Early-time thermal events behind a shock front and their relation to explosive initiation

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We consider the role, if any, of vibrational nonequilibrium in the ignition of solid explosives. Our recent theoretical work, as well as several large-scale molecular dynamics studies, all suggest that the initial nonequilibrium induced by a shock wave thermalizes far too quickly to influence shock initiation. In light of this, we examine some of the experimental correlations that have been cited as possible evidence that these nonequilibrium “up-pumping” processes may be involved in sensitivity. Particular attention is paid to recent studies of the vibrational anharmonicity and density of states of solid explosives based on temperature dependent Raman spectroscopy. Several authors have described good correlations between these properties and simple ignition tests such as a drop-weight impact. We investigate theoretically whether this correlation is even related to phonon-vibration up-pumping, or whether it is an artifact of unrelated aspects of the molecular decomposition kinetics and thermal transfer that occur during non-shock initiation.