WAITING-TIME COHERENCE DECAY IN METAL CARBONYLS AS A FUNCTION OF SOLVENT INTERACTION

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Multidimensional infrared (MDIR) spectroscopy has been used to study the properties of long-lived coherences in the carbonyl stretching region (1980-2050 cm^{-1}) of dimanganese decacarbonyl (DMDC, $Mn_2(CO)_{10}$) in different solvents. The coherences are created by the first two pulses in our three pulse sequence. The amplitudes of many peaks in the 2DIR spectrum oscillate as a function of the waiting time (between the second and third pulses); oscillation frequencies correspond to the difference frequency between the states involved in the coherence. The oscillations decay up to three times faster in a strongly interacting solvent (chloroform) than in a weakly interacting one (cyclohexane) despite similar overall signal decays in the two solvents for those peaks which do not oscillate. Further, chloroform is seen to interact differently with each of the three vibrational peaks in the region. These observations are discussed in terms of the effect of vibrational coherence on vibrational energy transfer. We explore the implications of the rate of coherence decay as an indicator of the relative frequency-fluctuation correlations of the excited states relative to one another, rather than referenced to the universal ground state.