PHOTOPHYSICS OF HOST–GUEST INCLUSION COMPOUNDS

A. GUARINO

Istituto di Chimica Nucleare, Consiglio Nazionale delle Ricerche, Casella Postale 10, Monterotondo Stazione, I-00016, Rome (Italy)

(Received November 11, 1985)

Summary

On the basis of a set of excitation decay functions developed recently (A. Guarino, *Chem. Phys.*, **86** (1984) 445), this paper describes numerical calculations carried out both on models of host–guest inclusion compounds and on true host–guest inclusion compounds in order to assess the spreading of electronic excitation inside these compounds under γ or UV photonic irradiation. These calculations are correlated with the experimental behaviour of irradiated inclusion compounds.

The influence of factors such as the anisotropy of the energy transfer process or the ratio of partially empty host cavities *versus* those filled by guest molecules has been investigated in detail.

There is interest in these correlations because of the possibility of determining the feasibility of utilizing the regiospecific and stereospecific reactions which occur inside inclusion compounds, *e.g.* syntheses of ethylenic polymers useful as organic semiconductors, isomerization processes etc.

1. Introduction

The study of host–guest inclusion compounds is a rapidly expanding research area; although mainly employed in the past decade for separation purposes [1], they are now a promising synthetic tool, particularly of stereospecific products [2, 3]. There is additional interest in their study because of the possibility of mimicking the catalytic behaviour of rather complex natural structures such as enzymes [4].

A significant contribution to the knowledge of the reactivity of an inclusion compound may be gained from the quantitative study of the photophysical and photochemical processes which occur in these compounds when subjected to light or γ radiation in the solid state [5].

Many theoretical and experimental approaches have been developed to explain the phenomena that take place on light irradiation of pure and mixed organic crystals or aggregates [6]; however, the photophysical

processes concerning inclusion compounds have been studied only scarcely [7]. For these compounds, electronic energy migration (EEM) (host* → host; guest* → guest) or electronic energy transfer (EET) (host* → guest; guest* → host, in case of energy back transfer) may occur by at least three different mechanisms: via an exciton energy transfer, via a resonance coulombic multipolar transfer or via a short-range exchange transfer.

It has been shown [8] that exciton transfer of energy predominates in molecular organic crystals and aggregates; this behaviour corresponds to a "strong coupling" between the electronic wavefunctions of the molecules involved, as evidenced by the shifts and splittings in the absorption and emission spectra of the molecules when in crystals rather than their free state.

The purpose of the present paper is to study the EEM and EET processes in models and in real host–guest inclusion compounds, and subsequently to correlate these calculations with the behaviour of these compounds under γ or UV photon irradiation [9, 10].

2. Photophysical processes in inclusion compounds

In the case of inclusion compounds, a "very weak coupling" among host and guest molecules seems to be the most probable interaction [5]: the microscopic energy migration or transfer law may be expressed as
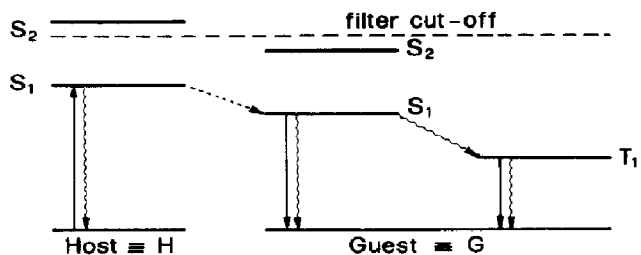
$$w(R_i) = \frac{1}{\tau_E}\left(\frac{d}{R_i}\right)^s \tag{1}$$

