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SEQUENCE CONGESTION EFFECTS IN OPTICAL SELECTION STUDIES OF ELECTRONIC RELAXATION

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We present a theoretical study of the non-radiative decay rate of an "isolated" large molecule characterized by displaced potential surfaces, which will exhibit temperature dependence due to sequence congestion effects.

Many theoretical studies of radiationless decay in an isolated large molecule focused attention on the electronic relaxation of the vibrationless level of an excited electronic state [1-3]. The non-radiative decay probability W_{si} of a single vibronic level $|si\rangle$ of a large molecule is of considerable theoretical and experimental interest in providing detailed information concerning intrastate coupling and intramolecular relaxation in the statistical limit [4-10]. We have recently derived general theoretical expressions for W_{si} in a large harmonic molecule characterized by displaced potential surfaces [9], and where the role of frequency changes can be also incorporated [10]. The utilization of the theoretical values of W_{si} to account for the experimental dependence of the non-radiative decay probability on the excess vibrational energy in an excited electronic state of a large molecule rests on two basic physical assumptions:

- (a) a single vibronic level of the upper electronic state can be optically excited by a short (relative to the molecular decay time) light pulse,
- (b) interstate electronic relaxation takes place on a time scale which is shorter than the intrastate energy redistribution due to anharmonic coupling within the excited electronic state.

Recently, Fischer et al. [11] have attempted to treat the problem of intrastate anharmonic vibrational energy redistribution, while an alternative approach to this problem was provided by us [12].

The present note is devoted to the investigation of the effects of sequence broadening* on optical selection studies in large molecules. Ross et al. [13] have conclusively demonstrated the crucial role of (temperature dependent) sequence congestion on "trivial" line broadening in the optical spectra of large molecules. From the experimental point of view, optical selection studies of radiationless decay in the low pressure gas phase are performed at moderately high temperatures (i.e., about room temperature) where the ground molecular state is not characterized by a single pure quantum state but rather involves a Boltzmann distribution of vibronic levels. Thus even when the exciting optical band width is narrow, different molecules will be excited to different electronically excited vibronic states (see fig. 1), the distribution of the electronically excited vibronic levels is determined by the ground state thermal distribution. Consequently, radiationless decay induced by excitation above the electronic origin of an excited electronic state in a large molecule (say, bigger than benzene) cannot be theoretically accounted for by the decay of a single vibronic level. To provide a proper theoretical scheme for optical selection studies under a real life situation we shall first consider the general expressions for the optical line shape, which will result in the excitation probability of a single vibronic level. The latter expression combined with our previ-

* One must distinguish between sequence broadening and hot bands effects. In the former no change in the quantum numbers of the non-totally symmetric modes occurs while the latter is characterized by such a change.

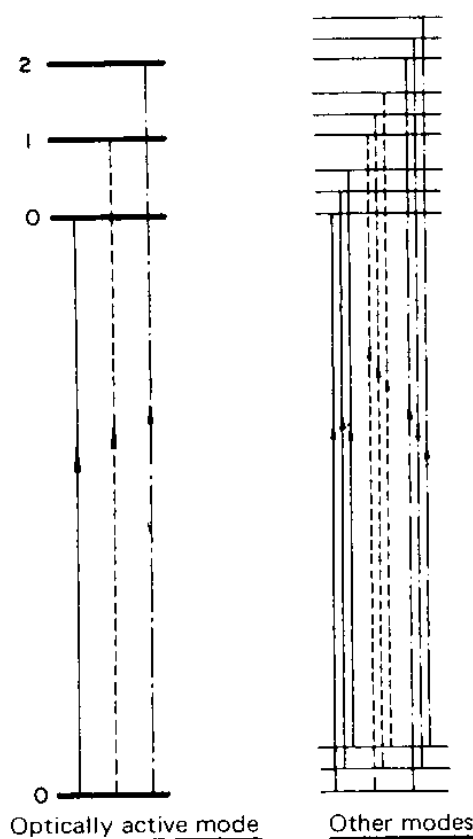


Fig. 1. A schematic representation of sequence congestion. — 0-0 transition; - - - 1-1 transition; 2-2 transition, etc.

ous results [9] will enable us to account for sequence congestion effects on the non-radiative decay probability of an isolated large molecule.

