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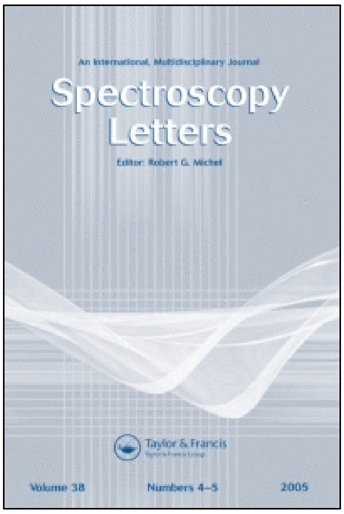

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INTERMOLECULAR ELECTRONIC ENERGY TRANSFER IN THE GAS PHASE

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ABSTRACT. The kinetics of triplet-triplet energy transfer in the gas phase has been studied for various donor-acceptor pairs of aromatic hydrocarbons and ketones. For all the donor-acceptor pairs investigated the triplet-triplet energy transfer efficiencies are much lower than unity. The triplet triplet energy transfer was used to gain insight into the paths of intramolecular excitation energy degradation in benzophenone and anthraquinone vapours and to obtain sensitized anti-Stokes annihilation delayed fluorescence of vapours of anthracene and its derivatives.

The intermolecular triplet-triplet transfer (T-T transfer) of excitation energy and sensitized phosphorescence were first discovered in 1952 by Terenin and Yermolayev in organic solutions[1]. Later these phenomena became known for liquid solutions[2], crystals[3], and also for vapours[4-10]. And though the nature of interactions underlying the T-T energy transfer phenomena in different aggregate states is the same, a number of specific features is observed in the vapour phase. The study of these processes makes it possible to obtain additional information on interacting molecules.

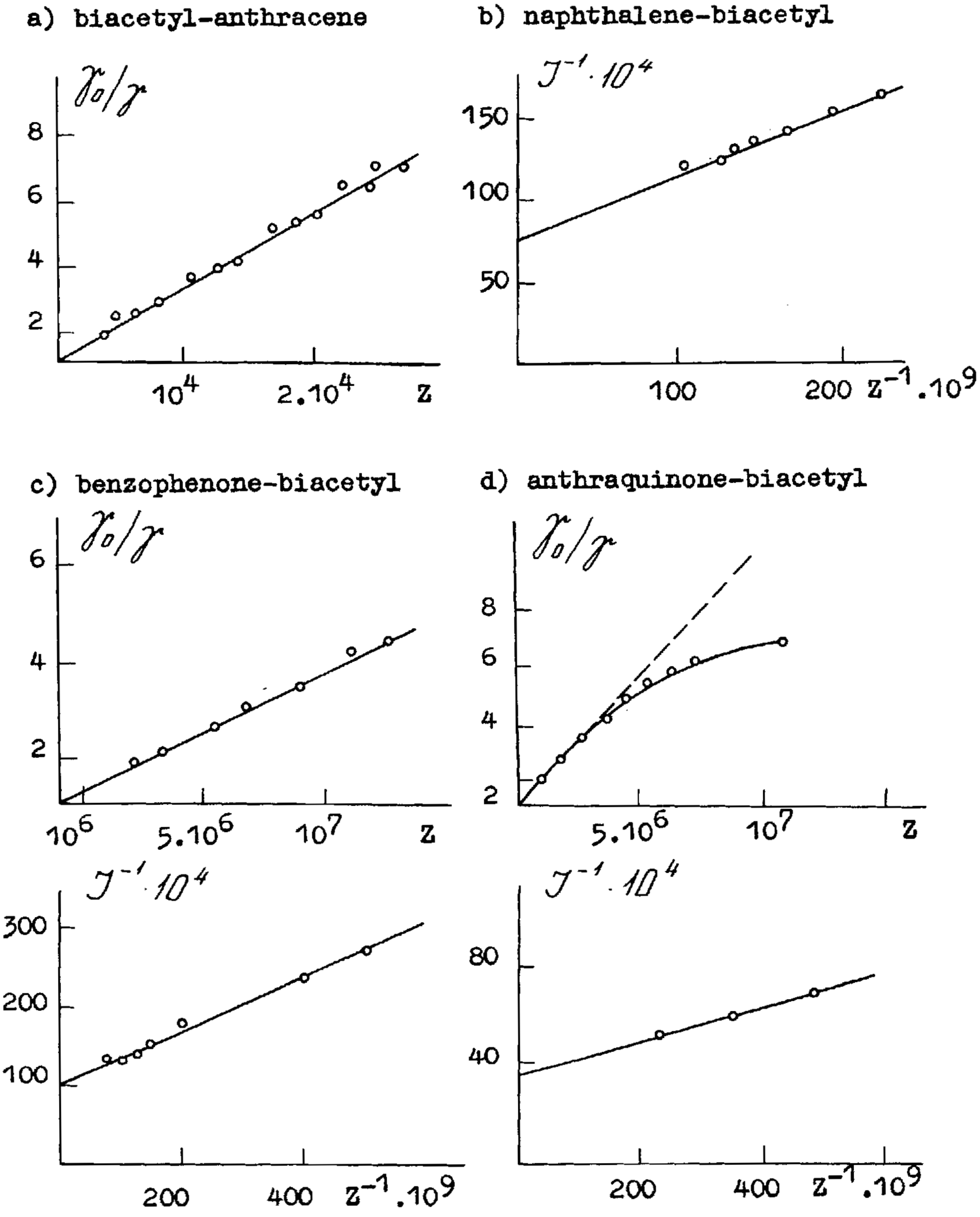
Let us first consider the kinetics of T-T energy transfer. As it is known, in some cases bimolecular reactions, including T-T energy transfer, proceed in liquid solutions at the "encounter" of reacting partners. Due to the fact that the reacting partners are surrounded by molecules of the solvent which hinder their fast departure, multiple collisions between the reacting molecules take place during the "encounter". Owing to this, T-T energy transfer in liquid solutions often takes place with a single efficiency per each "encounter" (transfer rate constant equals the diffusional one), i.e. it is diffusion controled, even when not every collision of the donor with acceptor results in energy transfer.