where $1/\tau_E$ refers to the transfer rate of any EEM or EET process, d is the nearest-neighbour host*–host or host*–guest distance, R_i is the host*–host or host*–guest crystallographic distance for any single site i occupied by an unexcited species and s refers to the kind of multipolar interaction (e.g. $s = 6$ in case of dipole–dipole interaction). It is worth observing that eqn. (1) assumes the rather unrealistic condition of an isotropic interaction among excited and unexcited species, which are taken as "points"; in order to account for the anisotropy of the interaction among the transition dipole moments of the host and guest molecules, a geometric parameter ψ_i has to be included in eqn. (1), giving an equation of the form [11, 12]
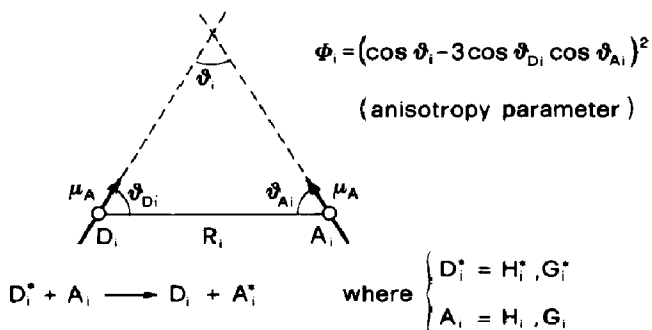
$$\psi_i = (\cos\theta_i - 3\cos\theta_{Di}\cos\theta_{Ai})^2 \tag{2}$$

where the θ_i are the angles between the donor transition dipole moment μ_H and the unexcited acceptor host or guest vectors μ_{Ai}, the θ_{Di} are the angles between the donor μ_{H*} and the distances R_{Hi} or R_{Gi} and the θ_{Ai} are the angles between the acceptor μ_{Ai} and R_{Hi} or R_{Gi}. Consequently, under anisotropic conditions, eqn. (1) becomes

$$w(R_i) = \frac{1}{\tau_E}\left(\frac{d}{R_i}\right)^s \psi_i \tag{3}$$

ⓐ Host—Guest electronic energy transfer diagram

$$\Phi_i = \left(\cos\vartheta_i - 3\cos\vartheta_{Di}\cos\vartheta_{Ai}\right)^2$$

(anisotropy parameter)

$$D_i^* + A_i \longrightarrow D_i + A_i^* \qquad \text{where} \quad \begin{cases} D_i^* = H_i^* , G_i^* \\ A_i = H_i , G_i \end{cases}$$

ⓑ The Host—Guest electronic energy transfer process.

Fig. 1. Electronic energy transfer processes for an inclusion compound.

The photophysical processes which occur inside a host—guest inclusion compound may be studied, as shown in diagram (a) of Fig. 1, by choosing host and guest molecules which possess suitable excited states, and by exciting the inclusion compound by means of adequately filtered UV photons. Figure 1, diagram (b), shows the excitation dipole moments of a donor D and an acceptor A, and their relative angles.

For the sake of simplicity, the study will be restricted to the specific situation in which the host molecules possess excited energy levels higher than those of the guest molecules, *i.e.* no excited guest → unexcited host energy back transfer may occur. Consequently, two possible photophysical processes may take place: (a) the host molecules remain totally inert to the radiation; (b) the radiation is absorbed by the host molecules which then transfer their excitation to the guest molecules.

2.1. Host molecules inert to radiation: guest molecules absorb radiation directly

In this case, host molecules act as an inert matrix, giving rise to an ordered spatial distribution of guests. This condition is to be found in many particularly useful photoprocesses such as the stereospecific polymerization of acetylenic guests or the photoisomerization of norbonadiene to quadricyclene [13].

The directly excited guest molecules deactivate via intramolecular radiative and non-radiative processes, as well as via intermolecular energy migration to other unexcited *ordered* guest molecules.

The time evolution of the EEM process is given by [5, 14, 15]

$$E_i(t) = \exp\{-tw(R_i)\} \tag{4}$$

The decay of the excitation consequent to any guest*–guest interaction is given by the product of the $E_i(t)$ functions which account for any crystallographic site i where unexcited guest molecules are present, with the exception of the site occupied by the excited guest:

$$\rho_{\mathrm{Et}}(t) = \prod_i E_i(t) \tag{5}$$

In the case of anisotropic guest*–guest interactions, the geometric parameters ψ_i of eqn. (3) become

$$\psi_i = (1 - \cos^2\theta_i)^2 \tag{6}$$

where the θ_i refer to the angles between the guest*–guest transition dipole moments μ_{Gi} and the guest*–guest distances R_i.