The well known expression for the absorption line shape from an initial state $|gk\rangle$ is

$$L^k(E) = -\pi^{-1} \text{Im} \langle gk | \mu G(E) \mu | gk \rangle, \quad (1)$$

where Im refers to the imaginary part, $\mu = (\boldsymbol{\mu} \cdot \boldsymbol{\epsilon})$ represents the projection of the dipole operator $\boldsymbol{\mu}$ on the polarization vector $\boldsymbol{\epsilon}$ and $G(E)$ is the molecular Green's operator. The experimental line shape function is given by the thermal average

$$\langle L(E) \rangle_T = (1/\pi Z) \sum_k \exp(-\beta E_{gk}) (-\text{Im} \langle gk | \mu G(E) \mu | gk \rangle), \quad (2)$$

where $Z = \sum_k \exp(-\beta E_{gk})$, $\beta = (k_B T)^{-1}$ and $\langle \rangle_T$ denotes a thermal average.

Neglecting interference effects between the optically active states $|si\rangle$, and using the well-known form of the diagonal matrix element of the Green's operator, eq. (2) readily yields

$$\langle L(E) \rangle_T = \frac{1}{2\pi Z} \sum_k \exp(-\beta E_{gk}) \sum_i \frac{\Gamma_{si} |\langle gk | \mu | si \rangle|^2}{(\Delta E_{ki})^2 + (\frac{1}{2}\Gamma_{si})^2}, \quad (3)$$

where Γ_{si} is the total (radiative and radiationless) width of the state $|si\rangle$ and

$$\Delta E_{ki} = E + E_{gk} - E_{si} = E + E_g^0 - E_s^0 + \sum_{\mu} \hbar(\nu_{\mu}^k \omega_{\mu}^g - \nu_{\mu}^i \omega_{\mu}^s), \quad (4)$$

where E_n^0 ($n = g, s$) denotes the vibrationless energy level of the n th electronic manifold, ν_μ^k and ν_μ^i represent the occupation numbers of the μ vibrational mode in the vibrational states $|gk\rangle$ and $|si\rangle$ respectively, while ω_μ^n is the μ mode frequency in the n th electronic state. Eq. (3) may be represented as a Fourier transform of a generating function and evaluated by the formalism of multiphonon processes [1-3]. This result yields the line shape function including sequential broadening effects (but excluding interference between resonances). This line shape function may be recast in terms of a summation over the contributions from different $|si\rangle$ states

$$\langle L(E) \rangle_T = \sum_i A_{si}(E), \quad (5)$$

where

$$A_{si}(E) = \frac{\Gamma_{si}}{2\pi Z} \sum_k \exp(-\beta E_{gk}) \frac{|\langle gk | \mu | si \rangle|^2}{(\Delta E_{ki})^2 + (\frac{1}{2}\Gamma_{si})^2} \quad (6)$$

is the excitation probability of the state $|si\rangle$ by photons of energy E . In a more realistic manner we should take

$$B_{si}(E) = \int_{-\frac{1}{2}\Delta\epsilon}^{\frac{1}{2}\Delta\epsilon} A_{si}(E) dE \quad (7a)$$

for the excitation probability of the state $|si\rangle$ by a radiation source characterized by the energy E and by the band width $\Delta\epsilon$.

