# ACCOUNTS
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# Two-Dimensional Infrared Spectroscopy of Metal Carbonyls

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## CONSPECTUS

**M**etal carbonyl complexes offer both rich chemistry and complex vibrational spectroscopy due to strong coupling among the carbonyl stretches. Using two-dimensional infrared (2DIR) spectroscopy, it is possible to resolve the underlying transitions between vibrational energy levels, determine the orientations and relative magnitude of the corresponding transition dipole moments, measure the coupling between modes due to the anharmonicity of the potential, and probe energy redistribution among the modes as well as energy relaxation to other degrees of freedom.

Measurements on metal carbonyl complexes have played, and continue to play, a crucial role in facilitating the development of 2DIR spectroscopy. These compounds have provided powerful demonstrations of the unique ability of 2DIR spectroscopy to resolve vibrational structure and dynamics in multimode systems. In addition, invaluable new information has been obtained on metal-to-ligand charge transfer processes, solvent−solute interactions and fluxionality. Since transition metal complexes play important roles in catalysis and as dye sensitizers for semiconductor nanoparticle photocatalysis, detailed probes of equilibrium and phototriggered dynamics should aid our understanding of these key catalytic systems.

The richness and level of detail provided by the 2DIR spectra of metal carbonyl complexes turn them into extremely useful model systems for testing the accuracy of *ab initio* quantum chemical calculations. Accurate modeling of the 2DIR spectra of solvated metal carbonyl complexes requires the development of new theoretical and computational tools beyond those employed in the standard analysis of one-dimensional IR spectra, and represents an ongoing challenge to currently available computational methodologies. These challenges are further compounded by the increasing interest in triggered 2DIR experiments that involve nonequilibrium vibrational dynamics on multiple electronic potential surfaces.

In this Account, we review the various metal carbonyl complexes studied via 2DIR spectroscopy and outline the theoretical approaches used in order to model the spectra. The capabilities of 2DIR spectroscopy and its interplay with modern *ab initio* calculations are demonstrated in the context of the metal carbonyl complex $Mn_2(CO)_{10}$ recently studied in our lab. Continued progress in experimental implementation and theoretical analysis will enable transient 2D spectroscopy to provide structurally sensitive details of complex, highly interacting nonequilibrium processes that are central to diverse chemical transformations.
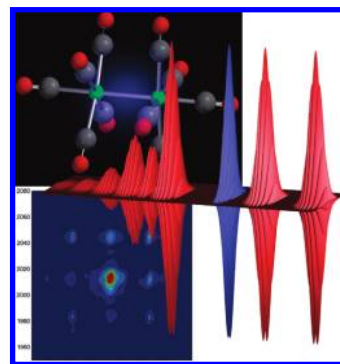
## I. Introduction

Transition metal complexes play key roles in many areas of synthetic chemistry and industrial processes. Linear IR spectroscopy has long been applied to the study of transition-metal carbonyl complexes due to the strong infrared (IR) terminal CO stretch absorption bands near 2000 cm$^{-1}$.[1,2] The enhanced oscillator strength of these bands can be attributed to back-bonding between the unoccupied antibonding $\pi^*$ orbitals and the metal d orbitals.[3] Interactions between multiple CO ligands split the vibrational bands, conveying structural information. Since the early 1990s significant experimental efforts have been directed toward understanding the dynamics of metal carbonyls using nonlinear
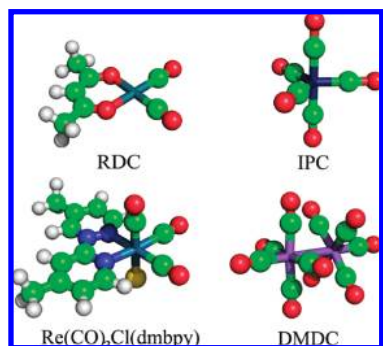
**FIGURE 1.** Structure of four metal carbonyls studied with 2DIR.

infrared methods such as transient-absorption and photon echo spectroscopy.[4] Two-dimensional IR (2DIR) spectroscopy is particularly well-suited to unraveling those spectral features and relating them to the underlying anharmonic vibrational Hamiltonian. In this Account, we review several metal carbonyl complexes studied using 2DIR spectroscopy (Figure 1) and various modeling approaches. We also report 2DIR spectra of the complex $Mn_2(CO)_{10}$ that were recently obtained in our lab, as well as results from *ab initio* calculations of the anharmonic shifts in this system.

