Transmission and Transformation of Vibrational Energy in a Molecular Donor–Acceptor System

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A system of two different organic molecules with specific properties is investigated in this article. It is assumed that only one of the two molecules has a permanent dipole momentum and is containing alkane chains (C_nH_{2n}), which can be excited by infrared (IR) fields with wavelengths in the range of $16 - 18\,\mu$m. This molecule can play the role of a donor in this system if the partner molecule (called acceptor) is an aromatic hydrocarbon and close enough to pick up the vibrational excitation energy acquired by the donor. As it was shown in our previous work [H. Jungclas, A. Wieghaus, L. Schmidt, A. M. Popova, and V. V. Komarov, J. Am. Soc. Mass Spectrom. 10, 471 (1999)], the C_nH_{2n}-structures of the donor molecule are able to act like IR antennas and thus store the energy of absorbed IR photons. Aromatic molecules can be polarized in the electric field of the IR antenna's dipole momentum. Thus the accumulated energy of the donor can be transferred to the acceptor by dipole–dipole interactions and finally will be emitted by fluorescence. These energy transmission and transformation processes are analyzed, and a practical application is proposed.

Key words: Molecular Donor–Acceptor System; IR Radiation; Vibrational Energy Transformation; Acceptor Fluorescence.

1. Introduction

There has been a substantial progress in the theoretical and experimental analysis of the photo-physical properties of a system consisting of two organic molecules, which are interacting at a distance of the centers of mass larger than the sum of their Van der Waals radii [1] If one of these molecules has no permanent dipole momentum but a significant polarizability, its electronic system can absorb vibrational energy from the other molecule due to Förster forces.

The main goal of the presented work is to investigate the energy transport in a molecular donor–acceptor system exposed to infrared (IR) fields with a wavelength in the range of $\lambda = 16 - 18\,\mu$m. In the considered system, excitation energy is transferred from one molecule (the donor) to the other (the acceptor) by dipole–dipole interactions. The donor in this system is an organic molecule, which has a permanent dipole momentum and an alkane-type hydrocarbon structure, which is able to be resonantly excited by IR fields like an antenna. We assume that the acceptor is a benzene-based aromatic compound, which has no permanent dipole momentum and cannot be excited by such IR fields. However, the aromatic molecules are characterized by a significant polarizability coefficient, i.e. the electron cloud of the aromatic molecule can be deformed in response to an external electric field. As a result, the permanent dipole momentum of the donor molecule can induce a dipole momentum in the acceptor molecule [2]. This special feature enables an energy transport and transformation process, which is described here in three steps: excitation of the donor molecules by a non-destructive method, transfer of the vibrational energy from the donor to the electronic system of the acceptor molecules, and finally emission of the electronic excitation by fluorescence.

As it was shown earlier, delocalized collective vibrational states (excimols) can be excited in an IR antenna by action of external IR radiation [3, 4]. The delocalization is defined by transition of vibrational excitation between identical dipoles in the antenna. The excimol energy is a lower limit of the spectral band of the vibrational states in a molecular structure of identi-

cal dipoles. This energy is lower than the corresponding fundamental frequency of the diatomic dipoles in the antenna. The eximol lifetime τ_{ex} is much higher than the lifetime of a vibrational state with frequency ω_d of an antenna dipole.

The most important IR antennas in organic donor molecules are of the type C_nH_{2n}, $n \geq 2$. For these antennas, the eximol parameters have the following values: $E_{ex} = 0.07$ eV; $\omega_{ex} = 1.1 \cdot 10^{14}$ s^{-1}; $\tau_{ex} = 10^{-11}$ s [3, 4]. An interaction between the permanent momentum of the donor molecule and the induced momentum of the acceptor molecule can occur if the center of mass (c.m.) distance between the molecules is limited by the interval $3\,\text{Å} - 5\,\text{Å}$. In this case, the eximol energy accumulated during the irradiation time $\tau_R \leq \tau_{ex}$ can be transmitted to the acceptor molecule by dipole–dipole interactions without decomposition of the donor–acceptor system and induce electronic excitation and possibly fluorescence.