2.2. Host molecules absorb radiation: guest molecules are excited by energy transfer

Under these circumstances, eqn. (4) refers to both EEM host*–host interactions (eqn. (7)) and EET interactions (eqn. (8)):

$$E_{\mathrm{H}i}(t) = \exp\left\{-\frac{t}{\tau_{\mathrm{EM}}}\left(\frac{d_{\mathrm{H-H}}}{R_{\mathrm{H}i}}\right)^s\right\} \tag{7}$$

and

$$E_{\mathrm{G}j}(t) = \exp\left\{-\frac{t}{\tau_{\mathrm{Et}}}\left(\frac{d_{\mathrm{H-G}}}{R_{\mathrm{G}j}}\right)^s\right\} \tag{8}$$

where $1/\tau_{\mathrm{EM}}$ and $1/\tau_{\mathrm{Et}}$ represent the EEM and EET rates respectively; $d_{\mathrm{H-H}}$ and $d_{\mathrm{H-G}}$ are the host*–host and host*–guest nearest-neighbour distances respectively and $R_{\mathrm{H}i}$ and $R_{\mathrm{G}j}$ are the distances between the excited host and any unexcited host present in site i or any unexcited guest present in site j. Consequently, the overall decay function for a specific inclusion compound of known crystallographic structure becomes

$$\rho_{\mathrm{Et}}(t) = \prod_i E_{\mathrm{H}i}(t) \prod_j E_{\mathrm{G}j}(t) \tag{9}$$

2.3. Partially filled host cavities

It is also useful to study the photophysical behaviour of an inclusion compound when the host to guest concentration ratio is different from that expected from the crystallographic cell molecular ratio, i.e. when not all the host cavities contain a guest molecule.

In such a case many different empty and/or filled host-cavity configurations exist, with different guest molecule distributions in the cavities. For

any specific host–guest configuration k the decay function becomes

$$\rho^k_{Et}(t) = \prod_i E_{Hi}(t) \prod_j E^k_j(t)$$

If a large number N of these $\rho^k_{Et}(t)$ functions is generated by Monte Carlo simulations, the usual $\rho_{Et}(t)$ functions may be obtained:

$$\rho_{Et}(t) = \lim_{N \to \infty} \left\{ \frac{1}{N} \sum_{k=1}^{N} \rho^k_{Et}(t) \right\}$$

It has been shown experimentally that the occurrence of partially guest-filled inclusion compounds is relatively frequent [14, 16]. In this case also, two irradiation conditions will be investigated: (a) the host molecules are inert to radiation; (b) the host molecules absorb radiation.

3. Numerical calculations and correlation with real inclusion compounds

The decay functions $\rho_{Et}(t)$ discussed in the previous paragraph are particularly suitable for a numerical evaluation of the photophysical processes which occur inside an inclusion compound.

To fulfil this task the following computations were carried out.

(i) By using the X-ray crystallographic unit cell parameters for a specific inclusion compound, the atomic coordinates were calculated for the host and guest molecules corresponding to a central unit cell. The atomic sites i forming the central host cavity and the atomic sites j occupied by the guest molecule included into this host cavity will be called a "computational cell" [17]; this cell is surrounded by equivalent "images", as shown in Fig. 2. It is worth noting that the inverse sixth power transfer law requires a relatively small number of image cells to obtain reliable excitation decay functions $\rho_{Et}(t)$.

(ii) It is assumed that photons of known energy impinge on a specific surface of the computational cell, exciting a host or a guest molecule depending on the particular case investigated, i.e. whether the host molecules are inert or absorb the radiation.

(iii) Whenever the crystallographic host to guest ratio for a specific inclusion compound did not correspond to the experimental ratio, i.e. when not all the available host cavities are filled by guest molecules, a Monte Carlo simulation was employed to obtain a random distribution of empty versus filled host cavity cells corresponding to a given host to guest experimental ratio.

