Radiationless Deactivation of Singlet Excited States of Complex Molecules in the Gas Phase

N. A. Borisevich[a]; L. M. Bolot'ko[a]; T. F. Raichyonok[a]
[a] Institute of Physics, BSSR Academy of Sciences, Minsk, USSR

PLEASE SCROLL DOWN FOR ARTICLE

RADIATIONLESS DEACTIVATION OF SINGLET EXCITED STATES

OF COMPLEX MOLECULES IN THE GAS PHASE

L.A. Borisevich, L.M. Bolot'ko and T.F. Raichyonok

Institute of Physics, BSSR Academy of Sciences,

220602 Minsk, USSR

ABSTRACT

The ways of degradation of electronic excitation energy of singlet states of complex molecules in the gas phase with various character of dependence of the quantum yield and lifetime of fluorescence on the excess vibrational energy of excited molecules, ΔE^{*}_{vib}, are discussed. From the analysis of literature data on phthalimide and anthracene derivatives and perylene, and also from the results of investigations conducted in the present study for 9,10-dimethylanthracene and 9,10-diphenylanthracene it follows that in the majority of cases radiationless degradation of electronic excitation energy is realized both by means of intersystem crossing and internal conversion. For all studied molecules, with the exception of anthracene, an increase in intersystem crossing with increasing ΔE^{*}_{vib} of excited singlet state is observed, while the internal conversion probability may either increase or decrease. In particular, an

increase in the quantum yield and lifetime of fluores-
cence of J,10-dimethylanthracene with increasing ΔE^{*}_{vib}
proved to be due to a decrease in the internal convers-
ion probability.

An increase in the excess vibrational energy of
singlet excited states of the majority of polyatomic or-
ganic compounds in the gas phase is known to be accompa-
nied with an increase in the probability of radiation-
less transitions[1]. As a result, the quantum yield, γ ,
and lifetime,τ , of fluorescence of free complex mole-
cules usually decrease with increasing energy of the
exciting radiation quantum, $h\nu_{exc}$, and vapour tempera-
ture, T.

Radiationless degradation of electronic energy of
the first excited singlet S_1 state can be realized in
two ways: by means of intersystem crossing ($S_1 \rightarrow T_n$ tran-
sition), and internal conversion ($S_1 \rightsquigarrow S_0$ transition).
The role of each of the channels in the radiationless
dissipation of electronic excitation energy of free po-
lyatomic molecules, however, remained uninvestigated
until recently. In our studies[2,3] it has been shown for
a series of phthalimide derivatives in the gas phase
that the S_1 state energy degradation is realized through
both channels. Moreover, with increasing excess vibrati-
onal energy of the excited molecules, ΔE^{*}_{vib}, the inter-
system crossing probability usually increases more ra-
pidly, thus causing a sharp decrease in γ and τ .

However, there are some compounds whose γ remains
practically constant with increasing ΔE^{*}_{vib} (anthracene,

perylene), or even increases (9,10-dimethylanthracene)[1].
For the anthracene molecule in the gas phase intersystem
crossing proved to be the main channel of radiationless
deactivation of the S_1 state, its probability being in-
dependent of ΔE^{*}_{vib}[3]. In the case of perylene molecules
in the gas phase, internal conversion effectively compe-
tes with intersystem crossing in the course of radiation-
less dissipation of the electronic excitation energy. The
probabilities of these processes change so that their sum
remains practically constant[4].

The principle aim of the present study was to estab-
lish the ways of the degradation of electronic energy of
the S_1 states of complex molecules in the case when the
fluorescence quantum yield and lifetime increase with in-
creasing ΔE^{*}_{vib}. Vapours of 9,10-dimethylanthracene
(9,10-DMA) and 9,10-diphenylanthracene (9,10-DPA) were
studied. The first compound is characterized by an inc-
rease of the values of γ and τ with increasing ex-
cess vibrational energy of the excited molecules,
ΔE^{*}_{vib}, while the second compound, by their decrease.
The triplet-triplet absorption spectra and quantum
yields of triplet state formation of the vapours of the-
se compounds were measured in order to determine the
probabilities of intersystem crossing, d_{ST}, and inter-
nal conversion, d_{SS}.