2. Dipole Momenta of Aromatic Molecules Induced by Electric Fields of Donor Molecules

To calculate the electronic excitation probability of the acceptor molecule due to energy transfer from the IR antenna of the donor molecule, we have to determine the induced dipole momentum of the aromatic acceptor molecule. The value of the permanent dipole momentum μ_0 of the C_nH_{2n}-antenna does not depend on the chain length of this structure and can be taken as $\mu_0 = 0.6D$ [2]. To determine the induced dipole momentum of the acceptor molecule, we apply the valence model, which is usually used for the analysis of electrical and optical properties of molecules. This means that each valence bond relates to an ellipsoid of polarizability with polarizability coefficients along the three main axes (a_1, a_2, a_3). The whole molecular dipole momentum can be defined as a sum of dipole momenta of valence bonds. Polarizability coefficients of molecules can be defined by a sum of polarizability coefficients of molecular bonds. The parameter a_1 is the polarizability coefficient along the ellipsoid's main rotation axis. The parameters a_2 and a_3 are polarizability coefficients perpendicular to each other and to the rotation axis. The values a_i of these coefficients ($i = 1$, 2, 3) are expressed in the form $a_i = \alpha_i \cdot 10^{-24}$ cm^3, where all α_i are dimensionless. The known values of polarizability coefficients are presented in Table 1 for some valence bonds and for C_6H_6 molecules.

Using the data of Table 1 [2], we calculated the polarizability coefficients for the following aromatic molecules: naphthalene, anthracene, and pyrene, see Table 2. The direction of the induced dipole momentum of the aromatic molecule coincides with the dipole momentum μ_0. We calculated the value μ_0 of the induced dipole momentum for the aromatic molecule versus its c.m. distance to the antenna of the donor molecule C_nH_{2n}. The electric field E_0 at the c.m. of the acceptor molecule generated by the IR antenna's dipole at distance R from the c.m. of the donor molecule can be presented in the form

$$E_0 = 2\mu_0/R^3 . \tag{1}$$

If θ is the angle between the direction of the dipole momentum μ_0 and the main axis of the ellipsoid of the aromatic molecule, the value of the induced dipole momentum is

$$D_{ind} = 2\mu_0/R^3 \cdot \left[a_1 \cos^2\theta + a_2 \sin\theta\right] \\ \text{for } a_2 = a_3 . \tag{2}$$

After averaging over θ in (2), the induced dipole momentum $\check{D}_{ind}$ is

$$\check{D}_{ind} = 2\mu_0/R^3 \cdot \left[a_1/2 + 2a_2/3\right] . \tag{3}$$

The calculated values of $\check{D}_{ind}$ for the aromatic molecules benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), and pyrene ($C_{16}H_{10}$) versus distance R are presented in Figure 1. The maximum and minimum values of the induced dipole momenta for these molecules can be obtained taking $\theta = 0°$

Table 1. Values of the polarizability coefficients a_i for some valence bonds and the molecule C_6H_6, ($a_i = \alpha_i 10^{-24}$ cm^3, $i = 1, 2, 3$, $\alpha_2 = \alpha_3$) [2].

Structure	α_1	$\alpha_2 = \alpha_3$
C–H	0.79	0.58
C–C	1.82	0.02
C=C	2.86	1.06
C_6H_6	6.35	12.31

Table 2. Values of the polarizability coefficients a_i for aromatic molecules ($a_i = \alpha_i 10^{-24}$ cm^3, $i = 1, 2, 3$, $\alpha_2 = \alpha_3$).

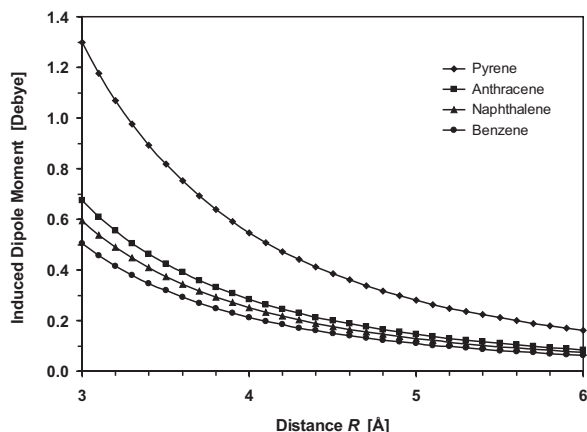| Molecule	α_1	$\alpha_2 = \alpha_3$
Naphthalene	8.15	14.0
Anthracene	9.5	15.6
Pyrene	9.2	29.4

Fig. 1. Induced dipole momentum $\check{D}_{\text{ind}}$ [Debye] for pyrene, anthracene, naphthalene, and benzene versus distance R induced by a C_nH_{2n} chain with $M_r = 10$, calculated by (3) after averaging over θ.

