ELECTRONIC ENERGY TRANSFER FUNCTIONS

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A central problem in photochemistry and radiation chemistry is the study of the overall deactivation channels of any excited metastable state created by the absorption of U.V. or gamma photons in molecules, atoms, ions, etc., from the gaseous to the solid state.

A significant channel of deactivation is the transfer of electronic excitation energy from excited to unexcited species; the quantitative aspects of this fundamental process have been thoroughly studied; however, as a consequence of the often different mathematical formalisms employed, the connections among these theoretical approaches have been often overlooked, giving rise to different interaction models. Purpose of this poster is not only to emphasize these connections but also to deduce, from the known treatments, a set of equations which may account for the various interaction models suggested; in particular, the process of transfer of electronic excitation energy may be described quantitatively by specific "energy transfer functions".

In a following poster, the functions derived, will be employed in connection with energy transfer experiments.

The overall deactivation processes of an excited species have been generally described quantitatively by the so-called decay functions, $\overline{\varphi}(t)$.

After suitable algebric manipulation, it can be shown that the decay functions correspond actually to a general formula :

$$\overline{\varphi}(t) = exp\left\{-\frac{t}{\tau_0} - c_A \, H(t)\right\}$$

where C_A is the acceptor concentration, in molecules per unit volume, and $H(t)$ is a time dependent function, in volume units, describing any energy transfer process between D^* and A .

In general, the energy transfer function can be expressed as a time dependent power series containing <u>both</u> multipolar, Coulombic terms, (which account for this type of interaction between an excited donor and acceptor), and exchange terms, (which account for exchange interactions) :

$$H(t) = \sum_{i=0}^{n} a_i \, t^{m_i} + \sum_{j=0}^{n} a_j \left(\ell_n A t \right)^{m_j}$$

where a_i and a_j are numerical factors, experimentally available, and A is a constant. This reduction has the advantage of putting in evidence an "energy transfer function", $H(t)$, which, more properly, describes the energy transfer process, whichever the type of interaction, of Coulombic or exchange nature. Once expressed the transfer processes by these $H(t)$ functions, the strict connections among the various reported theoretical approaches become apparent, and, in some cases, also their unexpected equivalence. This general equation gives also the opportunity of interpreting the Stern-Volmer, and the Perrin-Ermolaev relations as particular cases. As a consequence, the Förster, the intermediate, and the Stern-Volmer kinetics can be properly represented by the same model. This fact is significant because these relations are widely employed in treating experiments of energy transfer.