258

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Title:Terahertz spectroscopy and solid-state density functional theory simulations of the improvised explosive oxidizers potassium nitrate and ammonium nitrate

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Abstract:Terahertz spectroscopy provides a noninvasive and nondestructive method for detecting and identifying concealed explosives. In this work, the room-temperature and cryogenic terahertz spectra of two common improvised explosive oxidizers, namely, potassium nitrate (KN) and ammonium nitrate (AN), are presented, along with detailed solid-state density functional theory (DFT) analyses of the crystalline structures and spectral features. At both 294 and 78 K, KN exhibits two terahertz absorption features below 100 cm-1 that have been assigned through DFT simulations to arise from hindered nitrate rotations in the KN-II crystalline polymorph. The terahertz spectrum of AN exhibits a pronounced temperature dependence. The 294 K spectrum is free of any absorptions, whereas the 78 K spectrum consists of several narrow and intense peaks. The origin of this large difference is the polymorphic transition that occurs during cooling of AN, where room-temperature AN-IV is converted to AN-V at 255 K. The 78 K terahertz spectrum of AN is assigned here to various ion rotations and translations in the AN-V polymorph lattice. The analysis of the room-temperature AN-IV terahertz spectrum proved to be more complicated. The solid-state DFT simulations predicted that the room-temperature crystal structure of AN is not very well described using the standard Pmmn space-group symmetry as previously believed. The AN-IV polymorph actually belongs to the Pmn21 space group, and the perceived Pmmn symmetry results from vibrational averaging through nitrate rotations. This newly observed Pmn2 1 crystal symmetry for room-temperature AN is the reason for the absence of absorption features in the 294 K terahertz spectrum of AN and provides new insight into the polymorphic transitions of this ionic solid.

Number of references:53