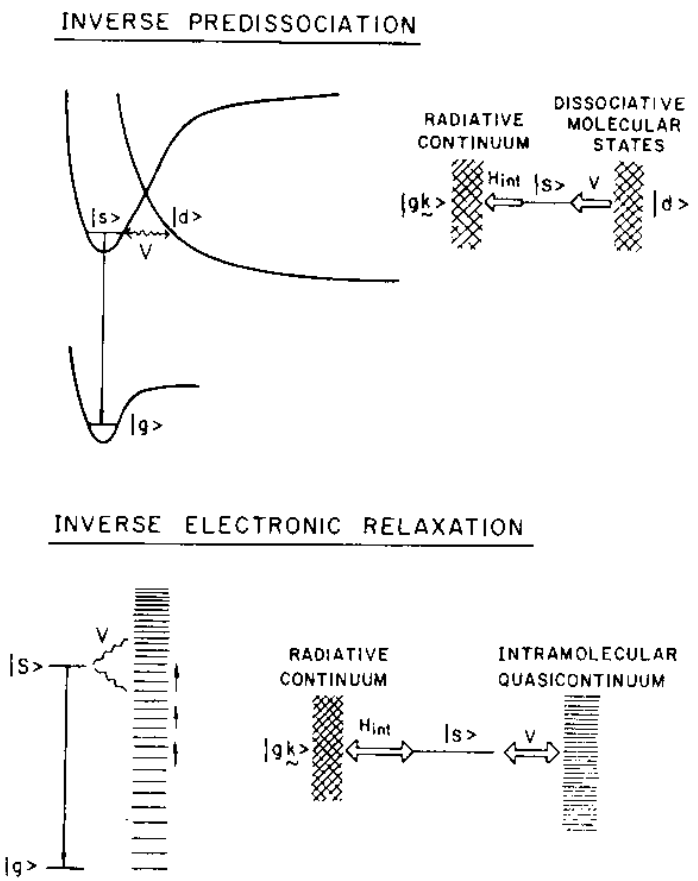

Fig. 1. Schematic representation of molecular inverse predissociation and of inverse electronic relaxation in range (A) of polyatomic molecules.

(b) In a higher energy range where the electronically excited state of the molecule corresponds to the statistical limit we propose the following mechanism for IER

$$\begin{array}{lcll} \text{ground state} & & \text{excited state} & \\ \text{molecular} & \overset{V}{\longleftrightarrow} & \text{molecular} & \overset{H_{\text{int}}}{\longleftrightarrow} \text{radiative} \\ \text{quasicontinuum} & & \text{quasicontinuum} & \text{continuum} \end{array} \qquad (2)$$

which rests on the nonadiabatic coupling between the ground-state quasicontinuum $\{|G\alpha\rangle\}$ and an electronically excited quasicontinuum $\{|S\beta\rangle\}$ which in turn is coupled to a radiative one-photon continuum. The physical picture (2) bears some analogy to the features of delayed fluorescence of a guest molecule in an inert medium [4], except that in the latter case thermal excitation prevails, while we consider multiphoton excitation of the $\{|G\alpha\rangle\}$ manifold.

It should be emphasized that the presence of a radiative continuum as the final decay channel ensures the irreversibility of the IER process. Multiphoton excitation of the ground-state manifold results in the excitation of scrambled ($\{|G\alpha\rangle\} + \{|S\beta\rangle\}$) molecular eigenstates which in principle exhibit radiative decay due to their $\{|S\beta\rangle\}$ character. Thus the IER induced by multiphoton excitation provides a new method for optical excitation of molecular eigenstates so that this novel phenomenon fits within the theoretical framework of the theory of electronic relaxation [1]. We now address ourselves to the question when is the IER process amenable to experimental observation?

In what follows we explore the consequences of interstate nonadiabatic coupling $V_{G\alpha,S\beta} = \langle G\alpha|V|S\beta\rangle$ between the ground electronic manifold $\{|G\alpha\rangle\}$, which is characterized by the density of states ρ_G and the lowest electronically excited manifold $\{|S\beta\rangle\}$, characterized by the density of states ρ_S. Each $|S\beta\rangle$ state decays via spontaneous one-photon emission to low-lying levels of the ground state. This radiative decay can be adequately described by assigning a radiative width $\Gamma_S^{(R)}$ to each of the states in the $|S\beta\rangle$ manifold. Furthermore, interference effects in this radiative decay can be safely disregarded. The $\{|G\alpha\rangle\}$ levels are assumed to be stable with respect to any decay process, which amounts to neglecting collisional deactivation and spontaneous infrared (IR) decay. This assumption is sensible as all time scales involved in the problem, i.e. the duration of the IR laser pulse exciting the $|G\alpha\rangle$ manifold and the optical decay times $\Gamma_S^{(R)}$, are considerably shorter than the IR decay times of the $\{|G\alpha\rangle\}$ manifold.