A two-dimensional spectrum spreads information along two axes, one of which corresponds to "excitation" and the other to "detection".[5,6] The amplitude at each point in the 2D spectrum indicates how much signal is emitted at a particular detection frequency $\omega_3$ given excitation at a specific frequency $\omega_1$. Fourier transform 2DIR employs three pulses separated by time delays $t_1$ and $t_2$ interacting with the sample producing a signal during $t_3$.[7] Heterodyne-detecting the field enables the $t_1$ time axis to be converted to a frequency axis ($\omega_1$) by Fourier transformation, while each $\omega_3$ spectral point is obtained in the spectrometer directly. Most 2DIR experiments employ 64- or 128-element HgCdTe (MCT) detectors, though recently frequency conversion methods have been used to shift the IR signal into the visible where silicon CCD cameras are sensitive.[8-13]

Several reviews of multidimensional optical spectroscopy, both broad[5,6,14] and more specifically focused,[15-17] have appeared recently. Generally speaking, the majority of reports of experimental and theoretical investigations largely fall into one of three classes: (1) analysis of coupling between transitions in order to extract information about the system's Hamiltonian as well as vibrational energy redistribution and relaxation; (2) characterization of the 2D line shape to uncover interactions between the system and its environment, including spectral diffusion and chemical exchange; (3) nonequilibrium 2D spectroscopy where the system is modified, either by

temperature jump or electronic excitation before or during a 2D experiment. Metal carbonyl complexes have provided tractable model systems for each of the above classes, and we will highlight those developments here.

Various approaches can be employed for modeling 2DIR spectra. Herein, we review the following three approaches in the context of metal carbonyls: (1) phenomenological fitting to a parametrized vibrational excitonic Hamiltonian; (2) direct diagonalization of the vibrational Hamiltonian using an *ab initio*-based potential surface; (3) an approach that avoids direct diagonalization by employing vibrational perturbation theory.

## II. Experimental Studies of Metal Carbonyls

The simplest vibrational system exhibiting coupling between modes is a dicarbonyl complex. In a series of papers,[18-25] the Tokmakoff group examined several aspects of dicarbonylacetonato rhodium(I) (RDC), whose two carbonyl oscillators are coupled to form one asymmetric and one symmetric mode with fundamental vibrational transitions at 2015 and 2084 $cm^{-1}$ in nonpolar solution.[21,22] A simulated 2DIR spectrum of RDC is shown in Figure 2. Like conventional pump–probe transient absorption spectroscopy, 2DIR is a third-order non-linear optical technique, and both methods are capable of discerning the ground state bleach (GSB) and excited state absorption (ESA). Because GSB leads to a loss of absorption and ESA an increase in absorption, the two contributions have opposite signs. The GSB signals appear on the frequency diagonal ($\omega_1 = \omega_3$), while the ESA is located immediately below the diagonal, and the frequency difference $\omega_3 - \omega_1 = \Delta$ is due to the anharmonicity.