Three different conditions of irradiation were simulated for each inclusion compound studied: (a) isotropic energy transfer, i.e. the excited donors and acceptors are treated like "points"; (b) anisotropic energy transfer, with consequent calculation of the orientation of the molecular host → host* or guest → guest* excitation dipoles with respect to the lattice axes; (c) anisotropic energy transfer in inclusion compounds which contain host cavities partially filled by guest molecules.

ⓐ Computational cell and images

● ≡ Host
○ ≡ Guest

ⓑ Guest centred square planar inclusion compounds

A)

B)
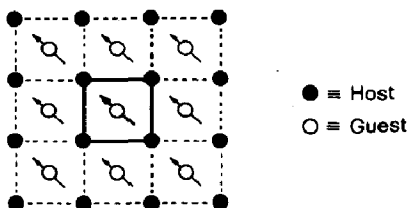
ⓒ Guest centred simple cubic inclusion compounds

A)

B)

Fig. 2. Computational host–guest cell of an inclusion compound.

The following inclusion compounds were simulated: a guest-centred square planar compound and a guest-centred cubic compound. Figure 2 shows the central cell of these two hypothetical inclusion compounds; for both, the host molecules are shown with different excitation dipole moments in order to illustrate the influence of anisotropy on the electronic energy transfer process.