The molecular eigenstates (ME's) $\{|j\rangle\}$ are obtained from the diagonalization of the hamiltonian $\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{M}} - \frac{1}{2}\,\mathrm{i}\boldsymbol{\Gamma}$ where $\mathbf{H}_{\text{M}}$ corresponds to the molecular hamiltonian and $\boldsymbol{\Gamma}$ is the damping matrix which in our case incorporates only electronic radiative damping. The ME's are characterized by the complex eigenvalues $\lambda_j = E_j - \frac{1}{2}\,\mathrm{i}\gamma_j$ where E_j is the energy and γ_j represents the decay width. The dephasing width of each $|S\beta\rangle$ state is $\Delta_{S\beta,G} = 2\pi\langle|V_{S\beta,G\alpha}|^2\rho_G\rangle$ where $\langle\ \rangle$ denotes configurational averaging over the $\{|G\alpha\rangle\}$ manifold. Two energy regions of ME's in the order of increasing energy are distinguished:

(a) Range (A) of sparse $|S\beta\rangle$ manifold for which

$$\rho_S \Delta_{S\beta,G} \ll 1\,. \qquad (3)$$

The level structure in range (A) consists of isolated groups of $\{|j\rangle\}$ states, each group having its parentage in a single $|S\beta\rangle$ level. These groups are separated by "black holes" containing uncontaminated $|G\alpha\rangle$ states. The total width of the $|j\rangle$ states in a range (A) is ap-

proximately

$$\gamma_j(E_j) \approx \sum_\beta \theta(E_j - E_{S\beta})\, \Gamma_S^{(R)}/N_A(E_{S\beta}), \quad (4)$$

$$N_A(E_{S\beta}) = \rho_G(E_{S\beta})\, \Delta_{S\beta,G}, \quad (5)$$

where $\theta(x)$ is the double step function

$$\theta(x) = 1, \quad -\tfrac{1}{2}\Delta_{S\beta,G} \leqslant x \leqslant \tfrac{1}{2}\Delta_{S\beta,G};$$

$$= 0, \quad \text{otherwise}, \quad (6)$$

while N_A is the dilution factor [5] in range (A).

(b) Range (B) is characterized by appreciable density of $|S\beta\rangle$ states

$$\rho_S \Delta_{S\beta,G} \geqslant 1. \quad (7)$$

The level structure consists of overlapping $\{|j\rangle\}$ states, each of which correspond to several $|S\beta\rangle$ levels. The interstate coupling of the $\{|G\alpha\rangle\}$ and $\{|S\beta\rangle\}$ quasicontinua in range (B) is essentially characterized by random $V_{S\alpha,G\beta}$ coupling terms [6–8]. Consequently, the dilution factor in range (B) is given by a statistical expression

$$N_B(E) = \rho_G(E)/\rho_S(E). \quad (8)$$

The total width of each of the ME's in range (B) is

$$\gamma_j(E_j) = \Gamma_S^{(R)}/N_B(E_j). \quad (9)$$

Obviously, IER taking place within range (A) must be described by scheme (1), while in range B scheme (2) provides a better description.

To gain some insight into the nature of the IER process consider a hypothetical experiment where during the duration τ of the IR pulse the molecule is excited within the $\{|G\alpha\rangle\}$ manifold to the energy range in the vicinity of and above the origin E_{S0} of the electronically excited configuration. τ is assumed to be shorter than the radiative decay time γ_j^{-1} of the ME's. For a polyatomic molecule containing more than three atoms $\rho_G(E_{S0})$ is high, for example, for the CrO_2Cl_2 molecule $\rho_G(E_{S0}) \approx 10^6 - 10^7$ cm. It was recently suggested [7,8] that the IR radiative coupling terms between groups of molecular states separated by the energy of the IR photon, are practically random with respect to magnitude and sign. Such random coupling results in intramolecular erosion of coherence effects, so that multiphoton excitation to the vincinity of E_{S0} will result in an incoherent superposition of ME's. Even without the random coupling assumption, the timescale orders stated above imply that all initial phase coherence in the $\{|G\alpha\rangle\}$ manifold will be erased before any appreciable radiative damping.

By the end of the IR pulse, at time $t = \tau$ the molecular state may thus be described by

$$\psi(t = \tau) = \sum_j c_j |j\rangle, \quad (10)$$

where c_j are complex amplitudes with random phases. The radiative decay rate is

$$R = \Gamma_S^{(R)} P_{S\beta}(t + \tau), \quad (11a)$$

where

$$P_{S\beta}(t + \tau) = |\langle S\beta|\psi(t + \tau)\rangle|^2. \quad (11b)$$

It can readily be shown that the occupation probability, eq. (11b), of the radiative zero-order state is

$$P_{S\beta}(t + \tau) = \sum_j \sum_{j'} c_j c_{j'}^* a_{j'}^{(S\beta)*} \times \exp[-i(E_j - E_{j'})t] \exp[-\tfrac{1}{2}(\gamma_j + \gamma_{j'})t], \quad (12)$$

where $a_j^{(S\beta)} = \langle S\beta|j\rangle$. The random phases of the coefficients c_j make it possible to neglect cross-terms in eq. (12) and we obtain

$$P_S(t + \tau) = \sum_j |a_j^{(S\beta)}|^2 |c_j|^2 \exp(-\gamma_j t). \quad (13)$$

