Overtones of νC≡N vibration as a probe of structure of liquid CH_3CN, CD_3CN, and CCl_3CN : combined infrared, near-infrared, and Raman spectroscopic studies with anharmonic density functional theory calculations.

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Streszczenie

The νCN band (νC≡N) is a sensitive probe of the state of molecules with nitrile groups. Hence, physicochemical properties of acetonitrile and its derivatives have been frequently investigated by means of vibrational (IR and Raman) spectroscopy. Near-infrared (NIR) spectroscopy combined with high-level quantum mechanical calculations offers deeper physical insight into the structure of liquid nitriles not available from the fundamental region. This results from unique information provided by the overtones of νCN. Here, we report an application of anharmonic vibrational calculations coupled with IR, NIR, and Raman spectroscopy for investigation of the structure of CH_3CN, CD_3CN, and CCl_3CN in the liquid phase. The computational part was based on generalized vibrational second-order perturbation theory (GVPT2) applied on the density function theory (B3LYP, M06-2X, and B2PLYP) level to monomers as well as linear and cyclic dimers. The obtained data were refined by counterpoise-corrected MP2 calculations to mimic the aggregation in the liquid state. Our results evidence that the intensity variations between the fundamental, first and second overtones of the νCN band depend on the symmetry of aggregated species. The symmetry of the cyclic dimers in liquid nitriles was elucidated from the relative intensity of the 2νCN band. This work advances our understanding of the vibrational spectra of acetonitrile and its derivatives by providing detailed band assignment of IR, NIR, and Raman spectra. For the first time, we reported the position of the first and second overtones of the nitrile group.

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