

Dynamics of Ground and Excited State Vibrational Relaxation and Energy Transfer in Transition Metal Carbonyls

Milan Delor , Igor V. Sazanovich , Michael Towrie , Steven J. P. Spall , Theo Keane , Alexander J. Blake , Claire Wilson , Anthony J. H. M. Meijer , and Julia A Weinstein

Abstract

Nonlinear vibrational spectroscopy provides insights into the dynamics of vibrational energy transfer in and between molecules, a crucial phenomenon in condensed phase physics, chemistry, and biology. Here we use frequency-domain 2-dimensional infrared (2DIR) spectroscopy to investigate the vibrational relaxation (VR) and vibrational energy transfer (VET) rates in different solvents in both the electronic ground and excited states of $\text{Re}(\text{Cl})(\text{CO})_3(4,4'\text{-diethylester-2,2'}\text{-bipyridine})$, a prototypical transition metal carbonyl complex. The strong $\text{C}\equiv\text{O}$ and ester $\text{C}=\text{O}$ stretch infrared reporters, located on opposite sides of the molecule, were monitored in the 1600-2100 cm^{-1} spectral region. VR in the lowest charge transfer triplet excited state (3CT) is found to be up to 8 times faster than in the ground state. In the ground state, intramolecular anharmonic coupling may be solvent-assisted through solvent-induced frequency and charge fluctuations, and as such VR rates are solvent-dependent. In contrast, VR rates in the solvated 3CT state are surprisingly solvent-insensitive, which suggests that predominantly intramolecular effects are responsible for the rapid vibrational de-activation. The increased VR rates in the excited state are discussed in terms of intramolecular electrostatic interactions helping overcome structural and thermodynamic barriers for this process in the vicinity of the central heavy atom, a feature which may be of significance to non-equilibrium photo-induced processes observed in transition metal complexes in general.

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