Influence of non-fundamental modes on mid-infrared spectra : anharmonic DFT study of aliphatic ethers.

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Streszczenie

Fundamental and non-fundamental vibrational modes, first overtones, and binary combination modes of selected aliphatic ethers (di-n-propylether, di-iso-propylether, n-butylmethyl ether, n-butylethyl ether, di-n-butyl ether, tert-buytlmethyl ether, and tert-amylmethyl ether) were modeled in a fully anharmonic generalized second-order vibrational perturbation theory (GVPT2) approach on the DFT-B2PLYP/SNST level. The modeling procedure of theoretical line shapes took into account conformational isomers of studied molecules. The calculated spectra of the above ethers were compared to the corresponding experimental spectra in the infrared (IR) region (4000-560 cm^{-1}) of the absorption index k(ν) derived from the neat liquid thin-film transmission data. It was found that IR spectra of aliphatic ethers are heavily influenced by the bands originating from non-fundamental modes, particularly from the combination modes in the C-H stretching region (3200-2800 cm^{-1}). Because of the effects of vibrational resonances, the intensities of overtones and combination bands originating from methyl and methylene deformation modes increase sufficiently to influence the experimental line shape in this region. Less significant contributions from non-fundamental vibrational modes were noticed in the lower IR region (1600-560 cm^{-1}), particularly in the vicinity of the C-O stretching band. The 2700-1600 cm^{-1} region, which is rich in weak bands due to non-fundamental vibrations, was reproduced accurately as well. It was concluded that a fully anharmonic approach allows significantly more accurate reproduction of the complex IR line shapes, particularly in the C-H stretching region of aliphatic ethers. On the basis of the achieved agreement between the experimental and calculated spectra, it may be concluded that the anharmonic GVPT2 method can adequately reproduce the anharmonic effects and vibrational resonances in particular, influencing the IR spectra of aliphatic ethers. The results obtained in this study show that the non-fundamental modes may play a significant role in shaping the IR spectra of aliphatic ethers and similar molecules in the neat liquid phase.

Adres publiczny

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