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Photophysical Radiationless Transitions

PHOTOPHYSICAL RADIATIONLESS TRANSITIONS AS A FORM OF ELECTRONIC RELAXATION

The portion of the working paradigm of molecular organic photochemistry that involves the photophysical radiationless transitions that are initiated from excited states of organic molecules, in particular those that are initiated from the lowest excited singlet (*R = S_1) state and triplet state (*R = T_1).

The importance of the *R(S_1) and *R(T_1) states in organic photochemistry results from the operation of Kasha's rule for Photophysical and photochemical processes in solution and solids: namely that the radiationless deactivations *R(S_n) $\rightarrow$ *R(S_1) and *R(T_n) $\rightarrow$ *R(T_1) are much faster than any photochemistry or radiative emission from S_n or T_n. As a result the simplified state energy is the starting paradigm for the analysis or organic photochemistry in solution. Radiationless processes from S_n or T_n deactivations may be purely vibrational or both electronic and vibrational.

Radiationless transitions between electronic states may be considered as a form of electronic relaxation by which electronic energy is converted into the kinetic energy associated with nuclear motion. What factors determine the rates and efficiencies of internal vibrational and electronic radiationless transitions (which involve no change of electron spin) and intersystem crossings (which involve a change of electron spin)? What are the relationships between the rates

and probabilities of radiationless processes and the electronic configurations of the states undergoing the processes?

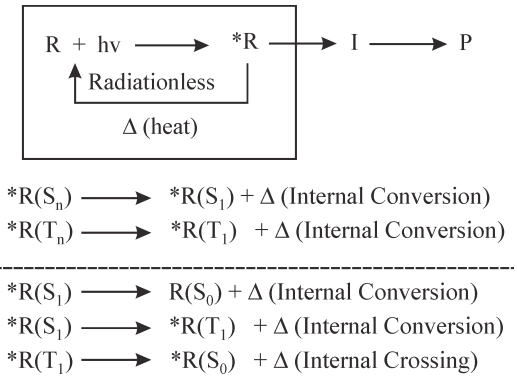

Fig. Radiationless photophysical transitions of interest to molecular organic photochemistry.

What are the relationships between the rates and probabilities of radiationless processes and quantum mechanical concepts? How can radiationless processes by visualized in terms of molecular mechanisms and representative points on energy surfaces? How are radiationless photophysical processes related to radiationless photochemical processes?

A structural and mechanistic basis for answering these questions, based on fundamental quantum mechanical principles. Photophysical and photochemical radiationless transitions may not always be sharply distinguished.

The latter can be treated as being analogous to photophysical processes, except that the conversion of electronic energy into nuclear energy causes such a distortion of the original ground state structure that the molecule does not return to its original nuclear geometry of the ground state spectroscopic minimum, S_0 (a photophysical process) but a new species, I or P is formed (a photochemical process has occurred).

A CLASSICAL INTERPRETATION OF RET AS THE MOTION OF A REPRESENTATIVE

Radiationless transitions between two electronic states in quantum mechanics corresponds to a radiationless