

FTIR Study of the Reactivity of Solid CO at High Pressure

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The advent of Diamond Anvil Cell (DAC) has paved the way for the spectroscopic study of matter under extreme conditions of P and T (0.1-500 GPa, 10-5000 K) [1]. In such high density conditions simple molecular systems containing unsaturated bonds typically undergo a redistribution of the electronic density with the formation of reaction products. The reversible formation of extended polymeric solids has been reported for molecular systems like CO₂ and N₂. In other cases, like unsaturated hydrocarbons, the bond reconstruction process is irreversible and allows the recovery of reaction products at ambient conditions. Under suitable reaction conditions, such processes may show high yields and selectivity in total absence of solvent, catalysts and radical initiators, leading to the synthesis of new classes of materials with advanced optical, mechanical and energetic properties, while fulfilling the requirements for a green chemistry [2, 3]. CO is a challenging molecular system both from a theoretical and applicative point of view. The phase diagram of CO shows very strong analogies with that of nitrogen in the low P-T region. Nevertheless with increasing pressure, despite being isoelectronic, the two molecules show a very different behaviour. As a matter of fact, while the transformation of N₂ to a non-molecular solid occurs above 110 GPa and 2000 K [4], CO reacts in much milder conditions at 5.5 GPa and 300 K. The high pressure reactivity of solid CO has been investigated in several experimental and theoretical studies [5], nevertheless up to now many aspects of this subject remain unclear. These aspects, mainly related to the employment of laser light to probe the sample, concerns the PT stability region of CO, the identification of the reaction mechanism and the characterization of the reaction products. Here we report the results of a FTIR study on the high pressure reactivity of solid CO at different temperatures avoiding any exposition of the sample to laser light. The pressure was measured by means of the IR active band of a vibrational pressure sensor calibrated with respect to the ruby fluorescence scale. The reaction pressure threshold has been individuated for every investigated temperature and for each P-T point in the phase diagram we monitored the reaction kinetics in constant thermodynamic conditions until the achievement of the equilibrium. Different behaviours have been observed at 300 K and 400 K, with different reaction mechanisms and products. In both cases a bright orange solid sample is recovered at ambient conditions, but while at 300 K this is the main reaction product, at 400 K CO₂ massively forms together with the solid product. The FTIR spectra show a clear evidence of the formation of CO₂ and provide a fine insight in the different composition of the solid products.

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