PHOTOCHEMISTRY, THERMOCHEMISTRY AND SPECTROSCOPY OF CARBENES

JOSEPH GUSS, PAMELA KNEPP, TIMOTHY SCHMIDT and SCOTT H. KABLE, School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia.

We have been investigating the spectroscopy and photochemistry of small carbenes for a number of years. Four triatomic fluorocarbenes, namely CF₂, CHF, CFCI and CFBr, have been the focus of our attention to date. In these experiments, we create free jet expansions of carbenes by either pyrolysis or photolysis at the nozzle orifice of appropriate halomethane precursors. Several spectroscopic techniques have been employed to probe their electronic and vibrational structure, including laser induced fluorescence, dispersed fluorescence, and photofragment excitation spectroscopy. Excited state dynamics have been probed by measuring their fluorescence lifetimes and by measuring the internal energy distribution of the nascent CF photofragment. Ab initio theoretical calculations of the X and A-state potential energy surfaces support the experimental investigation. Although members of a closely related family, the spectroscopy, photophysics and photochemistry of the first excited singlet states of each carbene is quite different. The reason for this lies in the variation in the heights of two barriers on the A-state surface: the barrier to XCF bond cleavage, and the "barrier" to linearity. The A and X-states are Renner-Teller pairs and are degenerate at linearity. Efficient crossing back to the ground state in the region of this "barrier" ensues. In CFBr, the barrier to bond cleavage is below the Renner-Teller intersection and it hence undergoes direct C-Br bond cleavage for A-state vibrational energies in excess of 3360 cm⁻¹. In HCF, on the other hand, the Renner-Teller intersection, which lies 6400 cm⁻¹ above the zero-point level in the A-state, is below the barrier for bond cleavage and hence no reaction takes place. CF₂, is remarkably stable, because the increased symmetry and strong electronegativity of the fluorine ensures that neither barrier is reached within the Franck-Condon region of the A-state. The bond cleavage barrier and linearity region have been calculated to be nearer to each other in energy for CFCI. We are currently undertaking experiments on this molecule to determine which barrier is higher, and whether any unusual dynamics might result if they turn out to be very close in energy. In this seminar, the data and calculations to support these statements will be presented, along with any new data and conclusions on CFCI.