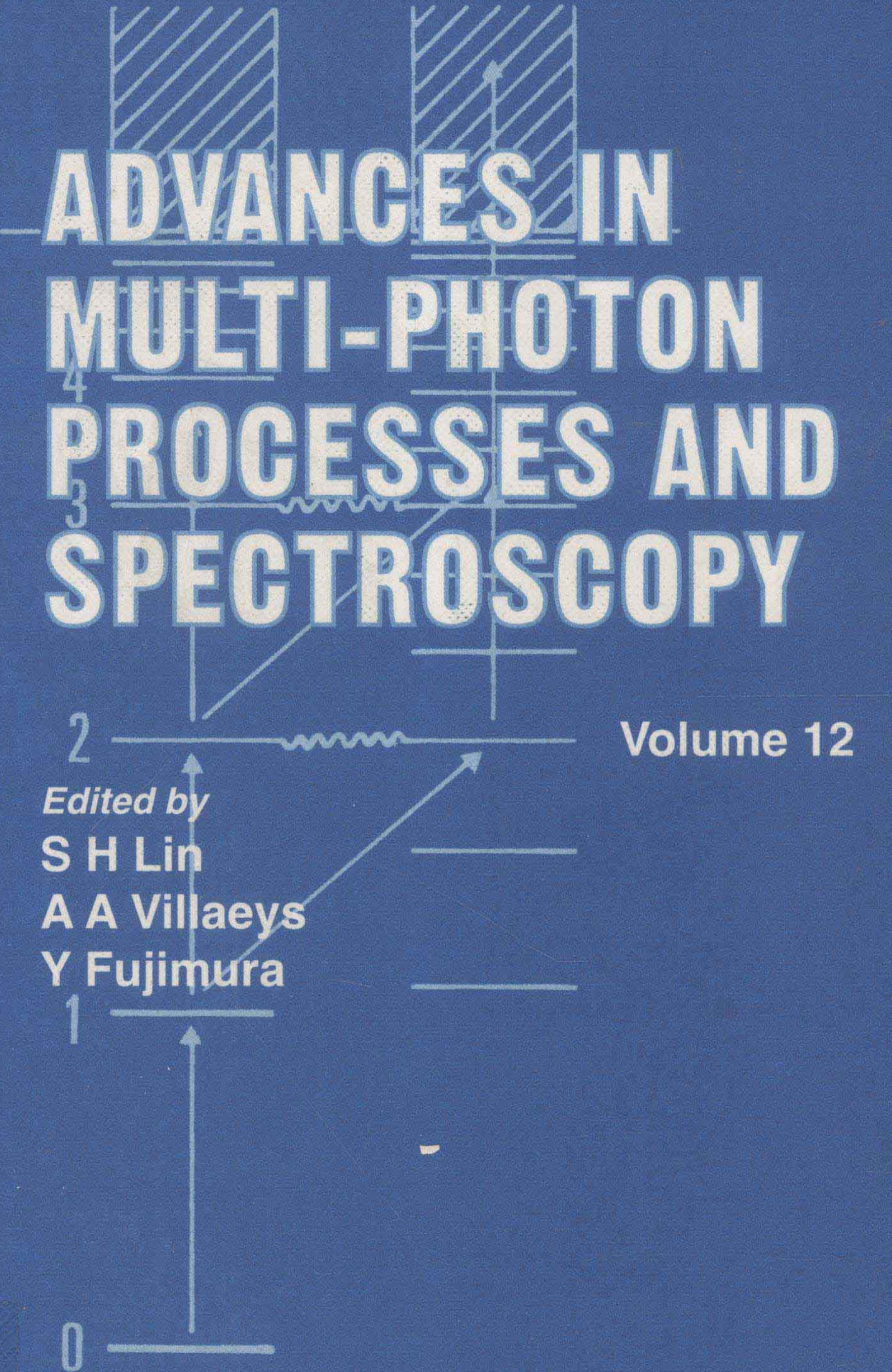

ADVANCES IN MULTI-PHOTON PROCESSES AND SPECTROSCOPY

Volume 12

Edited by

S H Lin
A A Villaeys
Y Fujimura

World Scientific

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Edited by

S H Lin
Institute of Atomic and
Molecular Sciences, TAIWAN

A A Villaeys
Université Louis Pasteur, FRANCE

Y Fujimura
Tohoku University, JAPAN

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PREFACE

In view of the rapid growth in both experimental and theoretical studies of multiphoton processes and multiphoton spectroscopy of atoms, ions and molecules in chemistry, physics, biology, materials science, etc., it is desirable to publish an advanced series that contains review papers readable not only by active researchers in these areas but also by those who are not experts in the field but who intend to enter the field. The present series attempts to serve this purpose. Each review article is written in a self-contained manner by the experts in the area so that the readers can grasp the knowledge in the area without too much preparation.

