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How much anharmonicity is in vibrational spectra of CH_3I and CD_3I?

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Streszczenie

This work presents new experimental and theoretical insights on vibrational spectra of CH_3I and CD_3I in the liquid phase. For the first time, we provided the contributions from different vibrational modes to mid-infrared (MIR) and near-infrared (NIR) spectra and estimated the extent of anharmonicity in the MIR region. Direct comparison of the intensities from ATR-IR and NIR transmission spectra was possible due to normalization of ATR-IR spectra. As a reference for normalization, we applied the area of the $\nu_s(CH_3)/\nu_s(CD_3)$ band recorded in transmission mode. Our results show that the corresponding vibrational modes of CH_3I and CD_3I have similar contributions to the total intensity (MIR + NIR), however, these contributions are distributed in a different way between MIR and NIR regions. As expected, most of intensity in MIR spectra originates from the fundamental transitions (>90%). The fundamental bands together with the first overtones and the binary combinations contribute to more than 99% of MIR intensity for both compounds. Therefore, reliable reconstruction of MIR spectra can be achieved by considering only these vibrational modes. On the other hand, accurate simulation of NIR spectra requires including the higher-order transitions. In the case of CD_3I, the fourth-order transitions contribute to 12.7% of NIR intensity. The contributions from NIR region are significantly smaller than those from MIR range and were estimated to be 6.7% for CH_3I and 2.3% for CD_3I. The theoretical calculations provide a reasonable estimation of the total contribution from the fundamental bands. Yet, the calculated contributions from the anharmonic transitions are different from those obtained from the experimental data. MIR spectra of CH_3I and CD_3I reveal an unexpected increase in the intensity of some overtones and combination bands indicating the presence of Fermi resonances. These resonances are responsible for differences in contributions from the first overtones and binary combinations between CH_3I and CD_3I.

Słowa kluczowe

Vibrational spectroscopy, Mid-infrared (MIR), Near-infrared (NIR), CH3I, CD3I, Vibrational intensities, Anharmonicity, Anharmonic calculations, Band assignments

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