Taking $|a_j^{(S\beta)}|^2 \approx N_A(E_{S\beta})^{-1}$ in range (A) we finally obtain (using also $\Sigma_j |c_j|^2 = 1$)

$$R = \Gamma_S^{(R)}/N_A(E_{S\beta}). \quad (14)$$

The IER rate is thus essentially determined by the diluted radiative decay time. In range (A) the IER rate is given by [using eq. (5)]

$$\gamma_j \approx \rho_G^{-1}(E_{S\beta})\, \Gamma_S^{(R)}/\Delta_{S\beta,G}, \quad (15)$$

which exhibits the following features:

(1) It is determined by the average inverse level spacing in the background $\{|G\alpha\rangle\}$ manifold and by the ratio, r, of the radiative and dephasing widths of a zero-order doorway state.

(2) As in general $r \leqslant 1$ we expect that the mean level spacing of the effectively coupled $\{|G\alpha\rangle\}$ background levels constitutes a upper limit for the IER rate.

(3) Only a part of $\{|G\alpha\rangle\}$ background levels which are

quasidegenerate with a certain $|S\beta\rangle$ level are effectively coupled to this $|S\beta\rangle$. This selective interstate coupling increases the effective value of ρ_G^{-1} in eq. (15) and enhances the rate of IER.

(4) The IER is amenable to experimental observation in a polyatomic molecule where γ_j is not too small. For exceedingly long lifetimes γ_j^{-1} of the (incoherently) excited ME's these high-lying ME's are damped by IR emission or by collisions. Denoting the combined IR and collisional damping width of the levels $|j\rangle$ by δ_j, the condition for observation of fluorescence in range (A) is

$$\gamma_j > \delta_j . \tag{16}$$

For $\delta_j^{-1} \approx 10^{-3}$ s (IR lifetime) this implies that IER will be amenable to experimental observation in range (A) provided that the density of effectively coupled background states is $\rho_G < 10^8$ cm. As $r < 1$ a conservative realistic estimate of this density of states is $\rho_G < 10^7$ cm. In the more common case where collisional damping takes place with lifetime $\approx 10^{-6}$ s we need $\rho_G < 10^4$ cm.

(5) When IER is observable in range (A), fluorescence on the time scale γ_j^{-1} should also be detectable following conventional one-photon electronic excitation of the "isolated" molecule. The electronic excited state which exhibits a long time tail of fluorescence induced either by the novel process IER or by one-photon electronic excitation corresponds to the case of intermediate level structure [1,5].

Next considering the features of IER in range (B) of a large molecule, where according to eqs. (8) and (9) the rate of the IER is

$$\gamma_j(E) = [\rho_S(E)/\rho_G(E)]\,\Gamma_S^{(R)} . \tag{17}$$

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

$$\rho_S(E)/\rho_G(E) \approx [(E - E_{S0})/E]^K , \tag{18}$$

where E is the energy above the electronic origin of the ground state and K is the number of vibrational degrees of freedom. In range (B) where $E > E_{S0}$ and $K \gg 1$

$$\rho_S(E)/\rho_G(E) \approx \exp(-KE_{S0}/E) , \tag{19}$$

so that

$$\gamma_j \approx \Gamma_S^{(R)} \exp(-KE_{S0}/E) . \tag{20}$$

The following features of the IER in range (B) should be noted:

(1) γ_j increases with increasing excess vibrational energy. This feature of enhancement of the IER rate in range (B) at higher E is qualitatively different than that in range (A) where γ_j decreases with increasing E.

(2) The dilution factor in range (B) is appreciable for a typical medium-sized molecule with $K = 12$ at $E_{S0}/E = 0.6$, $\gamma_j \approx 10^{-3}$, $\Gamma_S^{(R)} \approx 10^6$ s^{-1}. In this case increasing the excess vibrational energy helps, provided the molecule does not decompose in that energy range.

We conclude that the IER process is amenable to experimental observation in medium-sized isolated molecules characterized by a low-lying electronically excited state. The CrO_2Cl_2 molecule where IER was recorded [3] falls in this category. The IER process in medium-sized polyatomic molecules involves one-photon spontaneous radiative decay of molecular eigenstates of ME's reached by incoherent multiphoton excitation. The phenomenon of IER provides a nice demonstration for the wide applicability of the theoretical concept of scrambled ME's of a single polyatomic molecule, which can now be excited by the novel multiphoton process and interrogated by their characteristic radiative decay.

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