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Radiationless Transition between Randomly Fluctuating Levels. S_1-T_2-T_1 Intersystem Crossing in Condensed Phase

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Radiationless transitions in aromatic molecules in condensed phase are examined for the case where sparse intermediate levels are involved. Effects of surrounding mediums on radiationless transitions are also discussed in which the random fluctuation of the vibrational manifolds in the solvent cages is shown to be important to meet the resonance conditions in the transitions. The theory is applied to explain the "unusually" fast S_1-T_2-T_1 intersystem crossing in the system such as anthracene derivatives.

The radiationless transitions in aromatic molecules have been studied quite extensively both theoretically and experimentally.[1)] However, the quantitative interpretation of the experimental facts are not always in the stage of a good consensus. One of the examples is S_1-T_2-T_1 ISC of aromatic molecules (especially of anthracene derivatives) which may be the case where sparse intermediate levels are involved in the transitions.[2)]

In this paper, brief but general discussion of the effect of solvent on the radiationless transitions will be presented. Particularly, the random fluctuations of the vibrational manifolds in the solvent cage is shown to be important to meet the resonance conditions[1b)] in the transitions. This is closely related to the earlier discussion by the present author concerning the choice of basis sets in radiationless transitions.[3)] Actually, several key features in this paper were already suggested in that paper. So, the present paper is intended to give more quantitative interpretation of S_1-T_2-T_1 ISC of some anthracene derivatives which was not the major subject of the previous paper, by taking the recent experimental data into account.[2,4–6)] Thus, the "unusually" fast ISC of these compounds (even without heteroatoms), hardly explained by intramolecular mechanism (*e.g.*, the third triplet state had to be invoked),[2)] is now interpreted by taking the effect of solvent cage into account.

Mechanism

Just like the presentation in the previous paper, we'll give kinetical arguments which could be converted into a quantum mechanical picture as a branched sequential decay in a system composed of both aromatic molecules and surrounding medium.[3)]

However, before going into mechanism of ISC, we had better to discuss the effect of the medium on the radiationless transition in general which was discussed only implicitly in the previous paper.[3)] Most recognized is the vibrational relaxation (VR) between vibrational levels in the same electronic state which allows for rapid communication (as fast as $10^{12}\,s^{-1}$) within the vibrational manifolds generally accepted as a cause for the thermally activated processes of electronic relaxations.[1)] In addition, VR works to give uncertainty widths to the initial and the final states of radiationless transitions allowing for transfer from the intermediate case to the statistical limit case as was actually discussed to explain the collisional effect in vapor phase[7)] (*vide infra*). Another mechanism is a solvent effect on the location of energy levels (especially energy gap between the ground vibrational levels of the electronic states) which may partially explain the solvent effect on ER's. And thirdly, as was not widely recognized in spite of the earlier suggestions,[3)] the location of energy levels are fluctuating with the change of the structure of solvent cages so that the resonance conditions towards the radiationless transition are sometimes met between some levels for every transient conformation of a system composed of a solute molecule plus surrounding solvent molecules. Actually, the interpretation of the collisional effects of S_1-T_1 ISC rates of naphthalene by Fung and Freed[8)] and the theory of delayed fluorescences by van der Werf *et al.*[9)] as well as that of electronic relaxation (ER) of small molecules in a densed medium by Nitzan and Jortner[10)] are just like what to be supplemented by this scheme. The transition through this mechanism may be named as a nonadiabatic transition between randomly fluctuating levels[3)] because the initial state and the final state represent different potential curves of the whole system (the solute molecule and the solvent molecules). In this quantum mechanical description, vibrational modes of solvent molecules (phonon modes) may be regarded to be working as accepting modes. However, semiclassical interpretation would be rather suitable to describe the real event, because the initial and final states can not be well defined in solution against the case in gaseous state (or in mixed crystal).[11)] Uncertainty broadening of the energy levels due to vibrational relaxation might also give more probability for the resonance conditions to be met in such a way to

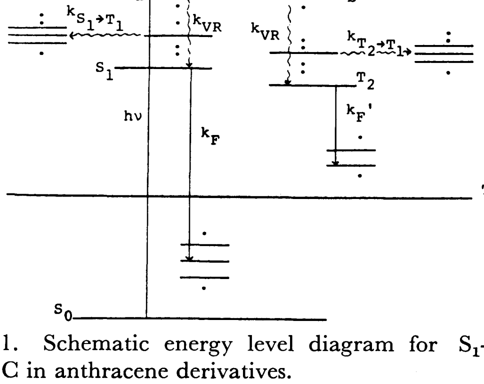

Fig. 1. Schematic energy level diagram for S_1-T_2-T_1 ISC in anthracene derivatives.

bring ER into the statistical limit[7,10] (*vide supra*). However, this VR effect appears to be minor compared to the preceding mechanisms. The most typical evidence to support this conjecture may be found in the "zeroth order" interpretation of the band shapes of radiative electronic transitions by the Franck-Condon intensity distribution of vibronic bands modified by broadening of the bands due to environmental (cage) effects[1,3] (inhomogeneous width), except for those in mixed crystal.[11],* A more quantitative account based on kinetics will be given later.