However, in gas phase systems the concepts "encounter" and "collision" are equivalent. Therefore, studying the kinetics of energy transfer between donor and acceptor molecules, it is possible to determine the transfer efficiencies per one gas-kinetic collision. Investigations of this kind have been carried out by the authors of this paper for the donor-acceptor pairs of aromatic hydrocarbons and ketones with lower triplet levels of different electronic configuration.

If donor molecules phosphoresced rather intensively, the transfer efficiency was determined by phosphorescence quenching of the donor. When donor had no marked phosphorescence in the gas phase, the transfer efficiency was determined by increasing the sensitized phosphorescence of the acceptor, as it was done for solutions in paper[11]. But in case the donor and acceptor phosphoresced, the transfer efficiency was determined by both methods. In calculating the number of gas-kinetic collisions the following radii values of colliding molecules were used: anthracene - 5Å, anthraquinone - 5Å, benzophenone - 4Å, biacetyl - 3Å, naphthalene - 3Å.

For the donor-acceptor pairs studied the singlet-singlet energy transfer was of no essential significance. Only at relatively high concentrations of the acceptor (1 mm Hg) in the naphthalene-biacetyl pair did this process become noticeable. The determination of T-T energy transfer efficiency was carried out for this pair at low concentrations of the acceptor.

Curves of phosphorescence quenching of the donor as well as of the increase of sensitized phosphorescence of the acceptor are given in Fig.1. As seen from Fig.1a,c phosphorescence quenching of biacetyl by anthracene and of benzophenone by biacetyl in coordinates of γ_0/γ (relation of quantum yield of non-quenched phosphorescence to quantum yield of the quenched one) and Z (number of collisions per second of the excited donor molecule with molecules of the acceptor) is described by the linear relation. The increase of sensitized naphthalene and benzophenone phosphorescence of biacetyl vapours represented as inverse intensity J^{-1} function of this phosphorescence versus the inverse number of Z^{-1} collisions of the triplet molecule of the donor with acceptor molecules is also linear. Phosphorescence quenching of anthraquinone vapours by biacetyl (curve 1 in Fig.1a) takes place with marked deviation from the linear law. This is due to the inverse energy transfer from biacetyl to anthraquinone and to the absorption, though small, of the exciting radiation by the acceptor. The phosphorescence quenching efficiency of anthraquinone vapours by biacetyl, on the


a) biacetyl-anthracene

b) naphthalene-biacetyl

c) benzophenone-biacetyl

d) anthraquinone-biacetyl

FIGURE 1. Donor phosphorescence quenching (γ_0/γ versus Z) and acceptor phosphorescence sensitization (J^{-1} versus Z^{-1}).

