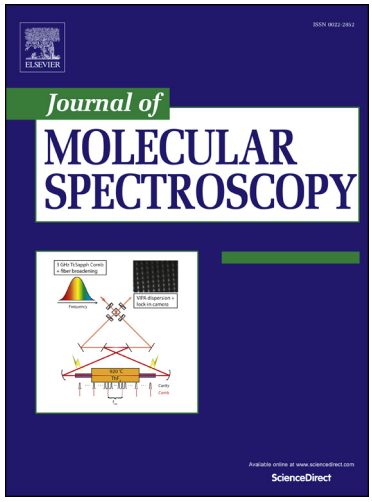

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Anharmonic, dynamic and functional level effects in far-infrared spectroscopy: phenol derivatives

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Keypoints

- Gas phase far-infrared spectra of phenol and phenol derivatives
- Comparison of Born-Oppenheimer Molecular Dynamics and Static DFT
- Calculations of hydrogen bonding, flexibility, couplings and anharmonicity
- Coupling of functional groups and their influence on theories match to experiment

Abstract

The far-infrared (far-IR) spectra of phenol and four ortho-substituted phenol derivatives, including three deuterated analogs, are presented. These spectra, measured using the free electron laser FELIX, are used to compare the performance of Born-Oppenheimer Molecular Dynamics (BOMD) with several commonly used levels of static density functional theory in the far-IR region. The molecules studied here form intramolecular hydrogen bonds of different strengths (except phenol), display diverse degrees of flexibility, and the OH moieties of the molecules provide large amplitude, anharmonic OH torsional modes. Since several of the molecules contain two OH groups, strong anharmonic couplings can also be present. Moreover, the experimental far-IR spectra of phenol and saligenin show overtones and combination bands as proven by the measurements of their deuterated analogs. All these characteristics of the molecules enable us to test the performance of the applied levels of theory on different complicating factors.