Unveiling the mysteries of L-serine pressure-induced polymorphism. Why do phase transitions occur?

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Polymorphism of molecular solids has an impact on almost all physical and chemical properties. Its control is important for new medical formulations, explosives, food, semi-conductors, optics, etc. Interest to new forms can only grow through years. In 60's Walter McCrone stated that "every compound has different polymorphic forms, and that, in general, the number of forms known for a given compound is proportional to the time and money spent in research on that compound". Controlling polymorphism, and not just obtaining new forms is the key question of modern chemistry. The control requires understanding the mechanisms of phase transitions and the interplay of thermodynamic and kinetic factors. Theoretical modelling can be helpful when moving in this direction.

Pressure-induced polymorphism has been studied for many years on a large number of systems. Unfortunately, even for relatively simple systems there is no full understanding of the changes in the lattice energy and intermolecular interactions in the course of phase transitions. An example is L-serine. This amino acid was examined carefully under pressure. Two reversible isosymmetric polymorphic transitions were reported for L-serine, giving polymorph II at 5.3 GPa , and polymorph III at 7.8 GPa. Transition from form I to form II shows a significant hysteresis as confirmed by Raman spectroscopy, optical microscopy, X-ray diffraction. The phases can co-exist in a wide pressure range.

The aim of the present study was to study the changes in the crystals of L-serine resulting from pressure-induced phase transitions using computational techniques. We developed a technique to simulate the behavior of every polymorph at all pressures using widely used computational packages - VASP and Gaussian09. This helped us to understand, what would happen to a certain form of L-serine, if no pressure induced transition occurred. Total energy of the system, enthalpy and several other macro and micro parameters of the system were calculated. In other words, we compared the enthalpies, the energies of inter- and intra-molecular interactions of all three forms. We also evaluated energy profiles of every H-bond and showed that calculations of hypothetical crystal structures help to understand what would happen to bonds (energies and geometries) if no phase transition occurred.

As a result we could suggest an interpretation, what drives the two phase transitions. It was shown that every next L-serine polymorph has *less* preferable energy of the unit cell (intermolecular plus intramolecular contributions), and the phase transitions occur due to the PV term contribution. It means that decrease of volume is the driving force at the macroscopic level, but not the lattice energy term. A careful simulation and examination of the H-bond energy profile made it possible to suggest which of the H-bonds is overstrained with increasing pressure and triggers the phase transition. The second phase transition from phase II to phase III was shown to be very different in its nature.

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