SPECTROSCOPIC STUDIES OF PHOTOCHEMICALLY INDUCED ENERGY TRANSFER IN VAN DER WAALS MOLECULES [a]

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Energy transfer plays an important role in a wide variety of processes, spanning from biological to atmospheric in nature. Most of the commonly encountered energy transfer processes can be understood in terms of near-resonant transition dipole induced (Förster type) or electron exchange (Dexter type) mechanisms. However, there have been rare examples of energy transfer, where the resonance criterion has severely been violated. In such cases a variety of terminologies have been used to identify these energy transfer processes. A common aspect among the different postulates is the encounter of the energy donor (D*) and energy acceptor (A) species below the van der Waals separation.

We have discovered such an energy transfer process in van der Waals O$\cdot\cdot\cdot$CO molecules, which have been generated through vacuum ultraviolet photolysis of CO_2 in rare-gas matrices using synchrotron radiation [1]. Electronic excitation of CO in the O$\cdot\cdot\cdot$CO species leads to the formation of excited CO_2, which dissociates to excited O and ground-state CO in the O$\cdot\cdot\cdot$CO species. As the first half of this process is photochemical formation of CO_2, we named this process as "photochemically induced energy transfer", whose general form of mechanism is: D* + A $\rightarrow$ (DA)* $\rightarrow$ D + A*, where * represents the localization of excitation.

Photochemically induced energy transfer (a) need not be a resonant process, like Förster or Dexter type processes, (b) there need be no spin-selection rules to be fulfilled nor the total spin angular momentum to be conserved.

Examples of photochemically induced energy transfer and other energy transfer processes in van der Waals molecules/complexes generated and stabilized in rare-gas matrices will be presented.

[1] Wagner, R., Schouren, F., and Gudipati, M. S.; **Journal of Physical Chemistry, A.** *104*, 3593, **2000**

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