The spectrum also shows distinct cross peaks because both fundamental transitions are located on the same molecule, and the amplitudes of the cross peaks relative to those on the diagonal indicate the relative orientations of the transition dipole moments.[18,26] The cross peak at $\omega_1 = 2015$ $cm^{-1}$ and $\omega_3 = 2084$ $cm^{-1}$ indicates that the sample was stimulated to emit at 2084 $cm^{-1}$ (symmetric stretch) given that it was excited at 2015 $cm^{-1}$ (asymmetric stretch). Since the spectrum is shown at zero waiting time ($t_2 = 0$), there is no time for energy transfer between the modes, indicating that the cross peak is due solely to the sharing of a common ground state. In RDC, the ESA peaks are red-shifted by 14 $cm^{-1}$ (asymmetric) and 11 $cm^{-1}$ (symmetric). Finally, there is another set of cross peaks in the RDC spectrum which appear below the cross peaks that arise from emission at the combination band following excitation of one of the fundamentals.
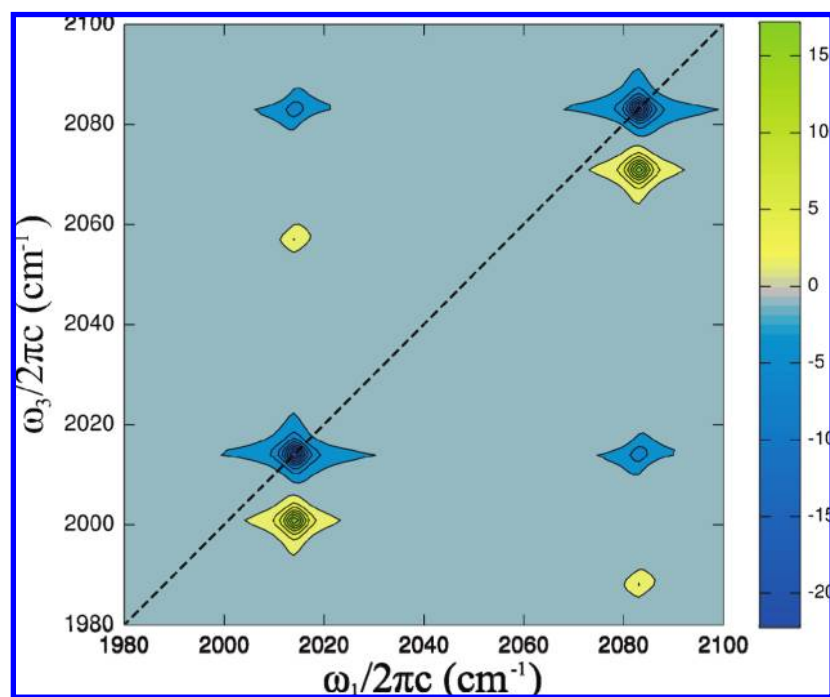
**FIGURE 2.** Absorptive 2DIR spectrum of RDC computed using the experimentally derived Hamiltonian parameters in ref 18.

The 2D spectrum provides a direct probe of the time scale of spectral diffusion. At zero waiting time, before the molecules have had time to sample other configurations, the spectrum contains correlation within a single spectral band. The signature in a 2D spectrum is the slant of the spectrum parallel to the diagonal, and the antidiagonal width reveals the actual width of the underlying transition. Using traditional language, the width along the diagonal is the *inhomogeneous* width, and that along the antidiagonal is the *homogeneous* width, though these terms lose their clear meaning in systems with complicated interactions, such as liquid water.[6] As an example, RDC in the more polar solvent chloroform exhibits inhomogeneous broadening at the initial waiting time, and as the waiting time is increased the molecules sample different environments, losing the correlation with the initially excited frequency.[21,22] The loss of correlation is evident in the relaxation of the line shape asymmetry. For RDC in chloroform, the relaxation of the asymmetry was seen to occur in ~2 ps, in agreement with three-pulse photon echo spectroscopy, a method widely used to monitor the loss of frequency memory.[21]