Fig. 2. Induced dipole momentum D_{ind} [Debye] for pyrene versus distance R calculated by (2) for $\theta = 90°$ and $\theta = 0°$.

and $\theta = 90°$ in (2) correspondingly. As an example, the values D_{ind} (max–min) for pyrene are presented in Figure 2. The same behaviour of the induced dipole momenta can be expected for other aromatic molecules.

The comparison of the induced dipole momenta for pyrene presented in Figures 1 and 2 shows that the polarization maximum of the aromatic acceptor molecule is reached when μ_0 is perpendicular to the rotation axis of this molecule. This is due to the fact that the coefficients a_2 and a_3 are much bigger than a_1. It means, that the aromatic acceptor molecules are oriented in the electric field of the IR antennas in a way that their rotation axes are directed nearly perpendicular to the dipole momentum μ_0, and the induced dipole momentum is on the plane perpendicular to their rotating axis.

3. Electronic Excitation of Acceptor Molecules by Excimol Energy from Donor Molecules

We consider the picoseconds processes which occur in molecular donor–acceptor systems in a field of IR radiation if the participating molecules have specific properties. Donor molecules with IR antennas can collect collective vibrational excitations (excimols) under action of the IR radiations [5]. The maximum number K of excimols accumulated in an IR antenna for the irradiation time τ_R can be defined by the expression

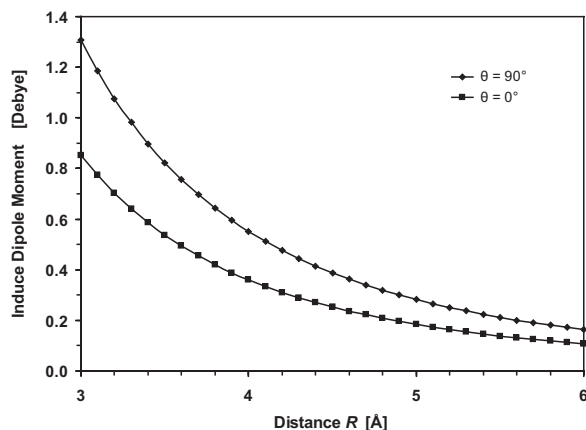$$K = P_{\text{ex}} \cdot M_R \cdot \tau_R / \tau_{\text{tr}} = P_{\text{ex}} \cdot M, \qquad (4)$$

where M_R is the real number of antenna dipoles; τ_{tr} is the time of energy transmission between neighboured dipoles; the relation τ_R/τ_{tr} defines the possible number of excimols excited in one IR antenna dipole. Thus M is considered as the effective number of antenna dipoles participating in the excimol excitation. P_{ex} is the probability function for excitation of one excimol, defined by the equation

$$P_{\text{ex}} = 4\pi^2/\hbar c \cdot (eD_0/r_0)^2 \cdot 2M_{01}^2 J\tau_R/E_{\text{ex}}, \qquad (5)$$

where eD_0 and r_0 are value and length of the dipole momentum; M_{01} is the matrix element of the interdipole energy transition; J is the flux of the primary IR radiation. The maximum number K of excimols can be defined by the probability

$$P_M^K = [2\pi K \cdot (1 - P_{\text{ex}})]^{-1/2}. \qquad (6)$$

The excimol energy $E(K)$ accumulated within the irradiation time τ_R is $E(K) = K \cdot E_{\text{ex}}$.