The molecules under study were excited by the se-
cond harmonic radiation of a giant-pulse ruby laser.
Triplet-triplet absorption was recorded 100-200 nsec
after the excitation of molecules. Photoelectric method

was used to determine the intensity of the radiation of
the spectroscopic flash after passing through an unexci-
ted sample, I_{unexc}, and through the excited one, I_{exc}.
The experimentally measured ratio, I_u/I_e, was used to
determine the excited sample optical density:

$$D^T = \lg \frac{I_u}{I_e} = (\mathbf{\mathcal{X}}^T - \mathbf{\mathcal{X}}^S)n_T 1,$$

where n_T is the triplet state population; $\mathbf{\mathcal{X}}^S$ and $\mathbf{\mathcal{X}}^T$,
molecular coefficients of singlet and triplet absorpt-
ion, respectively; 1, optical path length in the sample
(14 cm). The excess vibrational energy was varied by
means of introduction into the vapour of the foreign gas
- pentane - at different pressures. It is known[5] that
the interaction of foreign gases with molecules in elect-
ronic excited states results in vibrational energy excha-
nge which leads to the change of radiationless transition
probabilities. The studied molecules, excited by the ruby
laser second harmonic radiation into the S_1 state, may be
considered isolated under the vapour pressures used, and
have the vibrational energy excess of 2600 cm^{-1}. As a re-
sult of introducing of the foreign gas (400 mm Hg) into
the vapour, the practically equilibrium distribution of
molecules over the S_1 state vibrational levels is reali-
zed. Figure 1 displays spectra of triplet-triplet absor-
ption of 9,10-DMA and 9,10-DPA in pure vapour and in the
presence of the foreign gas.

To determine n_T and $\mathbf{\mathcal{X}}^T$, we used here as well as in
our previous works the method suggested in Ref.[6]. The
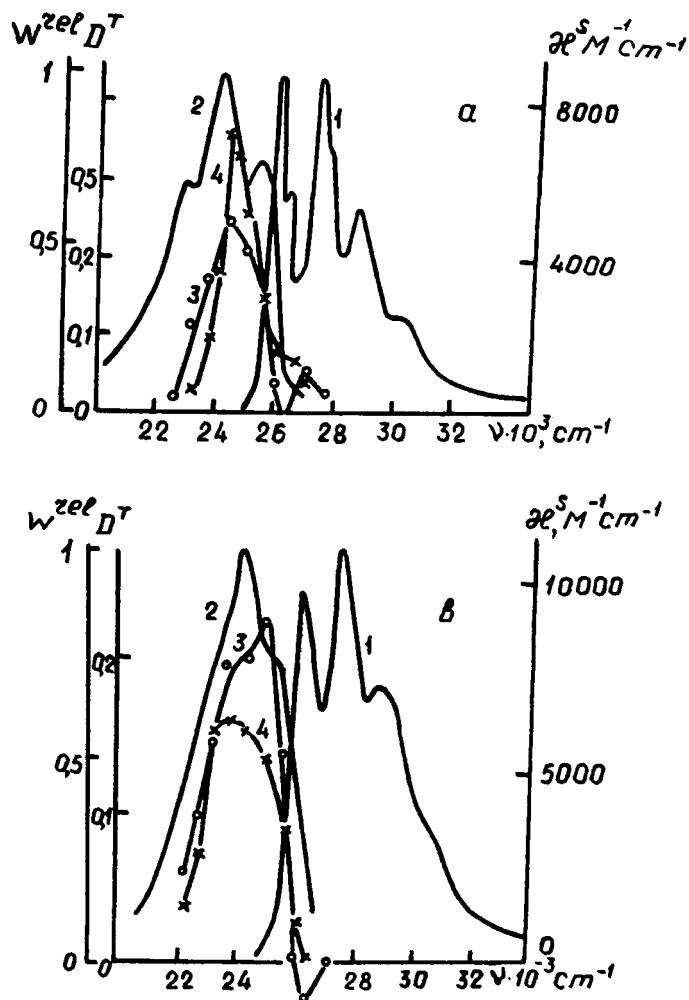absolute values of the triplet state formation quantum

Fig.1. Spectra of singlet absorption (1), fluorescence (2) and optical density, D^T, (3.4 - at different pressures of pentane, P):
a - 9,10-dimethylanthracene vapours
(P = 0.23 mm Hg, T = 443 K), 3 - P_p = 0;
4 - P_p = 360 mm Hg;   b - 9,10 -diphenyl-anthracene vapours (P = 0.3 mm Hg,
T = 525 K), 3 - P_p = 0,   4 - P_p = 400 mm Hg.

yield, η . were found from the ratio of the concentrat-
ion of triplet molecules to that of molecules which ab-
sorbed the exciting radiation. In these experiments
nearly a half of the incident exciting radiation energy
was absorbed in the cuvette. The exciting radiation po-
wer density was maintained practically constant alone
the entire cuvette length ov means of decreasing of the
cross-section area of the light beam from the beginning
of the cuvette towards its end with tne help of a focus-
ing lens. No more than 15% of molecules present in the
excited volume were converted into the triplet state.
The error of determination of the absolute values of η
did not exceed 40%, errors in relative measurements of
η were less than 15%. Using tne values of η obtain-
ed and those of γ and τ from the literature data, we
estimate the probabilities of intersystem crossing, d_{ST},
and internal conversion, d_{SS}, from the S_1 states of the
molecules under study, at various excesses of vibratio-
nal energy (see Table 1).