grounds mentioned above, was determined from the slope of curve 2, Fig.1 which is tangential to curve 1 at the point corresponding to zero vapour pressure of the acceptor. Though for the naphthalene-biacetyl pair $\mathcal{J}^{-1}$ versus Z^{-1} is linear, an inverse transfer is possible, since the energy difference of the triplet levels of these molecules is less than 2000 cm^{-1}, and the temperatures of vapours are comparatively high.

From the slope of quenching curves ($\mathcal{J}_0/\mathcal{J}$ of Z) and sensitization curves ($\mathcal{J}^{-1}$ of Z^{-1}) the product of the lifetime of donor triplet molecules τ_D and the donor phosphorescence quenching efficiency $\mathcal{E}_q$ are found, as well as the product of τ_D and the efficiency of acceptor phosphorescence sensitization $\mathcal{E}_S$. The values of τ_D necessary for the calculation of $\mathcal{E}_q$ and $\mathcal{E}_S$ efficiencies were determined experimentally. The measured lifetimes and estimated quenching and sensitization efficiencies are given in Table 1. Temperatures T^{o}K and vapour pressures P mm Hg of donor are also given in this table.

For the given donor-acceptor pair the efficiency values $\mathcal{E}_q$ and $\mathcal{E}_S$ are practically the same. The measured quantum yields of biacetyl phosphorescence sensitized by benzophenone and its phosphorescence at direct excitation in the quantum yield constancy region (λ_{ex}=436-405 nm) are equal. It follows that in the present case the only donor phosphorescence quenching process is T-T energy transfer to the acceptor. Therefore, the efficiencies $\mathcal{E}_q$ and $\mathcal{E}_S$ correspond to the efficiencies of the T-T energy transfer. The efficiency of energy transfer from benzophenone to biacetyl proved to be much lower than unity. In paper[6] efficiency of T-T energy transfer for this pair was assumed to be unity. The value $\tau_D \approx 10^{-8}$sec found on this basis turned out to be some orders of magnitude lower than the measured one (see Table 1).

The efficiency of the T-T energy transfer for the biacetyl-anthracene pair is two orders of magnitude higher than that for the benzophenone-biacetyl pair. It is probable that to perform the energy transfer act, a certain mutual orientation of partners is necessary. The localization of electronic excitation on carbonyl groups of both molecules of the benzophenone-biacetyl pair greatly decreases the probability of orientation of partners upon collision which results in the T-T energy transfer. This orientation is in the long run realized in solutions during "encounter" at multiple collisions.

TABLE 1

Efficiencies of donor phosphorescence quenching $\mathcal{E}_q$ and acceptor phosphorescence sensitization $\mathcal{E}_s$.

donor	acceptor	T^0K	p_D, mm Hg	$\mathcal{E}_q \cdot \tau_D$, sec	$\mathcal{E}_s \cdot \tau_D$, sec	τ_D, sec
biacetyl	anthracene	363	20	$2{,}3.10^{-4}$	-	$1{,}05.10^{-3}$
naphthalene	biacetyl	353	3,1	-	$1{,}9.10^{-7}$	$0{,}5.10^{-3}$
benzophenone	biacetyl	433	4,5	$2{,}8.10^{-7}$	$3{,}1.10^{-7}$	$0{,}14.10^{-3}$
anthraquinone	biacetyl	453	0,21	$7{,}3.10^{-7}$	$5{,}5.10^{-7}$	$0{,}15.10^{-3}$