The permanent dipole of the IR antenna in the donor molecule and the induced dipole of the acceptor molecule can interact if they get close enough. As a result of this interaction, the accumulated excimol energy $E(K)$ in the donor molecule can be transmitted to the acceptor molecule and induce its electronic excitation with the energy E_{el}. If the accumulated energy is $E(K) = E_{\text{el}}$, the probability function P_{el} of this process is obtained in the frame of the quantum perturbation theory in the form [6]

$$P_{el} = (4\pi^2/\hbar c) \cdot K P_M^K P_{ex} \cdot \left[(eD_0/r_0) \right.$$
$$\left. \cdot (e\check{D}_{ind}/R_A) \right]^2 \cdot (M_{01} \cdot M_{el})^2 \cdot R^{-6}, \tag{7}$$

where M_{el} is the matrix element of the electronic transition in the acceptor. The function P_{el} depends on the parameters $K = E_{el}/E_{ex}$, P_{ex}, and P_M^K, which are characterising the donor-molecule antenna, and the parameters $(e\check{D}_A/R_A)$ and M_{el}, which characterise the acceptor-molecule properties. Comparing (4) and (5), one can conclude that the excitation of a definite number K of excimols in antennas with different M_r numbers requires different values of the radiation flux J. With increasing M_r numbers, the flux J should be decreased, as a decreasing flux corresponds to a decreasing value of P_{ex} for a fixed τ_R and therefore a decreasing value of P_{el}.

To demonstrate this statement, we calculated the function P_{el} for donor molecules containing the C_nH_{2n} substructures for $n = 5$, 10, 15, 20, and 25, and for pyrene, see Figures 3a and b. For pyrene and naphthalene, we calculated the probabilities P_{el} for excitation of the electronic states with the energies 3.68 eV and 4.43 eV, correspondingly, induced by excimols accumulated during τ_R. It is known that these excited states are pronounced in the pyrene and naphthalene absorption spectra ($\lambda = 337$ nm and $\lambda = 280$ nm). The fluorescence probability is expected to be high in this process, because the electronic excitation probability of the aromatic molecules is high.

4. Fluorescence of Aromatic Molecules in Donor–Acceptor Systems Irradiated by 0.07 eV IR Photons

It is known from experiments [7] that the aromatic molecules pyrene and naphthalene excited to low-energy electronic states by photons with $\lambda = 300 – 400$ nm can emit light, as a radiationless process would be much too slow in this situation. It can be estimated by Einstein coefficients that the time of spontaneous emission or the fluorescence time for these molecules is about $10^{-7} – 10^{-8}$ s and depends on the kind and temperature of the solution in which the fluorescence of the aromatic molecules is measured.

In pure water, the fluorescence intensity of a pyrene solution is low but can be enhanced by other organic molecules (specific polymers), which are added to the
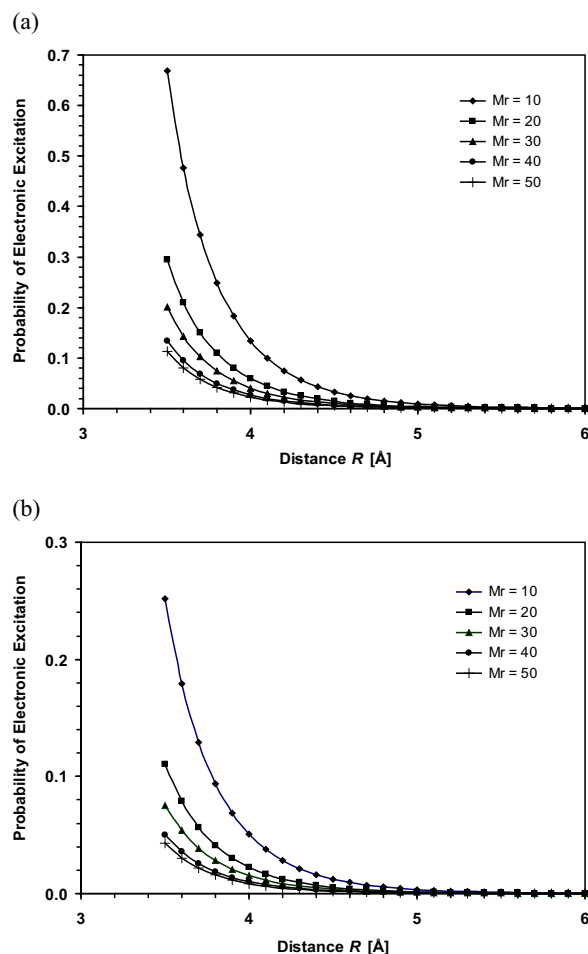
(a)