The topics covered in this volume are "Electronic Energy Transfer in Naphthalene – Anthracene Bichromophoric Molecular Systems Studies Under Supersonic Jet Cooling Conditions", "Optical Detection of Angular Momentum Polarization and Its Application to Photodissociation Dynamics", and "Two-Dimensional Vibrational Spectroscopy". The editors wish to thank the authors for their important contributions. It is hoped that the collection of topics will be useful not only to active researchers but also to other scientists in biology, chemistry, materials science and physics.

S. H. Lin

A. A. Villaeys

Y. Fujimura

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PART ONE

Electronic Energy Transfer in Naphthalene – Anthracene Bichromophoric Molecular Systems Studies Under Supersonic Jet Cooling Conditions

Electronic Energy Transfer in Naphthalene – Anthracene Bichromophoric Molecular Systems Studied Under Supersonic Jet Cooling Conditions

Gershon Rosenblum and Shammai Speiser

Department of Chemistry, Technion – Israel Institute Of
Technology, Haifa 32000, ISRAEL

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1. Introduction

1.1. Electronic energy transfer

The electronic energy transfer (EET) process is one of the most common relaxation mechanisms of an excited chromophore. Its understanding is important for studying the natural photosynthetic processes. The EET process also plays a major role in many technogenic processes such as synthetic light harvesting, polymer photophysics, dye laser operation, light interaction with molecular crystals and photochemical synthesis.

EET was studied extensively in condensed systems [1]. Its mechanisms are now thought to be well understood [*e.g.* 1-8].

In a simple model each of the two chromophores D and A can be found either in its ground or in its excited electronic state and also possesses several vibrational modes that can be excited. The electronic origin transition energy of donor chromophore E_D is higher than the acceptor energy E_A. Within the Born-Oppenheimer approximation the chromophore wavefunctions are

$$\begin{aligned} \Psi_D &= \phi_D(q_i^D, Q_j^D)\chi_D(Q_j^D) \\ \Psi_A &= \phi_A(q_i^A, Q_j^A)\chi_A(Q_j^A) \end{aligned} \tag{1}$$

here ϕ and χ are pure electronic and vibrational functions respectively, q_i and Q_j denote electronic and vibrational coordinate sets. The D and A superscripts mirror the fact that in the zero-order approximation at which there is no interchromophore interaction, the wavefunctions of one chromophore do not depend on the coordinates associated with the other one. Introducing the interaction mixes the wavefunctions, but as the interaction of interest is small compared to the vibronic transition energies, we will neglect this complication. Later we will refer to this approximation when speaking about "largely localized" excitations.

The goal of the following derivation is to obtain a rate expression for EET from the initial state in which the donor is vibronically excited and the acceptor is in its ground state to the final state in which the donor is in its ground state and the acceptor is in an excited vibronic state. The chromophore excitations are approximated by one-electron processes. In this case the total two-electron wavefunctions should be antisymmetrized according to the Pauli principle requirement:

$$\begin{aligned} \Psi_i &= 2^{-1/2}[\Psi_{D^\bullet v_{D^\bullet}}(1)\Psi_{Av_A}(2) - \Psi_{D^\bullet v_{D^\bullet}}(2)\Psi_{Av_A}(1)] \\ \Psi_f &= 2^{-1/2}[\Psi_{Dv_D}(1)\Psi_{A^\bullet v_{A^\bullet}}(2) - \Psi_{Dv_D}(2)\Psi_{A^\bullet v_{A^\bullet}}(1)] \end{aligned} \qquad (2)$$

here the right hand one-electron wavefunctions are described by eq.(1), the ones with a star corresponding to excited chromophore vibronic states, and the others to ground states. The the zero-order Hamiltonian of the system corresponds to no interchromophore interaction, and the interaction perturbation is

$$V = e^2 / r_{12} \qquad (3)$$

where r_{12} is the distance between the interacting electrons. The interchromophore interaction matrix element V_{DA} of perturbation responsible for the EET is

$$\begin{aligned} V_{DA} &= <\Psi_i | V | \Psi_f> \\ &= <\Psi_{D^\bullet v_{D^\bullet}}(1)\Psi_{Av_A}(2) | V | \Psi_{Dv_D}(1)\Psi_{A^\bullet v_{A^\bullet}}(2)> \\ &- <\Psi_{D^\bullet v_{D^\bullet}}(1)\Psi_{Av_A}(2) | V | \Psi_{Dv_D}(2)\Psi_{A^\bullet v_{A^\bullet}}(1)> \end{aligned} \qquad (4)$$

