

ENERGY TRANSFER PROCESSES IN LUMINESCENCE QUENCHING AND IN PHOTOLYSIS OF CLATHRATES

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i) Quenching of Organic Singlets and Triplets by Ni(II) and Co(II) complexes.

Systems are studied, in solution, at room temperature or at 77°K, consisting of the same molecules that form clathrates; in particular, the luminescence of the "guest" molecules (i.e. anthracene, I-Br-naphthalene, biacetyl) is quenched by increasing amounts of Ni(II) or Co(II) complex,  $(M(II)(4\text{-picoline})_4(NCS)_2$ . Under these circumstances, the organic molecules act as excited donors, and the Ni(II) or Co(II) complex act as acceptor. In these systems, the spatial distribution does not play the same rôle as in clathrates; i.e., electronically excited species,  $D^*$ , are now surrounded by a random distribution of acceptor species, A, and new parameters, like the presence of solvent molecules, and diffusion affect the energy transfer processes, applying the function described in another poster, to specific systems containing transition metal complex ions as acceptor.

The following points are put in evidence :

- a) The experimental quantum yield plots of  $\eta/\eta_0$  vs.  $C_A$  obtained in the quenching of anthracene excited singlet by two transition metal complex ions correspond to those calculated employing a dipole-dipole interaction mechanism; the experimental critical distance,  $R_0$ , agree with those calculated with the help of the spectroscopic overlapping integrals.
- b) The experimental quantum yield plots obtained in the quenching of biacetyl or I-Br-naphthalene triplets by the same transition metal complex ions do not agree with those obtained employing the equations for an exchange interaction transfer either in liquid or in glassy state. It seems reasonable to attribu-

te these discrepancies to the presence of impurities which act as competing triplet decay channels: particularly effective seems to be oxygen, owing its rather problematic total elimination from the irradiated samples. Further experiments are necessary in order to eliminate these secondary decay channels.

#### ii) Photolysis of Clathrates.

Purpose of these experiments is to describe the photolysis of two specific clathrates, formed by the same complex  $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$  and by 1-bromo-naphthalene or 2-bromo-naphthalene in order to study the electronic excitation energy transfer occurring, under irradiation, between the excited host, acting as the donor and the unexcited guest acting as the acceptor. The reason of employing these two compounds as acceptor, even if they possess very similar energetic, and spectroscopic properties, luminescence lifetimes, carbon-halogen bond strengths, etc..., is to emphasize, in these energy transfer processes, the rôle of the spatial relative orientation of donors and acceptors during the photolysis or radiolysis of a clathrate, as well as of the polarization of the excitation in these molecules.

The general equations for energy transfer reported in a separate poster will be employing in an attempt to rationalize the experimental results.

Two effects seem to contribute to the larger dissociation observed in the 2-Br-naphthalene clathrate: a better host-guest energy transfer, due to a larger value of the orientation parameter, and an internal effect due to the polarization direction of the excitation in the guest molecule. An additional minor effect may be attributed to recombination between naphthyls and  $\text{Br}\cdot$  radicals occurring in a different extent for the two clathrates. However, taking into account the spatial arrangement of the cages containing the halocompounds as guests, it seems reasonable to assume that the  $\text{Br}\cdot$  radicals easily diffuse, preventing significant recombination in both cases.