Anharmonicity Effects in IR Spectra of [Re(X)(CO)$_3$(α-diimine)] (α-diimine = 2,2′-bipyridine or pyridylimidazo[1,5-*a*]pyridine; X = Cl or NCS) Complexes in Ground and Excited Electronic States

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Streszczenie

Infrared spectra of [Re(X)(CO)3(α-diimine)] (α-diimine = 2,2′-bipyridine, X = Cl, NCS, or pyridylimidazo[1,5-a]pyridine, X = Cl) in the ground and the lowest triplet electronic states were calculated by a global hybrid density functional going beyond the harmonic level by means of second-order vibrational perturbation theory (VPT2) and including bulk solvent effects by the polarizable continuum model (PCM). The full-dimensionality (FD) VPT2 is compared with the reduced-dimensionality (RD) model, where only selected vibrational modes are calculated anharmonically. The simulated difference IR spectra (excited state minus ground state) in the ν(CO) region closely match experimental time-resolved infrared (TRIR) spectra. Very good agreement was also obtained for ground-state spectra in the fingerprint region. In comparison with the harmonic simulated spectra, the calculated anharmonic frequencies are closer to experimental values and do not require scaling when the B3LYP functional is used. Several spectral features due to combination bands have been identified by VPT2 simulations in the ν(CO) spectral region, which are of importance for a correct interpretation of TRIR experiments.

Słowa kluczowe

Approximation, Chemical calculations, Excited states, Infrared light, Oscillation

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