The first integral here corresponds to the simultaneous donor electron relaxation and acceptor electron excitation and it is known as the Coulomb integral [9]. The second integral describes energy transfer by electron exchange [10] and is known as the Dexter exchange integral. If one substitutes in eq.(4) the initial and final wavefunctions without omitting the spin parts, one obtains different spin selection rules for the two integrals. The exchange integral selection rules are less strict, and thus in some cases (*e.g.* triplet - triplet energy transfer) the first integral vanishes and the energy is transferred only via electron exchange. Generally, however, both integrals are non zero and the corresponding mechanisms interfere.

The perturbation affects only electronic wavefunctions, and the nuclear motion can be separated:

$$\begin{aligned} V_{DA} &= \{< \phi_{D*}(1)\phi_{A}(2)|V|\phi_{D}(1)\phi_{A*}(2) > - < \phi_{D*}(1)\phi_{A}(2)|V|\phi_{D}(2)\phi_{A*}(1) >\} \times \\ &\times \langle \chi_{D*v_{D*}}|\chi_{Dv_D}\rangle\langle \chi_{A*v_{A*}}|\chi_{Av_A}\rangle = V'_{DA}\langle \chi_{D*v_{D*}}|\chi_{Dv_D}\rangle\langle \chi_{A*v_{A*}}|\chi_{Av_A}\rangle \end{aligned} \tag{5}$$

where in order to separate the Franck-Condon factors an assumption was made that the vibrations of the two chromophores are uncoupled. The quantity V'_{DA} is the pure electronic matrix element.

In solution experiments the initially prepared vibronic states usually undergo vibrational relaxation to a temperature dependent solvent broadened set of states and the energy transfer proceeds from this set. In the supersonic free jet experiments the donor retains its excitation energy, and EET can be monitored from a specific vibronic state. At sufficiently high vibrational energies the initially prepared state is broadened by interaction with isoenergetic states. Even without this effect the initial state is broadened by the interaction with the radiation field and by the energy transfer process. The acceptor states are broadened by the interaction with the radiation field and by the possible back transfer. The energy profiles of the donor transition and of the acceptor transition can be defined:

$$P_D(E) \equiv \sum_{v_D} P\left(E - \Delta E_{Dv_D}\right), \qquad P_A(E) \equiv \sum_{v_{A*}} P\left(E - \Delta E_{Av_{A*}}\right),$$

here $\Delta E_{Dv_D} \equiv E_{D*v_{D*}} - E_{Dv_D}$, $\Delta E_{A*v_{A*}} \equiv E_{Av_A} - E_{A*v_{A*}}$, $\int P(E - \Delta E)dE \equiv 1$.

The total EET rate is obtained then from the Fermi Golden Rule:

$$k_{ET} = \frac{2\pi}{\hbar}\sum_{v_D}\sum_{v_{A*}}\int P\left(E - \Delta E_{Dv_D}\right)P\left(E - \Delta E_{Dv_{A*}}\right)dE \tag{6}$$

By neglecting the coupling between the vibrations of the two chromophores, we obtain

$$k_{ET} = \frac{2\pi}{\hbar}\left|V'_{DA}\right|^2\sum_{v_D}\sum_{v_{A*}}\left|\langle \chi_{D*v_{D*}}|\chi_{Dv_D}\rangle\right|^2\left|\langle \chi_{A*v_{A*}}|\chi_{Av_A}\rangle\right|^2\int P\left(E - \Delta E_{Dv_D}\right)P\left(E - \Delta E_{Dv_{A*}}\right)dE \tag{7}$$

Thus within the framework of the employed assumptions the EET rate is proportional to the square of the pure electronic interaction matrix element, Franck-Condon factor for the transition from the donor vibronic state and Franck-Condon weighted energy overlap integral between the donor level and acceptor levels. Usually the acceptor density of states is higher than the donor state width, and the integral in eq.(6) is approximated by the state density ρ or by the so-called Franck-Condon factor weighted state density ρ_{FC}:

$$k_{ET} = \frac{2\pi}{\hbar}|V_{DA}|^2\rho \quad \text{or} \quad k_{ET} = \frac{2\pi}{\hbar}|V'_{DA}|^2\rho_{FC} \qquad (8)$$

This simple picture can be substantially incorrect if the electronic levels are considerably mixed, if the vibrations of the two chromophores are coupled, if other electronic levels of the chromophores are coupled by vibrations to the levels involved in the EET, and so on.