(b)

Fig. 3. Probability of electronic excitation P_{el} versus distance R calculated by (7) for pyrene (a) and naphthalene (b) by C_nH_{2n} chains with $M_r = 10$, 20, 30, 40, 50.

solution on purpose. If these molecules have hydrophobic domains and are able to aggregate and form micelles in solution, they can interact with the co-dissolved pyrene molecules. The aggregation of the molecules starts at a certain concentration. Above this concentration value, the fluorescence intensity of pyrene is rising strongly, as the pyrene molecules are more and more binding to the hydrophobic parts of the micelle molecules [8]. If the concentration falls below this critical value, the micelles begin to disassemble again.

This special reaction of pyrene is used for clinical applications in an analytical method to determine the so-called critical micelle concentration (CMC) [9]. Ultraviolet (UV) lasers with a wavelength of $\lambda =$

300 – 400 nm or a photon energy of 3 – 4 eV are usually applied to induce the electronic excitation and fluorescence of pyrene in solution. Such high photon energies can dissociate some covalent bonds of the organic molecules, which are forming the mentioned micelles. Thus, commonly used fluorescence probe techniques may run into problems caused by misinterpretations of the probe results [10].

The molecules mostly used for the formation of micelles are containing hydrophobic domains of the type C_nH_{2n} ($n = 5$), which are able to interact with pyrene probe molecules by Förster forces [9]. We suggest to apply these structures as an internal source of energy for selective electronic excitation of probe molecules and their subsequent fluorescence. As it was shown in our previous works [3, 4], this source can be obtained by accumulation of vibrational energy in molecular C_nH_{2n} structures which act as antennas for IR radiation. In our method, we propose to irradiate micelle solutions containing pyrene probe molecules by IR photons with wavelengths of $16 – 18\,\mu$m. It is possible to estimate the required flux of IR photons depending on τ_R. As an example, if the IR antenna is C_5H_{10}, the radiation flux should exceed the value $J = 3.3 \cdot 10^{10}\,\text{J/cm}^2\text{s}$ for $\tau_R = 10^{-12}$ s. This excludes possible UV-induced dissociation of the dissolved micelles and probe molecules. Using this method, the first appearing of the fluorescence will allow determination of the CMC easily.

5. Conclusion

In the frame of a suggested quantum model, we describe the process of vibrational energy transport in a donor–acceptor system consisting of two specific organic molecules. The vibrational energy is acquired by absorption of IR photons during an irradiation period of $\tau = 10 \cdot 10^{-12}$ s. It is assumed that the donor molecule has a permanent dipole momentum and contains a C_nH_{2n} IR antenna. Collective vibrational excitations (excimols) appear in the antenna with a lifetime of $\tau_{ex} = 10^{-11}$ s and the energy 0.07 eV. The aromatic acceptor molecule has no permanent dipole momentum and is not sensitive to IR radiation. It is shown that a dipole momentum is induced in the acceptor molecule if it resides in the influence range of the electric field of the IR antenna. In this case, the vibrational energy can be transferred from the donor to the acceptor by dipole–dipole interactions.

The value of the induced dipole momentum of the acceptor depends on the distance R between the interacting molecules; R is in the interval $[3 – 6\,\text{Å}]$. This value also depends on the polarizability coefficients of the aromatic molecules, predominantly of those coefficients corresponding to the plane perpendicular to the rotation axis. These results are in a good agreement with experimental data [1].

We analyzed the probability function for electronic excitation of the aromatic acceptor molecules in the considered system and defined the proper conditions for the appearance of fluorescence. The mentioned donor–acceptor system can serve as an alternative and non-destructive analytical method using aromatic molecules as a fluorescence probe [8].

In summary, the proposed model of the donor–acceptor system is considered as an energy transformer which is able to collect vibrational energy by multi-excitations to convert it into electronic excitation by dipole–dipole interactions and to release the energy again by fluorescence or even by ionization of the acceptor molecules.

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