Now provided that $\Delta\epsilon$ is much smaller than the spacing between the optically active states (accessible from a single $|gk\rangle$ level) but much larger than Γ_{si} (for any $|si\rangle$) we get

$$B_{si}(E) = \int_{\Delta\epsilon} A_{si}(E) dE = Z^{-1} \sum_k \exp(-\beta E_{gk}) |\langle gk | \mu | si \rangle|^2 D(\Delta E_{ki}, \Gamma_{si}), \quad (7b)$$

where we have defined the function*

$$\begin{aligned} D(a, b) &= 0 \quad \text{for } |a| - |b| > 0, \\ &= 1 \quad \text{for } |a| - |b| < 0. \end{aligned} \quad (8)$$

The definition (8) is a trivial extension of the Kronecker delta function, being valid for $\Delta\epsilon \gg \Gamma_{si}$. Utilizing eq. (4) we have

$$D(\Delta E_{ki}, \Gamma_{si}) = D \left[\hbar \sum_\mu (\nu_\mu^k \omega_\mu^g - \nu_\mu^i \omega_\mu^s) - (E_{sg}^0 - E), \Gamma_{si} \right], \quad (8a)$$

where $E_{sg}^0 = E_s^0 - E_g^0$. Finally the averaged absorption coefficient in the energy region $(E - \frac{1}{2}\Delta\epsilon, E + \frac{1}{2}\Delta\epsilon)$ is given in the form

$$A_t(E) = \sum_i B_{si}(E), \quad (9)$$

so that the normalized excitation probability of $|si\rangle$ is just given by $B_{si}(E)/A_t(E)$.

The non-radiative decay probability, $W_s(E)$, resulting from optical excitation of the s electronic state at the

* The definition (8) amounts to replacing the lorentzian distribution in eq. (6) by a rectangular distribution.

energy E and excitation band width $\Delta\epsilon$ is

$$W_s(E) = A_t^{-1} \sum_i B_{si}(E) W_{si}, \quad (10)$$

where W_{si} represents the non-radiative decay probability of a single vibronic level $|si\rangle$. Eqs. (7)–(10) can be now considerably simplified by utilizing the conventional Condon approximation (in the case of an allowed $g \rightarrow s$ optical transition) so that $|\langle gk|\mu|si\rangle|^2 = |M_{gs}|^2 |\langle \chi_{gk}|\chi_{si}\rangle|^2$, where M_{gs} is the electronic transition moment while $\langle \chi_{gk}|\chi_{si}\rangle$ is the vibrational overlap Franck–Condon integral. Eq. (10) takes the form

$$W_s(E) = (|M_{gs}|^2/A_t) \sum_i W_{si} \sum_k Z^{-1} \exp(-\beta E_{gk}) |\langle \chi_{gk}|\chi_{si}\rangle|^2 D \left[\hbar \sum_\mu (v_\mu^k \omega_\mu^g - v_\mu^i \omega_\mu^s) - (E_{sg}^0 - E), \Gamma_{si} \right]. \quad (11)$$

Eq. (11) provides the general formal answer for the effects of sequence broadening on the non-radiative decay of an isolated molecule. This general formula may be considerably simplified by considering a model system which rests on the following assumption:

- (a) the vibrational frequencies are the same for the s and g electronic states,
- (b) there is only one optically symmetric mode (that will be denoted by α).

We thus replace the absorption spectrum (fig. 2) by a manifold of lorentzians characterized by a width $\langle \Gamma_{si} \rangle$ and spaced by $\hbar\omega_\alpha$. Consequently, we have

$$\sum_\mu (v_\mu^k \omega_\mu^g - v_\mu^i \omega_\mu^s) = \sum_\mu (v_\mu^k - v_\mu^i) \omega_\mu, \quad (12)$$

and also (using the definitions $|\chi_{gk}\rangle = \prod_\mu |\chi_{k\mu}^g\rangle$ and $|\chi_{si}\rangle = \prod_\mu |\chi_{i\mu}^s\rangle$),

$$|\langle \chi_{gk}|\chi_{si}\rangle|^2 = \left(\prod_{\mu \neq \alpha} \delta_{v_\mu^k, v_\mu^i} \right) |\langle \chi_{k\alpha}^g|\chi_{i\alpha}^s\rangle|^2. \quad (13)$$



Fig. 2. Lineshapes of a large molecule with sequence congestion effects at a finite temperature. a) All frequencies equal in ground and excited states, b) a real life situation. Frequencies in excited state are lower than in ground state.

