Spectroscopy and Monitoring of High Pressure Phenomena

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Physical and chemical transformations of matter at very high pressures are of interest in many areas of research including geochemistry and planetary science, synthesis of novel materials of technological interest to be quenched at normal conditions, basic understanding of electronic properties, and behaviour of biomolecules in extreme and hostile environments. With the advent in high pressure science of the diamond anvil cell and the use of appropriately selected diamonds that are transparent in most of the optical region between the far infrared and the visible-UV, spectroscopic methods have become techniques of election, and in many instances unparalleled, to study properties and transformations of materials at very high pressures. The information obtained by optical spectroscopic techniques on materials in extreme conditions of pressure are fundamental and unique.

The purpose of this contribution is to report on studies of the mechanisms of chemical reactions and phase transformations of molecular systems at pressures above 1 GPa, using infrared, Raman and electronic spectroscopy and two-photon absorption and fluorescence methods. It will be shown that by the combined use of high pressure and photochemical activation highly selective reaction pathways (dimerization vs. polymerization) can be induced in liquid and solid butadiene and isoprene. From the time evolution of the spectral profiles of reactants and products the activation volumes can be obtained as a function of pressure and from these important information on the reaction mechanisms can be sorted out. The formation at ultrahigh pressures of polymeric materials with interesting structural and mechanical properties will be illustrated with reference to the ethylene polymerization. Infrared spectroscopy and two-photon absorption and fluorescence, in conjunction with x-ray diffraction using synchrotron radiation, have allowed to unveil the role of the changes in the electronic configurations, of the structural reorganization and of the phonon modulation of the interatomic distances as precursors of the benzene amorphization to produce an amorphous hydrogenated carbon. The microscopic counterpart (interatomic distances and molecular orientations) of the high pressure-high temperature reaction thresholds will also be discussed. Finally, the subtleties of conformational and phase transformations at very high pressure, up to the reaction threshold, will be illustrated with reference to the nitromethane crystal, a prototype system for many explosive materials.