

A Study of Equilibrium Isomerization Dynamics of Dicobalt Octacarbonyl via Ultrafast 2DIR Spectroscopy

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Abstract. Ultrafast multidimensional infrared spectroscopy was used to study the equilibrium dynamics of dicobalt octacarbonyl, a model carbonyl complex that exists as three isomers, using the terminal carbonyl stretches as probes of the equilibrium exchange. The positions of the crosspeaks in the 2DIR spectra reveal the pathways of interconversion and monitoring the crosspeaks as a function of waiting time, t_2 , yields the equilibrium rate constants. Through temperature dependent studies, the activation energies required for isomerization were determined from an Arrhenius plot.

The study of equilibrium dynamics is becoming increasingly important in understanding complex biological systems and two dimensional infrared (2DIR) spectroscopy is a powerful tool that can be used to investigate these equilibrium dynamics. The 2DIR spectra of large, complex systems can be complicated and congested making the dynamic information contained in the spectra difficult to extract. In order to gain insight into how to extract this information we have chosen to study the metal-carbonyl complex, dicobalt octacarbonyl.

Dicobalt octacarbonyl (Fig. 1) is an ideal model system: it exists as three isomers (I, II, III) in equilibrium at room temperature which have distinct terminal carbonyl stretching frequencies between 2000 cm^{-1} and 2100 cm^{-1} . Using these carbonyl stretches as a probe, 2DIR spectroscopy was employed to study the equilibrium interconversion between the three isomers. 2DIR spectroscopy has been previously applied to study chemical exchange between two different species such as solvent-solute complexes¹ and free solute rotation about a carbon-carbon single bond², hydrogen bond formation³ and fluxionality⁴. Applying 2DIR spectroscopy to dicobalt octacarbonyl extends equilibrium exchange to systems with more than two equilibrium species.

Figure 1 displays absolute value of rephasing spectra for waiting times $t_2=0\text{ps}$ and $t_2=30\text{ps}$. The peaks lying along the diagonal are due to the fundamental transitions of the different isomers. Based on previous 1D IR measurements, peaks 1a, 1b and 1c are assigned to isomer I; 2a and 2b are assigned to II; and 3a and 3b are assigned to III. The off diagonal peaks at $t_2=0\text{ ps}$ indicate the corresponding diagonal peaks have a common ground state. As t_2 increases there is a growth of off-diagonal peaks, exchange peaks, indicating that the different isomers are undergoing interconversion. From the position of the exchange peaks the mechanistic pathway by which the isomers undergo interconversion may be determined. There is evidence that isomers I and II (peaks 2a1c and 1c2a) and isomers I and III (peaks 1a3a and 3a1a) undergo interconversion; however, there is not direct evidence of interconversion between isomers II and III. By monitoring the modulations of the crosspeaks as a function t_2 the exchange times ($1/\text{rate constants}$) for the interconversions are obtained. We have determined the exchange time for the conversion of isomer I to II (1c2a) is 26 ps while the exchange time for isomer II to I (2a1c) is 30 ps. Through the use of a temperature dependent sample cell the rate constants' dependences on temperature were studied and the activation energies required for isomerization were obtained from an Arrhenius plot. The activation energy required for the isomerization of isomer I to II was determined to be $\sim 2\text{ kcal/mol}$.

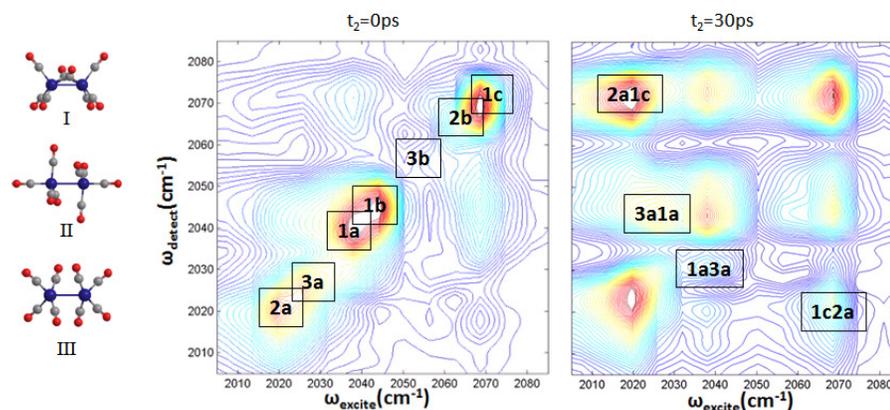


Fig. 1. The three different isomers of dicobalt octacarbonyl (B3LYP/6-31G). Absolute value of the rephasing spectrum of dicobalt octacarbonyl at $t_2=0\text{ ps}$ and $t_2=30\text{ ps}$.

References

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