Light Induced Reactions in Cryogenic Matrices

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The investigation of light induced reactions in cryogenic matrices is nowadays a hot topic in chemistry and physics. Interesting chemical systems with potential application as molecular optical devices have been described [1-3], and new materials, such as stable covalently bound noble gas containing molecules, have been produced and characterized [4,5]. In recent years, besides the more classic photochemical processes involving electronic excited states, studies have also included hot vibrational chemistry processes, in which vibrationally excited molecules in their ground electronic state undergo chemical transformations upon infrared excitation. Matrix-isolation spectroscopy has been the main technique used in these investigations, revealing itself to be specially powerful in the identification of reaction intermediates and establishment of reaction mechanisms. Interestingly, the success of this approach may also be ascribed to the concomitant development of computational chemistry, supported by an enormous quality jump regarding both hardware and software capabilities, which provided sound theoretical foundations for the interpretation of the experimental data, and the availability at relatively low cost of tunneable lasers that could be used as adequate irradiation sources to investigate specific processes in an elegant and powerful way.

In this lecture, both UV/visible induced photochemical processes and IR induced ground state hot vibrational chemistry will be considered. The described case studies will include photochemical reactions induced by UV/visible irradiation of matrix isolated organic compounds ranging from conformational isomerizations to complex bond-breaking/bond-forming processes, a well as IR induced reactions and the intramolecular vibrational energy relaxation/redistribution processes involved in these reactions. Effects of the media on the chemical processes will also be addressed.

References

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