Now, let us discuss the mechanism of ISC. The energy level scheme suitable for the kinetical interpretation is given in Fig. 1 where only concerned evells and processes are indicated. This may appear to be practically the same as Fig. 2 of the previous paper which is purely intramolecular scheme.[3] However, it has to be noted that these levels are fluctuating under the influence of the medium, thus allowing for the resonance conditions to be met between some vibrational levels of S_1 and T_2. In fact, there always exist the coupled pairs (resonance states) as shown by a-b in the figure which can be populated by thermal activation and fluctuation of the levels. Thence, presentation of the mechanism for S_1-T_2-T_1 ISC would be straightforward:

(1) The first step is of course the optical preparation of an excited level, say, a higher vibrational level of S_1 indicated in the figure.

(2) It is immediately followed by vibrational relaxation ($k_{VR}\approx 10^{12}\ s^{-1}$) so that thermal equilibrium between vibrational manifolds may be reached unless subsequent processes are extremely fast.

(3) Thenceforth, radiative and radiationless transitions from this manifolds (S_1) to S_0 and T_1 (T_2) would start, if we apply the general picture presented in the previous paper (*e.g.* Fig. 1 therein[3]). However, this is not the case for the present system because of the resonance coupling between some S_1 and T_2 vibronic levels (to be represented by pure spin adiabatic Born-Oppenheimer basis[3]) assisted by the medium. The alternative explanation is based on the assumption of the near (not strictly) thermal equilibrium between S_1 and T_2 manifolds supported by the kinetical argument using the estimated numbers of the rates: *e.g.* for the case of anthracene molecule, $k_F\approx 5\times 10^7\ s^{-1}$, $k_{S_1\to T_1}\lesssim 10^5\ s^{-1}$, $k_{T_2\to T_1}\approx 10^{10}\ s^{-1}$, $k_{VR}\approx 10^{12}\ s^{-1}$ and $k_{S_1\leftrightarrow T_2}\lesssim 10^{11}\ s^{-1}$ (H_{SO} matrix element including FC factor suitable for the coupling may be estimated to be $(\lesssim 1)\times(\lesssim 1)$ *i.e.* $\lesssim 1\ cm^{-1}$, indicates which the upper limit of the rates due to unknown effective Boltzmann factors[1,2]). In other words, the initial states for the following steps are not always represented by PS ABO basis (At least a-b level is a exactly spin contaminated level.[3]). This may be the reason why triplet-triplet fluorescence quantum yield corresponding to k_F' in the figure estimated from the intensity of T-T absorption (which may be that between PS ABO states) was much larger than the experimentally observed values[2a] (*vide infra*). Actually, possibility of thermal equilibration between S_1 and T_2 is already suggested by Campbell and Liu to account for sensitized chemical reactions from "T_2" states of anthracene derivatives.[12] Recent experimental results by Wilson and Halpern indicating fast T_2-S_1 ISC competing with T_2-T_1 internal conversion also conform to this. Thus, the observed decay rates of S_1 fluorescences should not be taken to be nearly equal to $k_{S_1\to T_1}$ plus $k_{S_1\to T_2\to T_1}$. For, S_1-T_2-T_1 and S_1-T_1 processes interfere with each other. In this respect, no "important" difference[2b] isseen between quantum mechanical and kinetical arguments, where kinetical scheme is represented by $S_1\rightleftarrows T_2\rightarrow T_1$ instead of $S_1\rightarrow T_2\rightarrow T_1$. The more quantum mechanical picture may be given as a behavior of a resonance state which arises from both S_1 and T_2 states with resonance conditions being satisfied and decays to either S_1 or T_2 state with probabilities proportional to the squares of their mixing coefficients.