Inserting these relations into eq. (11) we note that the sum over k may be written in the form

$$\begin{aligned} \sum_k Z^{-1} \exp(-\beta E_{gk}) \left(\prod_{\mu \neq \alpha} \delta_{\nu_{\mu}^k, \nu_{\mu}^i} \right) |\langle \chi_{g\alpha} | \chi_{s\alpha} \rangle|^2 D \left(\nu_{\alpha}^k - \nu_{\alpha}^i - \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}}, \frac{\Gamma_{si}}{\hbar \omega_{\alpha}} \right) \\ = \prod_{\mu \neq \alpha} \left(\sum_{\nu_{\mu}^k=0}^{\infty} Z_{\mu}^{-1} \exp(-\beta \hbar \omega_{\mu} \nu_{\mu}^k) \delta_{\nu_{\mu}^k, \nu_{\mu}^i} \right) \sum_{\nu_{\alpha}^k=0}^{\infty} Z_{\alpha}^{-1} \exp(-\beta \hbar \omega_{\alpha} \nu_{\alpha}^k) |\langle \chi_{g\alpha} | \chi_{s\alpha} \rangle|^2 D \left(\nu_{\alpha}^k - \nu_{\alpha}^i - \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}}, \frac{\Gamma_{si}}{\hbar \omega_{\alpha}} \right) \\ = \prod_{\mu \neq \alpha} Z_{\mu}^{-1} \exp(-\beta \hbar \omega_{\mu} \nu_{\mu}^i) \left| \langle \chi_{g\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) | \chi_{s\alpha}(\nu_{\alpha}^i) \rangle \right|^2 Z_{\alpha}^{-1} \exp \left[-\beta \hbar \omega_{\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) \right]. \quad (14) \end{aligned}$$

Utilizing the same procedure we easily obtain for A_t the following expression

$$\begin{aligned} A_t = \sum_i \sum_k Z^{-1} \exp(-\beta E_{gk}) |\langle gk | \mu | si \rangle|^2 D(\Delta E_{ki}, \Gamma_{si}) \\ = |M_{gs}|^2 \sum_i \left\{ \prod_{\mu \neq \alpha} Z_{\mu}^{-1} \exp(-\beta \hbar \omega_{\mu} \nu_{\mu}^i) \left| \langle \chi_{g\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) | \chi_{s\alpha}(\nu_{\alpha}^i) \rangle \right|^2 Z_{\alpha}^{-1} \exp \left[-\beta \hbar \omega_{\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) \right] \right\} \\ = |M_{gs}|^2 \sum_{\nu_{\alpha}^i} \left| \langle \chi_{g\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) | \chi_{s\alpha}(\nu_{\alpha}^i) \rangle \right|^2 Z_{\alpha}^{-1} \exp \left[-\beta \hbar \omega_{\alpha} \left(\nu_{\alpha}^i + \frac{E_{sg}^0 - E}{\hbar \omega_{\alpha}} \right) \right], \quad (15) \end{aligned}$$

where Z_{μ} is the single mode partition function, $Z_{\mu} = \sum_{\nu_{\mu}} \exp(-\hbar \omega_{\mu} \nu_{\mu})$. Thus, A_t depends only on the optically active mode.

