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Accession number:20112814146418

Title:Terahertz spectrum and normal-mode relaxation in pentaerythritol tetranitrate: Effect of changes in bond-stretching force-field terms

Authors:Pereverzev, Andrey (1); Sewell, Thomas D. (1)

Author affiliation:(1) Department of Chemistry, University of Missouri-Columbia, Columbia, MI 65211-7600, United States

Corresponding author:Pereverzev, A.(pereverzeva@missouri.edu)

Source title:Journal of Chemical Physics

Abbreviated source title:J Chem Phys

Volume:134

Issue:24

Issue date:June 28, 2011

Publication year:2011

Article number:244502

Language:English

ISSN:00219606

CODEN:JCPSA6

Document type:Journal article (JA)

Publisher:American Institute of Physics, 2 Huntington Quadrangle, Suite N101, Melville, NY 11747-4502, United States

Abstract: Terahertz (THz) active normal-mode relaxation in crystalline pentaerythritol tetranitrate (PETN) was studied using classical molecular dynamics simulations for energy and density conditions corresponding to room temperature and atmospheric pressure. Two modifications to the fully flexible non-reactive force field due to Borodin et al. [J. Phys. Chem. B 112, 734 (2008)] used in a previous study of THz-active normal-mode relaxation in PETN [J. Chem. Phys. 134, 014513 (2011)] were considered to assess the sensitivity of the earlier predictions to details of the covalent bond-stretching terms in the force field. In the first modification the harmonic bond-stretching potential was replaced with the Morse potential to study the effect of bond anharmonicity on the THz-region mode relaxation. In the second modification the C-H and nitro-group N-O bond lengths were constrained to constant values to mimic lower quantum occupation numbers for those high-frequency modes. The results for relaxation times of the initially excited modes were found to be insensitive to either force-field modification. Overall time scales for energy transfer to other modes in the system were essentially unaffected by the force-field modifications, whereas the detailed pathways by which the energy transfer occurs are more complicated for the Morse potential than for the harmonic-bond and fixed-bond cases. Terahertz infrared absorption spectra constructed using calculated normal-mode frequencies, transition dipoles, and relaxation times for THz-active modes were compared to the spectra obtained from the Fourier transform of the dipole-dipole time autocorrelation function (DDACF). Results from the two approaches are in near agreement with each other and with experimental results in terms of main peak positions. Both theoretical methods yield narrower peaks than observed experimentally and in addition predict a weaker peak at ω ~ 50 cm(-1) that is weak or absent.

Number of references:31