Similar but different mechanisms were already proposed for slow internal conversions between excited states in strongly coupled systems *i.e.* between singlet excitonic states of multiple molecules and triplet $n\pi^*$ and $\pi\pi^*$ states of 1-indanone in EPA where energy gaps were in the range of 50 to 500 cm^{-1}.[3]

One of the experiments to prove this scheme might be to show the multiple exponential decay of S_1 fluorescence with the fast component corresponding to $k_{S_1\to T_2}$ and slow component corresponding to the weighed average of k_F's, $k_{S_1\to T_1}$, and $k_{T_2\to T_1}$, if a single level a in the figure could be excited by light absorption. This seems to be practically impossible, however, because the molecules are in condensed phase *i.e.* $k_{S_1\to T_2}$ decay process in some molecules would be cancelled out by k_{VR} rise process towards $k_{S_1\to T_2}$ in the other molecules under observation. In case a ground vibrational level of S_1 state is accidentally degenerate with any level in T_2 manifold, solvent fluctuation would rather lower the rate. Difference of collisional effects between vapor phase and condensed phase seems to be taken as one of the evidences (*vide infra*).

Another proof of this mechanism is to explain the observed decay rates of S_1 fluorescences by setting reasonable values of k's and location of a-b levels (Experimentally obtained temperature effect on the rates *i.e.* activation energies might give the rough estimate of the location.). In the case of anthracene where $k_{S_1\to T_2}(\gtrsim 10^{11}\ s^{-1})$ is not fast enough compared to k_{VR}, the upper limit of the decay rate of the fluorescence is approximately $k_{T_2\to T_1}\approx 10^{10}\ s^{-1}$ (by taking account the effective Boltzmann factor suitable for near thermal equilibrium), only one order of magnitude larger than the experimental value,[1a] to be satisfactory. Therefore, the usual interpretation of the decay rate by thermally

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* To make the contention of this sentence clearer according to referees' suggestions, we can make the following statements:

(1) The locations and the shapes of potential energy surfaces of a solute molecule are regulated by the arrangement (locations and orientations) of solvent molecules and are thermally fluctuating *i.e.* change from time to time.

(2) Therefore, resonance conditions are satisfied within a time scale of solvent relaxation.

These assumptions, though being slightly oversimplified, seem to be fair as long as the "intramolecular" radiationless transition is concerned *i.e.* in case where intermolecular modes are not important due to *e.g.* their lower frequencies compared to intramolecular modes.

activated S_1-T_2-T_1 process would apply for this system although thermal equilibrium between S_1 and T_2 is not well established. For anthracene derivatives such as 9-bromoanthracene,[2,4] however, $k_{S_1\to T_2}$ would become orders of magnitude larger in spite of the possible reduction of FC factors by the increase of S_1-T_2 energy gaps. So thermal equilibrium between S_1 and T_2 is more reached by the heavey atom effect. Thus, the decay rates of T_2-T_1 fluorescences would not represent the rates ($k_{T_2\to T_1}$'s) indicated in the figure but rather represent the weighed averages of the decay rates among the S_1 and T_2 levels. This explains "the small TTF quantum yields and apparent internal heavey atom effect"[2,4a] in these systems.

Finally, the kinetical discussion is made to show why the present mechanism is prediminant over the possible alternative based on the statistical limit descriptions in both S_1-T_2 and T_2-S_1 ISC's (*vide supra*) as was implicitly assumed in most of the experimental papers[4–6] though no quantitative verification was given so far. Actually, Gillispie and Lim's papers which showed the need of the third triplet state to explain the rates with a formula given *e.g.* by Nitzan *et al.*[7,10] can be taken to indicate inadequacy of the statistical limit assumption. Somehow, it is almost certain that broadening due to solvent fluctuation (inhomogeneous width) is much larger than the uncertainty broadening (homogeneous width). In actuality, since the rates involved in the observation is$<10^{11}$ s^{-1} (according to the present interpretation), there is enough chance for solvent fluctuation to be involved in the mechanism.** Thus, the present mechanism can be taken as a sublation of the statistical limit picture and the previous mechanism.[2]

Concluding Remarks

Presentation of the mechanism is over. However, to seek other evidences than those presented above and in the previous paper[3] in different kinds of experiments to support this proposal would be desired to clear up some skepticisms. One of the key features in the mechanism is the importance of the resonance coupling. This may be actually evidenced in the recent experiments in isolated molecules.[1] For example, the steep rise of the decay rate of a single rotational level when it is brought into resonance with another by Stark field was suggested for H_2CO.[13] Recent results of Zeeman effect on the quenching rates of gaseous molecules[14] may also be related to this interpretation. Another important key feature is the existence of a possible two-step activation process of ER by a medium *i.e.* thermal activation and thermal fluctuation of energy levels. This may be related to the recent experimental facts of the temperature effect of T_1-S_0 ISC in anthracene and its deuterium substitute reported by Hung and Henry.[15]

