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Effect of high pressure on reaction profiles and energy surfaces

JACOB SPOONER, Simon Fraser University, BRANDON YANCIW, University of the Fraser Valley, NOHAM WEINBERG, University of the Fraser Valley; Simon Fraser University — Both experiment and first principles calculations unequivocally indicate that properties of elements and their compounds undergo a tremendous transformation at ultra-high pressures exceeding 100 GPa due to the fact that the difference between intra- and intermolecular interactions disappears under such conditions. Yet, even at much milder pressures of 5-30 GPa, when molecules still retain their individual identity, their chemical properties and reactivity change dramatically. Although first principles MD is perfectly suitable and, in fact, is being increasingly used to describe these systems, its applications are severely restricted by their size and complexity. Since, as long as transition state theory remains valid, the reaction kinetics and mechanisms can be described in terms of the free energy surfaces (FESs) of the solvated reaction systems, we propose to use classical molecular dynamics to describe effects of high pressure on condensed-phase FESs by calculating effects of solvation on the quantum mechanical gas-phase potential energy surfaces. We also show that high-pressure free energy surface $G(\mathbf{x};P)$ (\mathbf{x} is a multidimensional geometrical parameter) is well approximated by equation $G(\mathbf{x};P) \approx G(\mathbf{x};0) + PV(\mathbf{x})$, where $G(\mathbf{x};0)$ is the zero-pressure free energy surface and $V(\mathbf{x})$ is the volume of reaction system in configuration \mathbf{x} .

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