Harmonic vibrational frequencies in molecules at extreme high pressure: a novel QM method

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ABSTRACT:
The study of molecular systems at extreme high pressure (order of GPa) is a field at the frontier of contemporary Molecular Quantum Mechanics [1]. We present here a new contribution to this field with a Quantum Chemical method (PCM-XP) [2] for the calculation of harmonic vibrational frequencies for molecular systems in dense medium at high pressures. The PCM-XP method, which is an extension on the Polarizable Continuum Model (PCM) [3] amply used for the study of the solvent effects at standard condition of pressure, is here illustrated by the case of diborane as a molecular system under high pressure. The PCM-XP vibrational frequencies (DFT level) of diborane are in a satisfactory agreement with the corresponding experimental results [4] as a function of the pressure. Moreover, the PCM-XP method gets a new light on the effect of the pressure on the vibrational frequencies, showing how this effect can be ascribed to two physically distinct influences (curvature and relaxation) on the potential energy for the motion of the nuclei of the molecular system.

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