Finally, it should be mentioned that this mechanism of ISC is not purely intramolecular, different from those of ordinary ER's in aromatic molecules in condensed phase which have been always assumed to be followed by fast vibrational relaxation.[1,7,10] In this respect, a recent paper by Hirayama on the ISC in cyanoanthracenes[6] is worthwhile subject to discuss. Although these systems do not belong to the case where "sparse" intermediate levels are involved but rather are described by conventional statistical limit picture as is consistent with their not-"unusual" lifetimes, the result indicates the difference of collisional effects in vapor phase from that in condensed phase (in nonpolar solvent). This seems to be an indication of the fact that solvent molecules work not only as vibrational relaxers but also as energy level fluctuators causing enhancement of the rate. As is mentioned before, weakening by solvent fluctuation is also possible, because of dilution of the effect by either more broadening or more rapid thermal equilibration (Thermal equilibration between vibrational levels can not be attained by a few collisions in vapor phase.). This is actually evidenced in Hirayama's data. It should also be noted that this kinds of mechanisms are expected to be playing crucial roles in the more complicated processes such as photoionization in solution[16] or phenomena to be named as solvent induced charge separation.[17] Somehow, the most desired experiments of the anthracene derivatives are high resolution observations in gas phase at collision free condition. Very recently, a preliminary experiment on this line was performed showing longer lifetime in the collision free condition.[18] This seems to conform to the present arguments.

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References

1) See, for example, a) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970); b) "Radiationless Processes in Molecules and Condensed Phase," ed by F. K. Fong, Springer-Verlag, Berlin (1976).

2) a) G. D. Gillispie and E. C. Lim, *Chem. Phys. Lett.*, **63**, 355 (1979); b) *ibid.*, **70**, 532 (1980) and references therein.

3) N. Kanamaru, *Sci. Papers IPCR*, **71**, 85 (1977).

4) a) C. G. Morgante and W. S. Struve, *Chem. Phys. Lett.*, **68**, 272 (1979); b) K. Hamanoue, S. Hirayama, T. Nakayama, and H. Teranishi, *J. Phys. Chem.*, **84**, 2074 (1980) and references therein.

5) T. Wilson and A. M. Halpern, *J. Am. Chem. Soc.*, **102**, 7272, 7279 (1980).

6) S. Hirayama, *J. Am. Chem. Soc.*, **103**, 2934 (1981).

7) A. Nitzan, J. Jortner, and P. M. Renzepis, *Proc. R. Soc. London, Ser. A*, **327**, 367 (1972).

8) K. H. Fung and K. F. Freed, *Chem. Phys.*, **14**, 13 (1976).

9) R. van der Werf, D. Zevenhuijzen, and J. Jortner, *Chem. Phys.*, **27**, 319 (1978).

10) A. Nitzan and J. Jortner, *Theor. Chim. Acta*, **29**, 97 (1973).

11) See, for example, R. W. Olson and M. D. Fayer, *J. Phys. Chem.*, **84**, 2001 (1980).

12) R. O. Campbell and R. S. H. Liu, *J. Am. Chem. Soc.*, **95**, 6560 (1973).

13) J. C. Weisshaar and C. B. Moore, *J. Chem. Phys.*, **72**, 2875 (1980).

** The author has seeked for the formalism which suitably represents the scheme illustrated by the figure but has merely come up with the kinetical interpretation. For, the other formalisms so far the author has tried *e.g.* using a density matrix has become more phenomenological than that of kinetics.

14) See, for example, K. Hashimoto, S. Nagakura, J. Nakamura, and S. Iwata, *Chem. Phys. Lett.*, **74**, 228 (1980).

15) I-F. Hung and B. R. Henry, *Chem. Phys.*, **27**, 263 (1978).

16) See, for example, H. Nakamura, J. Tanaka, N. Nakashima, and K. Yoshihara, *Chem. Phys. Lett.*, **77**, 419 (1981).

17) See, for example, a) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **49**, 854 (1976); b) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978); c) K. Rotkiewicz and W. Rubaszewska, *Chem. Phys. Lett.*, **70**, 444 (1980).

18) T. R. Hays, W. Herke, H. L. Selzle, and E. W. Schlag, *Chem. Phys. Lett.*, **77**, 19 (1981).