The computed $\rho_{Et}(t)$ versus t/τ_E plots are reported in Figs. 3 - 6. The following observations may be deduced from these calculations.

(i) The $\rho_{Et}(t)$ values are strongly dependent on the lattice of the inclusion compound and particularly on the relative orientation of the excitation dipole moments of the host and guest molecules.

(ii) For a given structure, e.g. a guest-centred planar cell, the spreading of excitation is faster when the host molecules absorb radiation but slows down when the host molecules are inert to radiation.

(iii) Whenever the host moiety absorbs radiation but the host cavities are only partially filled by guest molecules, the spreading of excitation strongly depends on the specific host to guest ratio employed for the simulation.

In conclusion, provided the structure of the host–guest inclusion compound as well as the excitation singlet and triplet levels of the host and guest molecules are known, it is possible to estimate the EEM and/or the EET processes. These calculations may be used to make reasonable guesses
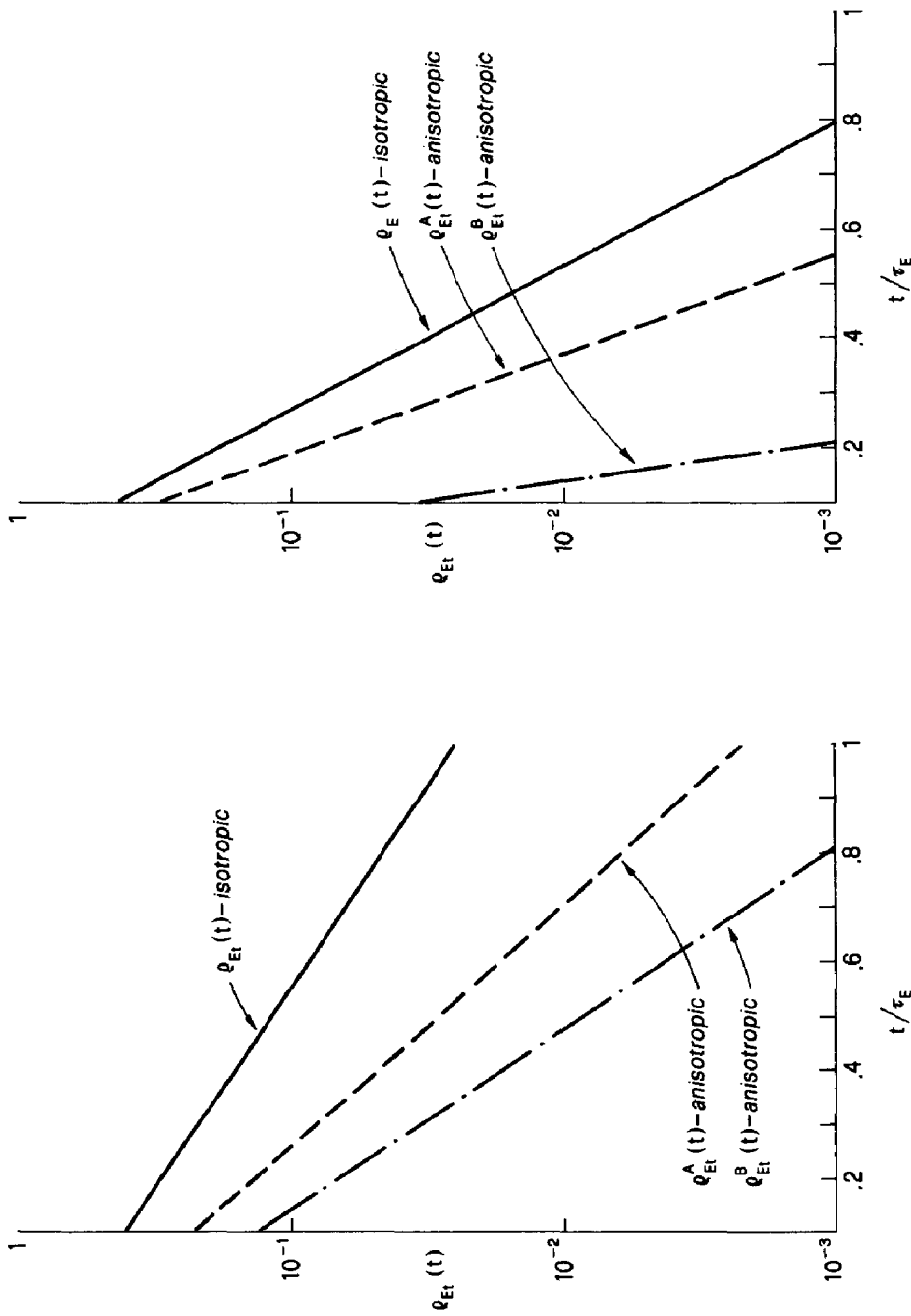
$\varrho_E(t)-isotropic$

