place at even lower excess energy. With the help of Eq. (1) the determination of the excess energy of the rate constant is reduced to the problem of finding the temperature dependence.

Nitzan and Jortner[5] recently critized this scheme because (a) they felt an isolated molecule can not act as its own heat bath, (b) they state that the predictions which result from this scheme are at variance with experiments if one incorporates the promoting mode process. It is the purpose of this note to demonstrate that there must be energy exchange between normal modes and that the excess energy dependence which is due to the promoting mode strongly supports this scheme of communicating states.

Even though the model of communicating states does not predict detailed structure it is interesting to observe that the range of applicability is rather large. Energy exchange seems to take place whenever different vibronic states are nearly degenerate. It is due to anharmonic coupling.[12] Direct evidence for such an energy redistribution in the low excess energy region has been found recently by Schlag *et al.*[13] who measured the lifetime of selected vibrational states of naphthalene and deuteronaphthalene. A b_{1_g} (936 cm^{-1}) mode of the electronically excited molecule is populated, and radiationless decay from an out-of-plane b_{3_g} mode which is almost isoenergetic with the b_{1_g} mode, is observed. The linear decrease of the naphthalene lifetime as observed by Loar and Ludwig[10] further supports this hypothesis. The detailed calculations[14,15] show that the linear increase of the rate of radiationless transition from the lowest singlet state S_1 to the second triplet T_1 is mainly due to a promoting mode ω_p of b_{3_g} symmetry. As a result the rate constant is proportional to $\coth(\hbar\omega_p/2kT)$. This factor converts into an excess energy dependence of

$$\coth(\hbar\omega_p/2kT)=1+2n_p=[1+(2E_{\text{ex}}/L_p\hbar\omega_p)],\qquad(2)$$

where L_p is defined via the equation

$$\sum_j^L \hbar\omega_j n_j=L_p\hbar\omega_p n_p.\qquad(3)$$

For a promoting mode frequency of $\omega_p=408$ cm^{-1}, (the lowest frequency of b_{3_g} symmetry) L_p turns out to be about 20 over the excess energy range of interest ($E_{\text{ex}}<8000$ cm^{-1}). The slope predicted from Eq. (2) compares favorably with the experiments. If there would be no energy exchange between the normal mode frequencies, the theoretically predicted rate constant would stay almost constant, unless the promoting mode is excited directly.

After we received the reply from Dr. Nitzan and Dr. Jortner, we became aware of two further experiments, which seem to be important in this context:

(a) Lim and Uy[16] have found a linear increase of the radiative transition from S^1 for naphthalene for increasing excess energy. In this case the promoting mode is of b_{1_u} symmetry ($\omega_p\sim500$ and $L_p\sim30$). The slope predicted from (2) is in surprisingly good agreement with their data.

(b) Werkhoven *et al.*[17] determined the rate for energy flow into the promoting mode for pyrene. They conclude that the decay from the indirectly activated mode is larger by a factor of 2 ($n_p\approx\frac{1}{2}$) and this way demonstrate the importance of the promoting mode for the over-all rate.

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Radiationless Decay and Intrastate Energy Equilibration in an Isolated Large Molecule

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The nonradiative decay probability (NRDP) W_{si} of a single vibronic level $|si\rangle$ in an isolated large molecule, can be conveniently displayed in terms of the generating function formalism[1] which is entirely equivalent to the correlation function method,[2] whereupon[3] $W_{si}=\hbar^{-2}\int dt L(t)\exp(i\Delta Et/\hbar)$ where ΔE is the electronic energy gap and $L(t) = \langle i \mid V_{sl} \exp(iH_l t/\hbar) V_{ls}^{+} \exp(-iH_s t/\hbar) \mid i\rangle$. For the simple model of displayed identical harmonic potential surfaces, where the initial vibrational state is $\mid i\rangle = \prod_\mu \mid v_\mu\rangle$, where $\{v_\mu\}$ denote the vibrational quantum numbers, we were able[3] to derive a general expression of $W_{si}(\{v_\mu\})$, which accounted qualitatively for the gross features of the dependence[4] of the NRDP on the excess vibrational energy E_V. Using W_{si} for optical selection studies involves two basic assumptions: (a) A single vibronic level $\mid si\rangle$ can be optically excited. (b) No intrastate mixing of vibronic levels due to anharmonic coupling is involved.