In the case of 9,10-dimethylanthracene, radiation-
less degradation of electronic energy proceeds through
both channels. The internal conversion yield in the S_1
state decreases with increasing excess vibrational ener-
gy (within the studied limits) from 0.52 to 0.17, the
internal conversion probability, d_{SS}, is reduced three-
fold, while the intersystem crossing probability, d_{ST},
increases approximately by a factor of 1.5. Thus an in-
crease of γ and τ with increasing $\Delta\Gamma^{*}$vib in this ca-
se is due to a more rapid decrease of d_{SS} as compared to
the increase of d_{ST}.

TABLE 1

Intersystem Crossing and Internal Conversion Probabilities

Compound	Vapour temperature, K	T-T absorption coefficient, $\mathscr{æ}^T$, $M^{-1}cm^{-1}$	T-state quantum yield, η	Fluorescence quantum yield, γ [7]	S state lifetime, τ ns [7]	$d_{ST} \cdot 10^{-3}$ s^{-1}	$d_{SS} \cdot 10^{-6}$ s^{-1}
9,10-di-methyl-anthra-cene	448	11900 ± 1700 (ν =24390 cm^{-1}) nonrelaxating molecules	0.67	0.14	3.5	1.9	0.5
		30100 ± 4500 (ν =24390 cm^{-1}) relaxating molecules (360 mm Hg pentane)	0.37	0.11	3.0	1.3	1.7
9,10-di-phenyl-anthra-cene	525	12400 ± 1800 (ν =25000 cm^{-1}) nonrelaxating molecules	0.34	0.76	3.3	1.0	–
		11000 ± 1600 (ν =23800 cm^{-1}) relaxating molecules (400 mm Hg pentane)	0.26	0.8	3.3	0.8	–

It can be seen from Fig. 1a that the optical densi-
ty, D^T, of 9,10-DMA vapours in the vicinity of the tri-
plet-triplet absorption band maximum in the presence of
pentane exceeds D^T of rarefied vapours, although the
triplet state formation yield is reduced on a decrease
of excess vibrational energy of singlet-excited molecu-
les caused by the foreign gas addition (Table 1). This
is due to an increase of the triplet-triplet absorption
coefficient resulting from vibrational relaxation of
complex molecules during interaction with the foreign
gas molecules. The increase of triplet-triplet absorp-
tion coefficient near the band maximum successfully com-
petes with the decrease of triplet molecules concentrat-
ion, n_T, due to a decrease of the probability d_{ST} upon
addition of pentane to the 9,10-DMA vapours. This can be
seen from the time dependencies of D^T (Fig. 2). In the
case of rarefied vapours, within the investigated time
interval, the intermolecular vibrational relaxation in
the triplet state does not occur, and D^T remains cons-
tant (curve 3). Contrary to this, with the pentane pre-
ssure being 360 mm Hg, the relaxation is already comp-
leted (curve 2). In the presence of pentane at 13 mm Hg,
the molecules of 9,10-DMA during their lifetime in the
excited singlet state undergo approximately one collis-
ion, and the probability d_{ST} must be less than in the
case of rarefied vapours. Consequently, at the initial
instant of observation, D^T (curve 1) is also less than
for rarefied gases. With time, D^T increases due to an
increase in triplet-triplet absorption coefficient du-
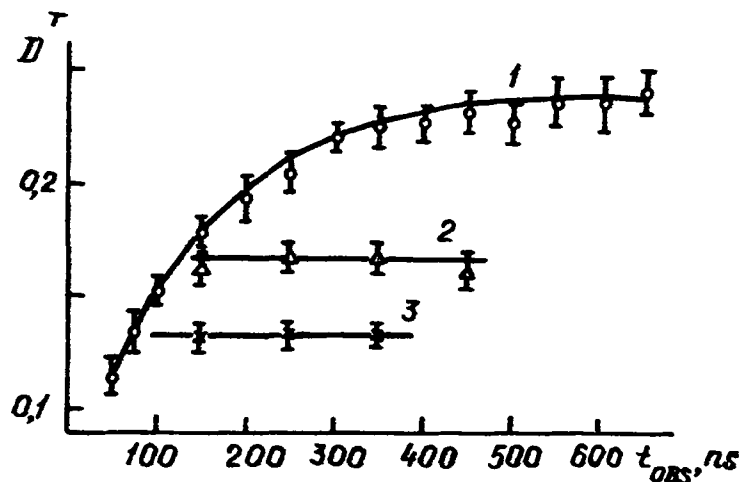ring intermolecular relaxation in the triplet state,