$\varrho^A_{Et}(t)-anisotropic$

$\varrho^B_{Et}(t)-anisotropic$

$\varrho_{Et}(t)$

t/τ_E

$\varrho_{Et}(t)-isotropic$

$\varrho^A_{Et}(t)-anisotropic$

$\varrho^B_{Et}(t)-anisotropic$

$\varrho_{Et}(t)$

t/τ_E

Fig. 3. Decay functions *vs.* t/τ_E plots for a guest-centred square-planar inclusion compound (inert host): ——, isotropic $\rho_{Et}(t)$; ———, anisotropic $\rho_{Et}(t)$ for case A of Fig. 2(b); — · —, anisotropic $\rho_{Et}(t)$ for case B of Fig. 2(b).

Fig. 4. Decay functions *vs.* t/τ_E plots for a guest-centred square-planar inclusion compound (absorbing host): ——, isotropic $\rho_{Et}(t)$; ———, anisotropic $\rho_{Et}(t)$ for case A of Fig. 2(b); — · —, anisotropic $\rho_{Et}(t)$ for case B of Fig. 2(b).
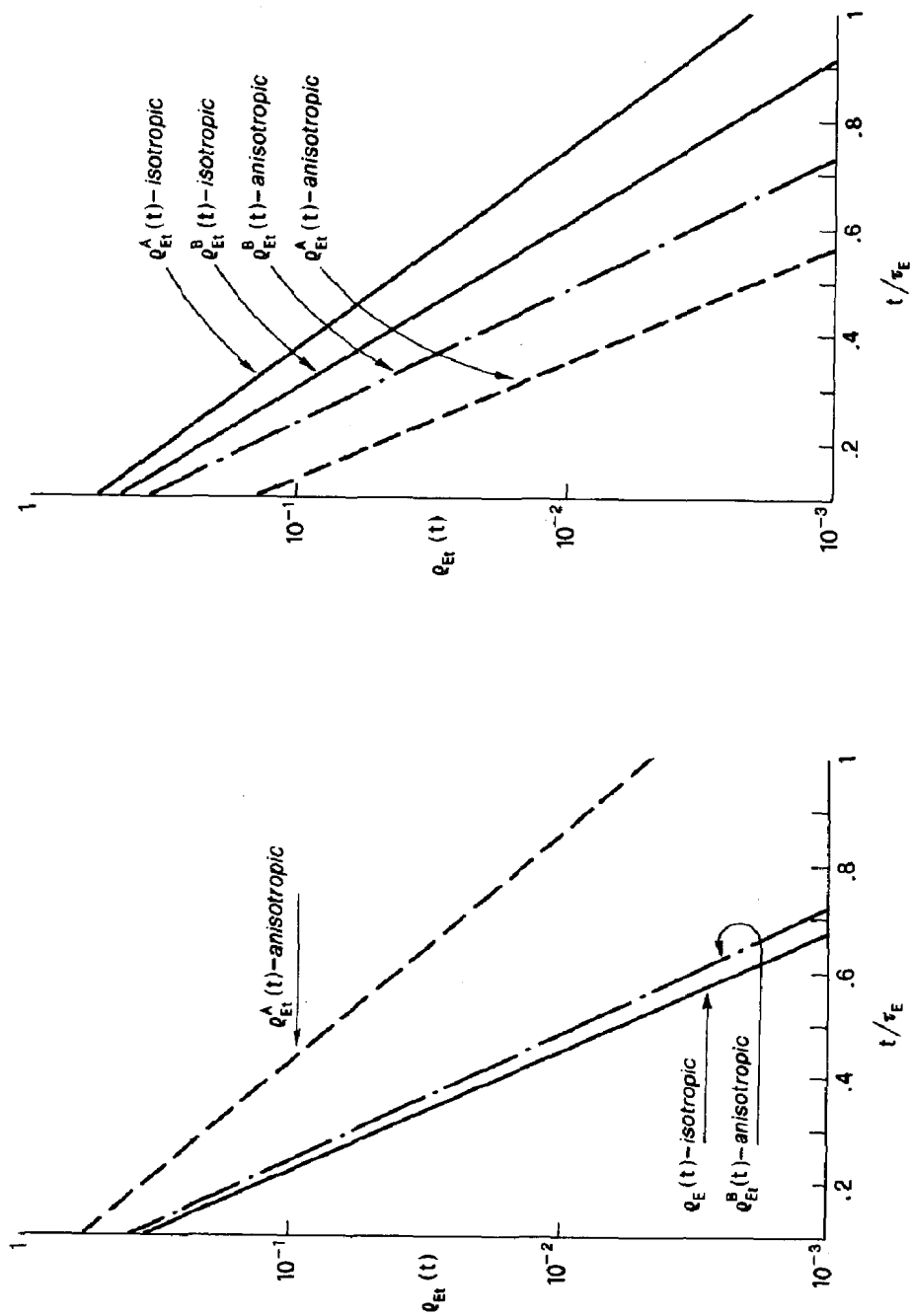
Fig. 5. Decay functions *vs.* t/τ_{Et} plots for a guest-centred cubic inclusion compound: ———, isotropic $\rho_{Et}(t)$; — — —, anisotropic $\rho_{Et}(t)$ for case A of Fig. 2(c); — · —, anisotropic $\rho_{Et}(t)$ for case B of Fig. 2(c).

Fig. 6. Decay functions *vs.* t/τ_E plots for a guest-centred cubic inclusion compound (50% of the cavities filled by guests): ———, isotropic $\rho^A_{Et}(t)$, in case A of Fig. 2(c); ———, isotropic $\rho^B_{Et}(t)$, in case B of Fig. 2(c); — — —, anisotropic $\rho^A_{Et}(t)$, in case A of Fig. 2(c); — · —, anisotropic $\rho^B_{Et}(t)$, in case B of Fig. 2(c).