	$\mathcal{E}_q$	$\mathcal{E}_s$
biacetyl-anthracene	0,22	-
naphthalene-biacetyl	-	$3{,}8.10^{-4}$
benzophenone-biacetyl	$2{,}0.10^{-3}$	$2{,}2.10^{-3}$
anthraquinone-biacetyl	$4{,}9.10^{-3}$	$3{,}7.10^{-3}$

We used the T-T energy transfer to study the degradation paths of energy excitation in anthraquinone and benzophenone molecules in the gas phase. As was shown earlier[12] luminescence bands of the above compounds represent α -phosphorescence. The luminescence of biacetyl vapours sensitized by these donors is the β -phosphorescence. Donor fluorescence is rather weak and makes no marked contribution into the lumiscence. If the probability of internal conversion processes $S_1^* \rightsquigarrow S_0$ is also small the quantum yield of intersystem crossing $S_1^* \rightsquigarrow T_1^*$ must be close to unity.

Quantum yield values of intersystem crossing obtained with the use of T-T energy transfer[10] are given in Table 2. From the data in the Table it follows that at excitation in the long-wavelength region of absorption spectrum covering the first two electronic bands, the quantum yield of intersystem crossing is constant and its value is close to unity. This means that the first act in excited singlet molecules of the mentioned donors, in spite of considerable variations in the quantity of their vibronic energy, is the transition to the

TABLE 2

Intersystem quantum yields.

λ_{ex},nm / Compound	405	365	334	313	302	297	280	265	248
anthraquinone (T=443°K)	0,90	0,93	0,88	1,00	0,94	0,89	0,87	0,62	0,18
benzophenone (T=393°K)	-	1,01	1,06	0,99	1,01	0,95	1,05	1,03	0,19

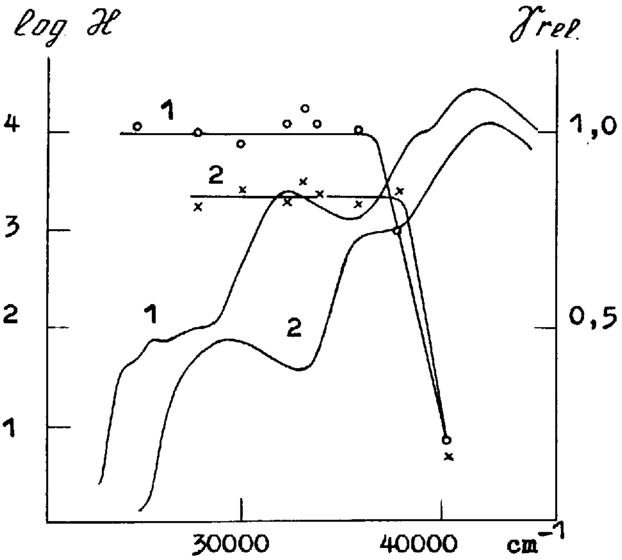


FIGURE 2. Absorption spectra and relative luminescence quantum yield of anthraquinone (1) and benzophenone (2) vapours.

triplet state which is the initial state for all further processes of emission and non-radiative degradation of electron excitation energy. However, at excitation in the third electronic absorption band the quantum yield of intersystem crossing of the compounds studied becomes much lower that unity.

The dependence of luminescence quantum yield of anthraquinone and benzophenone vapours upon the energy of excitation (Fig.2) corresponds to analoguos dependence of the quantum yield of intersystem crossing. The lifetime of their luminescence in the whole excitation region studied (405 - 248 nm) does not depend on the energy of excitation. Thus, additional processes of very efficient radiationless deactivation of the excited state arising at short-wavelength excitation (third absorption band) are not associated with the low triplet level of anthraquinone and benzophenone molecules. Probably, at the excitation of these molecules into the third electronic singlet state quickly progressing intensive photochemical processes take place.