Concerning assumption (a) it is well established[5] that "trivial" (temperature dependent) sequence congestion leads to line broadening in the optical spectra of large molecules. Invoking sequence broadening effects, the NRDP resulting from optical excitation at energy $\hbar\nu$ and excitation band width $\Delta\epsilon$ [where assumption (b) is still assumed to hold and interference effects disregarded] is

$$W^{sb} = \sum_{si} \int_{\Delta\epsilon} A_{si}(\hbar\nu) W_{si} d(\hbar\nu) \left[\int_{\Delta\epsilon} A_{si}(\hbar\nu) d(\hbar\nu)\right]^{-1},$$

where

$$A_{si}(\hbar\nu) = \sum_{gk} \exp(-E_{gk}/k_BT) \mid \langle gk \mid M \mid si\rangle \mid^2$$
$$\times \delta(E_{gk} - E_{si} - \hbar\nu) \Big[\sum_{gk} \exp(-E_{gk}/k_BT)\Big]^{-1}$$

is the optical excitation probability of $\mid si\rangle$, $\mid gk\rangle$ represents a ground state vibronic level, while M corresponds to the transition moment. The oscillatory dependence of the emission quantum yield on E_V for the isolated aniline molecule[6] may originate from sequence broadening effects.

Anharmonic intrastate scrambling at large E_V is of interest. Anharmonic coupling may affect the intensity distribution in absorption, rather than result in intrastate vibrational relaxation in the isolated molecule. Fermi resonances are rare in the electronic spectra of large molecules.[5] The anharmonic perturbation is characterized by the molecular symmetry and will couple vibrational states of the same symmetry, whereupon the number of vibrational states communicating with the optically accessible level $\mid si\rangle$ is enormously reduced. The correct way to handle this problem involves a consecutive decay scheme whereupon $\mid si\rangle$ is anharmonically strongly coupled to N states in a sparse manifold $\{\mid sj\rangle\}$, while $\mid si\rangle$ and $\{\mid sj\rangle\}$ are coupled to the dissipative intramolecular channel. Assuming strong anharmonic scrambling, the NRDP resulting from excitation of a single vibronic level [assumption (a) holds] is roughly

$$W^{as} \approx N^{-1} \sum_{\{v_\mu{}^i\}} W(\{v_\mu{}^i\}),$$

where the sum is restricted over $\{v_\mu{}^i\}$ levels such that

$$\sum_\mu v_\mu{}^i \hbar\omega_\mu = E_{si}.$$

Taking now into account both sequence broadening and anharmonic scrambling we have

$$W^{as+sb} \approx \sum_{si} \int_{\Delta\epsilon} d(\hbar\nu) N^{-1} \sum_{\{v_\mu{}^i\}} W(\{v_\mu{}^i\})$$
$$\times \left[\int_{\Delta\epsilon} d(\hbar\nu) A_{si}(\hbar\nu)\right]^{-1}.$$

Fischer's theoretical scheme for optical selection[7] is in our opinion open to criticism because of the following reasons:

(a) Suppose that rapid intrastate energy redistribution takes place. Fischer's assumption[7] concerning the attainment of a Bose distribution $v_\mu = [\exp(\hbar\omega_\mu/k_BT^*) - 1]^{-1}$ (with an effective temperature T^* determined by E_V and L)[7] is based on a grand canonical ensemble (variable "particle" number $\sum_\mu v_\mu$) and the replacement of the average energy by E_V. For moderate E_V values the role of fluctuations will be crucial, while for large E_V other effects (photochemistry) will set in.

(b) Care must be exerted in pursuing formal analogies. Fischer implies[7] that the initial phonon distribution is $v_\mu = \langle v_\mu\rangle_{T^*}$ (where $\langle\ \rangle_T$ is a thermal average). However, one cannot use the well-known expression for the thermally averaged nonradiative decay probability of the s state $\langle W_s\rangle_{T^*}$, replacing v_μ by $\langle v_\mu\rangle_{T^*}$. Such a procedure is valid[3] only for $\Delta_\mu \ll 1$, being applicable to solids but not for molecules. The correct expression for this situation is given by W^{as}. We thus conclude that *an isolated molecule cannot act as its own heat bath.*

(c) Fischer's claim[7c] that a promoting mode process is necessary to insure a linear dependence of the NRDP on E_V for small ΔE is unjustified as we have demonstrated[3] that in this case $W_{si}(\{v_\mu\})$ can exhibit all types of behavior (increase, decrease or even oscillatory) with increasing E_V.

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