To simplify eq. (11) further we utilize the relation [1-3]

$$W_{si} = \sum_{\kappa} |C_{sl}^{\kappa}|^2 \int_{-\infty}^{\infty} \exp(-iE_{sl}^0 t/\hbar) F^{\kappa}(t) dt, \quad (16)$$

where l is the electronic manifold which acts as a quasicontinuum for the radiationless decay of the $|si\rangle$ vibronic levels, $E_{sl}^0 = E_s^0 - E_l^0$ is the $s-l$ electronic energy gap, C_{sl}^{κ} is proportional to the matrix element [2] of the inter-state non-adiabatic coupling between the electronic states s and l induced by the promoting mode κ . $F^{\kappa}(t)$ is the generating function [1-3] for non-radiative decay due to the promoting mode. It is well established [1-3] that $F^{\kappa}(t)$ may be written as a product over contributions from all the vibrational modes.

$$F^{\kappa}(t) = \prod_{\mu} f_{\mu}(t). \quad (17)$$

Taking for simplicity the contributions of a single promoting mode and inserting eqs. (14)–(17) into eq. (11) we obtain

$$W_s(E) = |C_{sl}|^2 \int_{-\infty}^{\infty} \exp(-iE_{sl}^0 t/\hbar) \prod_{\mu \neq \alpha} \langle f_{\mu}(t) \rangle_T g_{\alpha}^T(t), \quad (18)$$

where

$$g_{\alpha}^T(t) = \left(\sum_{\nu_{\alpha}^i} \zeta^T(\nu_{\alpha}^i) \right)^{-1} \sum_{\nu_{\alpha}^i} f_{\alpha}(t) \zeta^T(\nu_{\alpha}^i), \quad (19)$$

with

$$\zeta^T(\nu_\alpha^i) = \left| \langle \chi_{g\alpha} \left(\nu_\alpha^i + \frac{E_{sg}^0 - E}{\hbar\omega_\alpha} \right) | \chi_{s\alpha}(\nu_\alpha^i) \rangle \right|^2 Z_\alpha^{-1} \exp \left[-\beta \hbar \omega_\alpha \left(\nu_\alpha^i + \frac{E_{sg}^0 - E}{\hbar\omega_\alpha} \right) \right]. \quad (20)$$

Eq. (18) bears a close analogy to the well-known form of the thermally averaged non-radiative transition probability

$$\langle W_s \rangle_T = |C_{sl}|^2 \int_{-\infty}^{\infty} \exp(-iE_{sl}^0 t/\hbar) \prod_{\mu} \langle f_{\mu}(t) \rangle_T.$$

The major difference between $W_s(E)$ and $\langle W \rangle_T$ involves the contribution of the optically active mode. As in general the promoting mode κ for radiationless $s \rightsquigarrow l$ non-radiative decay differs from the optically active mode α for $g \rightarrow s$ excitation; we may assume that the promoting mode and its equilibrium configuration are unmodified for both the $g \rightarrow s$ and for the $s \rightsquigarrow l$ transitions. Thus we take the thermal average for the contribution of the promoting mode to the generating function (17) [1-3]

$$\langle f_{\kappa}(t) \rangle_T = (\langle \nu_{\kappa} \rangle_T + 1) \exp(i\omega_{\kappa} t) + \langle \nu_{\kappa} \rangle_T \exp(-i\omega_{\kappa} t). \quad (21)$$

Utilizing the well-known form [1-3] for $\langle f_{\mu}(t) \rangle_T$ ($\mu \neq \alpha, \kappa$), then for the simple case of displaced identical potential surfaces we get

$$W_s(E) = |C_{sl}|^2 \int_{-\infty}^{\infty} \exp(-iE_{sl}^0 t/\hbar) [(\langle \nu_{\kappa} \rangle_T + 1) \exp(i\omega_{\kappa} t) + \langle \nu_{\kappa} \rangle_T \exp(-i\omega_{\kappa} t)] \\ \times \exp \left\{ \frac{1}{2} \sum_{\mu \neq \alpha} (\langle \nu_{\mu} \rangle_T + 1) \Delta_{\mu}^2 [\exp(i\omega_{\mu} t) - 1] + \frac{1}{2} \sum_{\mu \neq \alpha} \langle \nu_{\mu} \rangle_T \Delta_{\mu}^2 [\exp(-i\omega_{\mu} t) - 1] \right\} g_{\alpha}^T(t) \quad (22)$$

(where Δ_{μ} is the normalized displacement of the mode μ in the $s-l$ transition).

