# Spectroscopic and quantum mechanical calculation study of the effect of isotopic substitution on NIR spectra of methanol.

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Streszczenie

In this work we studied methanol and its deuterated derivatives (CH3OH, CH3OD, CD3OH, CD3OD) by NIR spectroscopy and anharmonic quantum chemical calculations. Vibrational bands corresponding up to three quanta transitions (first and second overtones, binary and ternary combination modes) were predicted by the use of VPT2 route. The accuracy of prediction of NIR modes was evaluated through density functional theory (DFT) with selected basis sets. Based on the theoretical NIR spectra detailed band assignments for all studied molecules were proposed. It was found that the pattern of bands in NIR spectra of deuterated methanols one can use for identification of isotopically equalized forms. Calculations of NIR spectra of all possible forms of CXXXOX (X=H,D) molecules demonstrated that the isotopic contamination can be identified due to a co-existence of bands specific to OH and OD groups. Also bands from partially deuterated methyl group can be distinguished in NIR spectra. Since VPT2 framework is known to be sensitive to inaccuracy in the case of highly anharmonic modes, we obtained an independent insight by numerical solving of the time-independent Schrödinger equation corresponding to O-X stretching mode scanned within -0.4 to 2.0 Å over a dense grid of 0.005 Å. This way the energies of vibrational levels of the CX1X2X3OX4 (X=H,D) isotopologues and the corresponding transition frequencies were obtained with high accuracy (<0.1 cm(-1)). The change in normal coordinate influences the reduced mass of the oscillator and thus its frequency. Our results lead to a conclusion that the effect of deuterization of the methyl group introduces very specific and consistent frequency shift of the first overtone of O-X stretching mode depending on the substitution of X1, X2 or X3 positions (<2 cm(-1)). However, the pattern of this shift is not reproduced accurately and also largely overestimated by VPT2 calculations.

Słowa kluczowe

near-infrared spectroscopy, quantum mechanical calculation, methanol

Adres publiczny

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