The Coulomb integral can be approximated by two separate integrals corresponding to the electronic transitions in the chromophores. These integrals can then be expanded in series, with the largest term being the dipole - dipole interaction term. If other terms are neglected as well as other contributions to the interaction integral, it can be expressed by the chromophore transition dipole moments:

$$V'_{DA} = \frac{|M_D||M_A|\Gamma}{R^3_{DA}} \qquad (9)$$

R_{DA} being the interchromophore distance and Γ being the mutual orientation factor of the two transition dipole moments M [1]. Together with the translation of the energy overlap integral and of the Franck - Condon factors into the spectral overlap between donor emission and acceptor absorption it yields

$$k_{ET} = \frac{9000 \ln 10\, \Gamma^2\, \Phi_D}{128\pi^5 n^4 N_A \tau_D}\frac{1}{R^6_{DA}}\int \overline{F_D}(\bar{\nu})\varepsilon_A(\bar{\nu})\bar{\nu}^{-4}d\bar{\nu} \equiv \frac{1}{\tau_D}\left(\frac{R_0}{R_{DA}}\right)^6 \qquad (10)$$

here Φ and τ are fluorescence quantum yield and lifetime, n is refractive index of the medium, F is fluorescence spectrum and ε is absorption spectrum. Thus Förster critical transfer radius R_0 defined here and the EET rate can be calculated from spectroscopic experimental data.

In cases where the Coulomb mechanism contribution is either small or spin forbidden, the interaction matrix element can be expressed via the exchange integral. At large enough separations this integral dependence on the interchromophore distance can be approximated by the exponential chromophore wavefunctions spatial overlap dependence [10]:

$$V'_{DA} = K\exp(-R_{DA} / L) \qquad (11)$$

here L is an average decay radius of the wavefunctions of the two interacting states.

It can be seen from eqs. (10) and (11) that the Förster mechanism rate is proportional to R_{DA}^{-6}, and this interaction is most important at intermediate separations. At larger distances the trivial EET due to interaction via the radiation field (photon emission and reabsorption) its rate being proportional to R_{DA}^{-2} becomes more important. At close separations were the wavefunctions overlap becomes considerable, the exchange mechanism dominates. At some separation the Coulomb and exchange contributions will be of equal size and may cancel out one another.

Förster critical transfer radius for most systems in solution is between 10 and 100Å. Eq. (10) is widely used to describe energy transfer in condensed phase [1]. At distances less than about 5Å the Dexter exchange mechanism usually becomes more important [1, 3]. In real systems the exchange integral evaluation by computational methods is extremely complicated, and without it the model mechanism can be employed only in some very limited cases. Still, such computations were performed in a study of a series of bichromophoric molecules, yielding good agreement with experimental data on distance and orientation dependence of the EET rate [11].

In addition, more complicated mechanisms than the two considered in eq.(5) can contribute to the pure electronic interaction matrix element. Notably, higher electronic levels for which wavefunctions are localized spatially between the two chromophores, can mediate the transfer. This effect ("superexchange") was detected in bichromophoric molecules, where the rigid bridge connecting the chromophores enhanced the exchange mechanism rate [5, 12-15].

Rigorously speaking, the localized excited states approximation is never correct, as the same interaction that leads to the EET delocalizes the interacting wavefunctions. The two electronic states then are

$$\begin{aligned}\Psi_1 &= a\Psi_A + b\Psi_D \\ \Psi_2 &= b\Psi_A - a\Psi_D\end{aligned} \qquad (12)$$

If the two weights are similar, EET will not be from one moiety to another but from one state of the molecular system to another. The chromophores can be defined only if the initially excited states are largely localized at different parts of the system, and the interchromophore interaction is weak. In systems involving two interacting identical moieties, the weights will be equal and the electronic degeneracy will be removed by exciton splitting. In systems involving two chromophores with large energy separation of the excited states the excitation will be localized to a high degree.

When the donor chromophore is excited to some specific vibronic state, it can undergo dephasing (intramolecular vibrational redistribution, IVR) involving other molecular states that have low Franck-Condon factors for excitation (dark states). These states should have the same energy in the sense of eq.(6). It also can undergo energy transfer to the isoenergetic levels of the acceptor chromophore. As all the described processes do not involve energy change, the excitation can be then transferred back, if the fluorescnce is sufficiently slow. Finally, a stationary state is achieved, in which the excitation is spread over the two chromophores in a ratio corresponding to the vibrational state density ratio of the chromophores.

Usually there is a considerable energy gap between the electronic states and thus the acceptor vibrational state density is much higher than the donor one at any given system energy. In this case the stationary state is localized on the acceptor, back energy transfer is negligible and an unimolecular EET rate can be defined. When the state density