Combined IR/NIR and density functional theory calculations analysis of the solvent effects on frequencies and intensities of the fundamental and overtones of the C=O stretching vibrations of acetone and 2-hexanone.

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Streszczenie

Vibrational overtone studies primarily focus on X—H stretching overtone transitions, where X is an atom like C, O, N, or S. In contrast, the studies on the C═O stretching overtones are very scattered. To advance the research in this field, we measured the fundamental, first, and second overtones of the C═O stretching vibration of acetone and 2-hexanone in *n*-hexane, CCl_4, and $CHCl_3$, as well as in the vapor phase using FT-IR/FT-NIR spectroscopy. Density functional theory (DFT) calculations have also been performed to help the assignment of the C═O stretching bands and to guide interpretation of the experimental results. It was found that the wavenumbers, absorption intensities, and oscillator strengths of the C═O stretching bands show marked solvent dependence. In the fundamental and the first overtone regions, the intensities of the C═O stretching vibration were found to be pronouncedly more intense than those of the C—H stretching vibration. In the second overtone region, the intensities of the C—H stretching vibration are comparable to those of the C═O stretching vibration. The theoretical and observed decrease in integrated intensity upon going from the fundamental to the first overtone of the C═O stretching vibration is around 50, which is significantly larger than those of the O—H, C—H, and S—H stretching vibration. Both the calculated and experimental results suggest that excessive weakness in the C═O stretching overtone was shown to be a result of both a low anharmonicity and a substantial reduction in the oscillator strength. These results provide new insight into our understanding of the C═O stretching vibration.

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https://www.acs.org/content/acs/en.html