TABLE 1

Structural parameters[a] and photochemistry[b] of the inclusion compound: $Ni^{II}(NCS)_2$-(4-picoline)$_4$ (host) and bromonaphthalenes (guests)

$$Br\text{-}NA + host \longrightarrow [Br\text{-}NA] \xrightarrow{h\nu} [Br\text{-}NA^*] \longrightarrow NA + Br + host$$
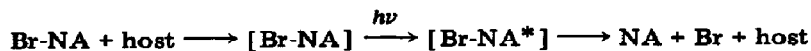
System	Space group	Molecules per unit cell		Naphthalene yield[c]
		Host	Guest	
Host plus 1-bromonaphthalene	$P2_{1/c}$	4	8	0.05
type A guest molecules[d]			4	
type B guest molecules			4	
Host plus 2-bromonaphthalene	$P\bar{1}$	1	1	0.81

[a] See ref. 19.
[b] See ref. 14.
[c] Percent of naphthalene formed at 1×10^{19} quanta cm^{-2}.
[d] Type A and B 1-bromonaphthalene molecules are differently oriented inside the host cavity.

on the extent of specific reaction processes which occur inside any real inclusion compound subjected to irradiation.

For example, it is possible to correlate the photochemical behaviour of two real inclusion compounds with the previously described numerical calculations: $Ni^{II}(NCS)_2$(4-picoline)$_4$ forms two different inclusion compounds with both 1-bromonaphthalene and 2-bromonaphthalene (which act as guests). The structures of the two complexes are rather different, as is their photochemical behaviour (see Table 1) [18].

When these two inclusion compounds are irradiated by UV photons, the dehalogenation product is formed, i.e. naphthalene. However, its yield is quite different for the two compounds.

By using the known atomic coordinates for both compounds, and by simulating the experimental host to guest ratios, numerical calculations were carried out, giving the $\rho_{Et}(t)$ versus t/τ_E plots shown in Fig. 7. It is worth noting that in the case of 1-bromonaphthalene the excited states involved are its first singlet states; these correspond to the excitation dipole moments passing through the long axis of the naphthalene rings.

By correlating the $\rho_{Et}(t)$ values for the 1-bromonaphthalene inclusion compound with those for the 2-bromonaphthalene inclusion compound, a significantly faster spreading of excitation energy may be obtained for the latter. Experimentally, this calculation corresponds to the observed larger yield of product, i.e. naphthalene, in the case where the inclusion compound contains 2-bromonaphthalene.
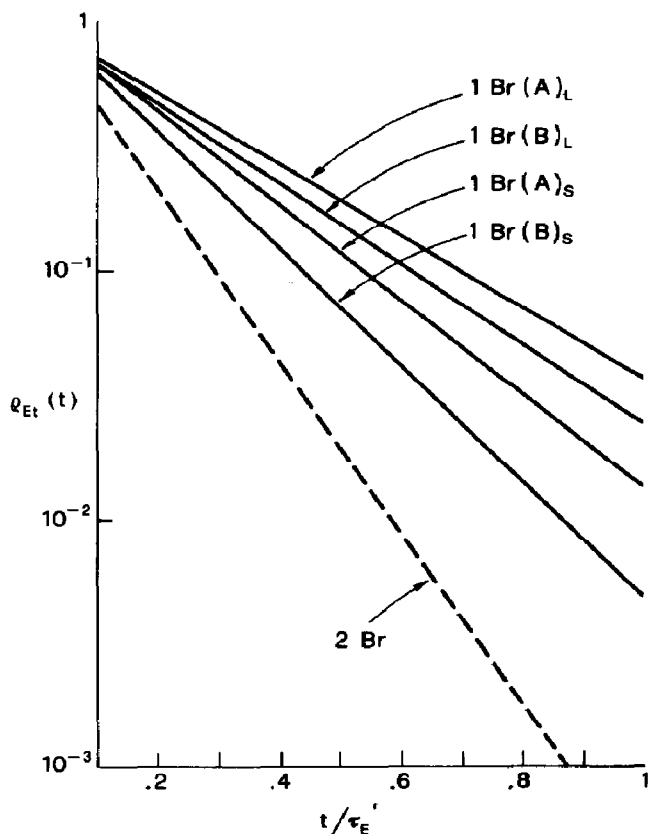
Fig. 7. Decay functions vs. t/τ_E plots for 1-bromonaphthalene (guest) and $Ni^{II}(NCS)_2$-(4-picoline)$_4$ (host): 1 Br(A)$_L$ represents the case of dipole moments of molecules A through their long axes and 1 Br(A)$_S$ the case of molecules A through their short axes: 1 Br(B)$_L$ represents molecules B through their long axes and 1 Br(B)$_S$ through their short axes. 2 Br are 2-bromonaphthalene guests.