Anthracene molecules in the gas phase in addition to fast fluorescence emit annihilation delayed fluorescence (AD-fluorescence) with a lifetime of the order of 10^{-3} sec. The appearance of AD-fluorescence results from the radiationless electronic energy transfer from one excited triplet molecule to the other excited triplet molecule with the formation of a higher energy singlet state. The AD-fluorescence spectrum is identical to the fast fluorescence spectrum. If for some donor-acceptor pair the first excited triplet level of the donor is higher and the first excited singlet level is lower than the corresponding levels of the acceptor one may expect for such a pair the appearance of sensitized anti-Stokes annihilation delayed fluorescence (SAAD-fluorescence) as a result of two consecutive radiationless electron energy transfer processes (T-T energy transfer from donor to acceptor and then T-T annihilation of acceptor molecules). This situation is realized for the biacetyl-anthracene pair[9].

At selective excitation of only biacetyl vapours by radiation λ_{ex}= 436 nm which is not absorbed by anthracene, delayed luminescence of anthracene is observed with a lifetime equal to the lifetime of AD-fluorescence ($\tau_{ADF} = 0{,}58.10^{-3}$ sec, P = 5.10^{-2} mm Hg, T = 400^{o}K; $\tau_{SAADF} = 0{,}57.10^{-3}$ sec, P = 5.10^{-2} mm Hg, T = 400^{o}K). The square-law dependence of SAAD-fluorescence intensity upon the intensity of exciting radia-

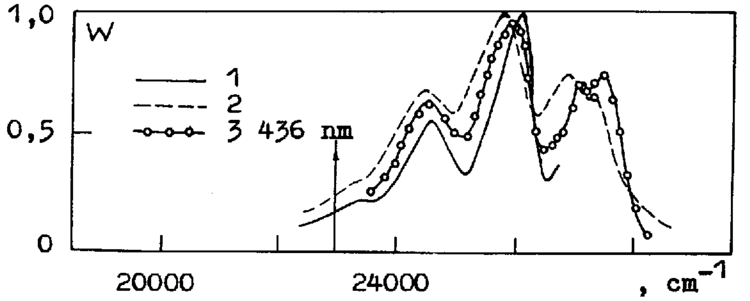


FIGURE 3. Fast fluorescence (1 - λ_{ex} = 365 nm, 2 - λ_{ex} = 313 nm) and SAAD-fluorescence (3 - λ_{ex} = 436 nm) spectra of anthracene vapours.

tion and upon the concentration of donor molecules points directly to the bimolecular annihilation nature of sensitized luminescence of anthracene.

The spectra of fast and SAAD-fluorescence of anthracene vapours are shown in Fig.3.

The dependence of the position and form of short-lived fluorescence spectrum upon a quantum of the exciting energy $h\nu_{ex}$ is typical for the rarified vapours. The comparison of fast and SAAD-fluorescence anthracene spectra makes it possible to determine the position of the lowest triplet energy of annihilating molecules. The average vibronic energy $\bar{E}_{S_1^*}$ of molecules in a singlet excited state produced by annihilation of two triplet molecules is twice the average vibronic energy $\bar{E}_{T_1^*}$ of molecules in the triplet state. Having found the value of the exciting quantum for which the fast fluorescence spectrum coincides with the SAAD-fluorescence spectrum, it is possible to estimate the triplet level energy of annihilating molecules as $\frac{h\nu_{ex}}{2}$. The value of the triplet level energy of anthracene is 15000

cm^{-1}, which is in agreement with the value found by other methods. This agreement, as well as the identity of properties of AD- and SAAD-fluorescence of anthracene vapours enables one to draw a conclusion that the appearance of SAAD-fluorescence does not result from mixed T-T annihilation of donor and acceptor molecules which could be expected, and in the present case encounters of two triplet acceptor molecules are needed.

AD-fluorescence in the gas phase is emited not only by anthracene molecules but also by its derivatives (9-methylanthracene, 9,10-dimethylanthracene, 9,10-diphenylanthracene) and pyrene. Using biacetyl as a donor of energy it was also possible to observe the SAAD-fluorescence of these compounds[9,10].

It is necessary to point out the prospects of using T-T energy transfer in investigations of delayed fluorescence of polyatomic molecules. There is no need to use the phosphoroscope to record the SAAD-fluorescence, as it was done previously, in studying AD-fluorescence. When the exciting radiation is absorbed by donor molecules and not absorbed by acceptor molecules (biacetyl-anthracene) a purely delayed fluorescence of the acceptor is observed without admixture of its fast fluorescence

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