Fig. 2. Dependence of triplet-triplet absorption of 9,10-dimethylanthracene vapours at the frequency $\nu = 24390$ cm^{-1} on time at different pressures of pentane (1 - 13, 2 - 360, 3 - 0 mm Hg)

and becomes larger than D^T at 360 mm Hg of pentane, which is attributable to a considerably lower intersystem crossing probability at high pressure of pentane.

The sum of quantum yields of triplet state formation and fluorescence of 9,10-diphenylanthracene vapours is equal to unity within experimental error limits, which means that the radiationless deactivation of the S_1 state of this compound proceeds by intersystem crossing and its probability increases with an increase in excess vibrational energy, thus causing the decrease of the fluorescence quantum yield.

From the analysis of the data obtained by us for different classes of compounds in the gas phase (phtha-

limide and anthracene derivatives, perylene) it follows
that in the majority of cases radiationless degradation
of electronic excitation energy is realized through both
channels. For all molecules studied, with the exception
of anthracene, an increase in intersystem crossing pro-
bability with increasing excess vibrational energy of
the excited state is observed, while the probability of
internal conversion may either increase or decrease, be-
ing practically negligible for some molecules. This does
not agree with the published calculation data^{3,9}, accor-
ding to which the internal conversion probability must
increase with increasing excess vibrational energy of
singlet-excited molecules.

In the solutions of the studied aromatic hydrocar-
bons - perylene, anthracene, 9,10-dimethylanthracene and
9,10-diphenylanthracene - the channel of electronic exci-
tation radiationless degradation is the intersystem cros-
sing^{10}. This result agrees with the empirical regularity
established for solutions of aromatic hydrocarbons^{11,12},
according to which the internal conversion probability
is reduced with an increase in the energy interval betwe-
en the combining singlet electronic states. Since the
value of energy gap between the S_0 and S_1 levels of the
above-mentioned compounds exceeds 20000 cm^{-1}, the inter-
nal conversion probability must not be more than $10^6 s^{-1}$
on the order of magnitude, which is much less than the
sum of probabilities of radiation transition and inter-
system crossing, $10^3 s^{-1}$.

As we have shown earlier, in the case of perylene
and 9,10-dimethylanthracene vapours, unlike the conden-

sed phase, internal conversion is an effective channel
of radiationless energy degradation. A possible reason
for this behaviour of free molecules, the importance of
which was underlined by Terenin[13], is the enhancement
in the gas phase of torsional and deformational vibrat-
ions causing a greater molecular skeleton mobility than
in the condensed phase.

REFERENCES

1. N.A.Borisevich, Excited States of Complex Molecules
   in the Gas Phase, Nauka i Tekhnika Press, Minsk,
   1967.

2. N.A.Borisevich, L.M.Bolot'ko and T.F.Raichyonok,
   Dokl. Akad. Nauk SSSR, 243, 590 (1979).

3. N.A.Borisevich, L.M.Bolot'ko, and T.F.Raichyonok,
   Optika i Spektroskopiya, 50, 137 (1981).

4. N.A.Borisevich, L.M.Bolot'ko, I.I.Kalosha and T.F.
   Raichyonok, Dokl. Akad. Nauk BSSR, 25, 402 (1981).

5. B.S.Neporent and N.A.Borisevich, Otkrytiya v SSSR,
   (Moscow, 1973), p. 21.

6. G.Hadly and R.A.Keller, J. Chem. Phys., 73, 4351
   (1969).

7. N.A.Borisevich and G.B.Tolstorozhev, Izv. Akad. Nauk
   SSSR, Ser. Fiz., 34, 652 (1970).

8. P.Avouris, W.M.Gelbart and M.A.El-Sayed, Chem. Rev.
   72, 793 (1977).

9. G.V.Mayer and V.G.Plotnikov, Optica i Spektroskopi-
   ya, 47, 310 (1979).

10. C.Parker, Photoluminescence of Solutions (Mir Press, Moscow, 1972).

11. V.L.Ermolaev and E.B.Sveshnikova, Acta Phys. Polon. 34, 771 (1968).

12. J.B.Birks, Photophysics of Aromatic Molecules, (Wiley-Interscience, London, 1970).

13. A.N.Terenin, Photonics of Dye Molecules, (Nauka Press, Leningrad, 1967).