Mechanisms of Photochemistry and Photobiological reactivity: Studies using Quantum Chemistry and Quantum Dynamics.

M A Robb Chemistry Dept. Imperial College London

Most chemists learn about chemical reactivity in a mechanistic way. Molecular orbital theory, resonance theory, and valence bond theory provide the basis for the rationalisation of most ground state reaction mechanisms. Photochemical mechanisms have not been developed to the same extent. This is because there are few mechanistic ideas based upon simple bonding considerations that enable the prediction or rationalisation of photochemical reactivity.

A photochemical reaction begins with the absorption of light, which promotes the system to an excited state. In order to understand photochemistry from a mechanistic point of view, we must understand how the bonding in an excited state differs from that in the ground state, since this determines the forces which govern the initial reaction path on an excited state. The other new mechanistic question arises from the fact that the photoexcited system must return to the ground state by changing from the excited state potential surface to the ground state potential surface at a conical intersection. We must thus understand how the nature of the bonding in both the excited state and the ground state balance each other to allow the radiationless transition to take place

It has now been 20 years[1] since we (together with Massimo Olivucci and Fernando Bernardi) published our first paper on a conical intersection in the prototypical organic photochemical problem: the $2_s + 2_s$ face-to-face cycloaddition of two ethylenes. In the intervening period we have systematically studied these two aspects of photochemical mechanisms using quantum chemistry and more recently using quantum dynamics. Our purpose in this lecture is to discuss some new theoretical and mechanistic ideas that have emerged. We shall choose examples from organic photochemistry and photobiology. (See recent reviews from our group [2]).

1 F. Bernardi, S. De, M. Olivucci, and M. A. Robb, Journal of the American Chemical Society **112** (5), 1737 (1990).

2 M. J. Paterson, M. J. Bearpark, M. A. Robb, L. Blancafort, and G. A. Worth, Physical Chemistry Chemical Physics **7** (10), 2100 (2005); G. A. Worth, M. A. Robb, and B. Lasorne, Molecular Physics **106** (16-18), 2077 (2008); M. J. Bearpark and M. A. Robb, in *Reviews of Reactive Intermediate Chemistry*, edited by M. S. Platz and R. A. Maitland (John Wiley & Sons, Inc 2007), pp. 379; G. A. Worth, M. J. Bearpark, and M. A. Robb, in *Computational Photochemistry* edited by M. Olivucci (Elsivier, 2005), pp. 171.