Consider now the factor $g_{\alpha}^T(t)$ which depends on the initial excess vibrational energy. Assuming that the frequency of the optically active mode is high so that at relevant temperatures ($\hbar\omega_{\alpha} \gg k_B T$) the only contribution to the sum in eq. (18) originates from the first term in the expansion (19) where ν_{α}^i satisfies the condition:

$$\nu_{\alpha}^k = \nu_{\alpha}^i + (E_{sg}^0 - E)/\hbar\omega_{\alpha} = 0, \quad (23)$$

so that

$$g_{\alpha}^T(t) = f_{\alpha}(t) \Big|_{\nu_{\alpha}^i = (E - E_{sg}^0)/\hbar\omega_{\alpha}}. \quad (24)$$

Utilizing the results of our previous work [9] for the generating function we get

$$g_{\alpha}^T(t) = \exp \left[\frac{1}{2} \Delta_{\alpha}^2 \exp(i\omega_{\alpha} t) - 1 \right] (\nu_{\alpha}^i)! \sum_{\nu=0}^{\nu_{\alpha}^i} (-\Delta_{\alpha}^2)^{\nu} \frac{[1 - \cos(\omega_{\alpha} t)]^{\nu}}{(\nu_{\alpha}^i - \nu)! (\nu!)^2}. \quad (25)$$

The non-radiative decay probability for an isolated "harmonic" molecule characterized by displaced potential surfaces is given in terms of eqs. (22) and (25). This simple model system exhibits the following characteristics of the non-radiative decay probability of the "isolated" molecule:

(a) temperature dependence of $W_s(E)$. The major temperature dependence originates from the contribution of the promoting modes,

(b) the non-radiative decay probability of our model system excited in the 0-0 band (which overlaps all the sequence bands) is higher (approximately by the factor $(2\langle \nu_{\kappa} \rangle_T + 1) \approx \coth(\frac{1}{2}\hbar\omega_{\kappa} \beta)$) than that of the same model

molecule imbedded in an inert dense medium at $T \rightarrow 0$,

(c) $W_s(E)$ depends on the excess vibrational energy in the s manifold only via the $s-l$ non-radiative coupling of the optically active mode.

It is amusing to notice that in a hypothetical system where the optically active mode is not displaced between the s and l states, $W_s(E)$ for our model system will be independent of the excess vibrational energy.

The physical situation is more complex for a real large molecule, where frequency changes [10] have to be incorporated, however, our general conclusions concerning the temperature dependence of $W_s(E)$ in an isolated molecule (collision free in respect to intramolecular decay) will be valid. As all sequence active frequencies decrease in the excited state, the 0-0 transition (and the higher 0- α transitions involving the optically active modes) should be located at the high energy end of a broad molecular absorption band group (corresponding to the same totally symmetric mode) and will in general exhibit a lower value of W_s relative to the value resulting from excitation at lower energy into the same band group. An oscillating dependence of the emission quantum yield on E was recorded for the case of the isolated aniline and naphthalene molecules [14-16] which we attribute to the effects of sequence congestion.

Note added in proof

In this work we have assumed that the initial population of the excited state of the isolated molecule is unchanged throughout the electronic relaxation process. The non-radiative decay probability [eq. (10)] represents faithfully just the initial decay rate. In a short time excitation experiment sequence congestion effects result in the population of a large number of vibronic levels all located within a narrow energy range. These levels will subsequently decay independently and may result in a decay pattern consisting of a superposition of exponentials. The non-exponential decay of pyrene vapor excited into the S_1 state at 28800 cm^{-1} [17] may originate from sequence congestion effects.

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