3. Conclusions

In conclusion, provided the crystallographic structure is known, the extent of any photochemical transformation in the cavities of an inclusion compound may be estimated by computing the spreading of energy.

This treatment seems particularly appealing when applied to the formation of polymeric semiconductors in host cavities. The length and the ordering of the product polymer may be studied by computing the best spatial arrangement of the host and guest molecules; work is in progress to exploit this opportunity.

In general, a simultaneous study of EEM and/or EET processes for inclusion compounds of known structure as well as of the photochemical processes which occur in their cavities may enhance the possibility of "engineering" compounds suitable for obtaining specific phototransformations.

References

1 R. Arad-Yellin, B. S. Green and M. Knossow, *J. Am. Chem. Soc.*, *102* (1980) 1157.
2 I. Tabushi, Y. Kimura and K. Yamamura, *J. Am. Chem. Soc.*, *103* (1981) 6486.
3 R. Arad-Yellin, S. Brunie, B. S. Green, M. Knossow and G. Tsoucaris, *J. Am. Chem. Soc.*, *101* (1979) 7529.
4 R. Breslow, M. F. Czarniecki, J. Emert and H. Hamaguchi, *J. Am. Chem. Soc.*, *102* (1980) 762.
5 A. Guarino, *Chem. Phys.*, *86* (1984) 445.
6 Th. Forster, in O. Sinanoglu (ed.), *Modern Quantum Chemistry*, Part III, Academic Press, New York, 1965, p. 63.
   A. Blumen and J. Manz, *J. Chem. Phys.*, *71* (1979) 4694.
   A. Blumen, *J. Chem. Phys.*, *72* (1980) 2632.
   A. Guarino, *J. Photochem.*, *11* (1979) 273.
7 A. Guarino, *Collect. Abstr. Int. Symp. on Clathrate Compounds and Molecular Inclusion Phenomena, Jachranka, Warsaw, September 22, 1980*, Academy of Sciences, Warsaw, 1980, p. 23.
8 M. Kasha, in D. Bartolo (ed.), *Spectroscopy of the Excited State*, Plenum, New York, 1976, p. 337.
9 A. Guarino, G. Occhiucci, E. Possagno and R. Bassanelli, *Spectrochim. Acta, Part A*, *33* (1977) 199.
10 A. Guarino, in J. L. Atwood, S. E. D. Davies and D. D. MacNicol (eds.), *Inclusion Compounds*, Vol. III, Academic Press, London, 1984, p. 147.
11 P. K. Wolber and B. S. Hudson, *Biophys. J.*, *28* (1979) 197.
12 A. Blumen, *J. Chem. Phys.*, *74* (1981) 6926.
13 A. Guarino, E. Possagno and R. Bassanelli, *Chem. Phys. Lett.*, submitted for publication.
14 A. Guarino, G. Occhiucci and A. Patacchiola, *J. Photochem.*, *12* (1980) 147.
15 A. Blumen and G. Zumofen, *J. Chem. Phys.*, *77* (1982) 5127.
16 R. Gerdil and J. Allemand, *Helv. Chim. Acta*, *63* (1980) 1750.
17 J. R. Beeler, Jr., *Radiation Effects Computer Experiments*, North Holland, Amsterdam, 1983, p. 64.
18 J. B. Birks, *Organic Molecular Photophysics*, Vol. I, Wiley, London, 1973, p. 313.
19 J. Lipkowski, P. Sgarabotto and G. D. Andreetti, *Acta Crystallogr., Sect. B*, *36* (1980) 51.