The 2D spectrum of metal carbonyls measured as a function of waiting time enables the separation of intramolecular vibrational redistribution (IVR) and vibrational energy relaxation (VER). Since the splitting of the carbonyl first excited states is small, between 20 and 70 cm$^{-1}$, rapid randomization of initial excitation leads to changes in the cross peak amplitudes relative to the diagonal peaks. Energy proximity is known to be insufficient to explain IVR and VER since spatial correlation is also a significant factor.[27] The most favorable conditions for IVR occur when modes involve the same atoms and when the energy gap is small. In RDC this situation is well satisfied since both eigenstates are composed of the same CO units, and IVR is observed to occur on the 1 ps time scale.[24] In a di-iron hexacarbonyl model compound of the [FeFe]-hydrogenase enzyme active site, Stewart et al. observed an alternative IVR-like process, where rapid ~5 ps vibrational redistribution was attributed to a solvent-mediated channel.[28] This relaxation mechanism may be found to play a role in describing the dynamics of the actual enzyme's function.

Pentacarbonyl iron(0) (IPC) exhibits fluxional structural interconversion through the mechanism of Berry pseudorotation.[29,30] Two of the three equatorial carbonyls exchange with the two axial carbonyls through a $C_{4v}$ transition state. Molecules are able to surmount the barrier during the time interval ($t_2$), exchanging the initially excited CO ligands, complete with their vibrational energy. The time-dependence of the cross peaks in the 2D spectrum directly probes the equilibrium interconversion.[31−33] Cahoon et al. used strong modes in IPC to track the fluxional motion through the transition state back to the starting geometry and found the 1/*e* exchange time to be 8 ps, and—using temperature dependence—a barrier of 1.6 ± 0.3 kcal/mol.[34]

The Hamm group developed methods for triggering photochemical and photophysical processes, probing them with 2DIR.[17,35−38] One variation places electronic excitation
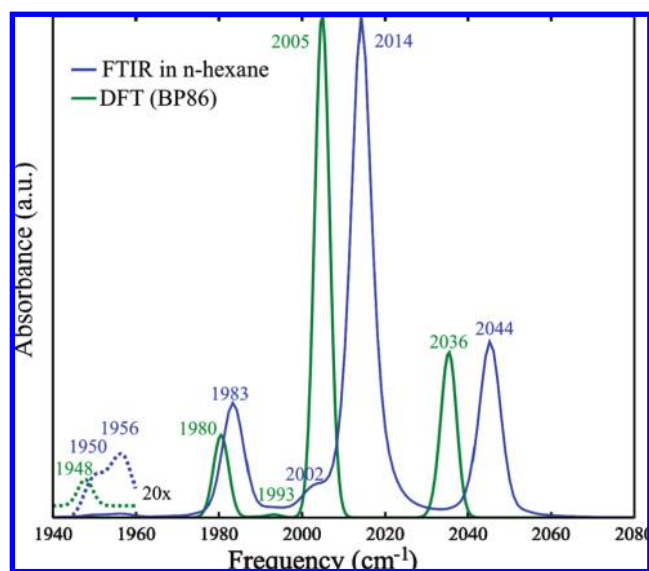
**FIGURE 3.** Experimental FTIR spectrum of 2.5 mM DMDC in *n*-hexane has peaks at 1983, 2014, and 2044 cm$^{-1}$ with weaker absorption peaks at 2002, 1950, and 1956 cm$^{-1}$ due to natural $^{13}$C isotopomers. *Ab initio* harmonic spectrum (see theory section). To simulate the isotopomer, a computed spectrum containing equatorial $^{13}$C was scaled according to natural abundance and added to the all-$^{12}$C spectrum.
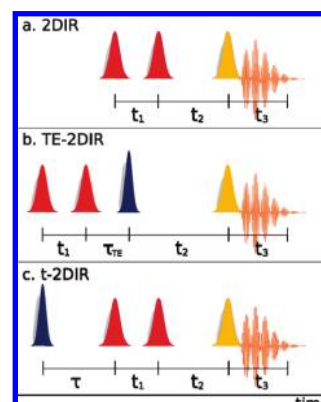


**FIGURE 4.** Fourier transform (a) 2DIR, (b) triggered-exchange 2DIR, and (c) transient-2DIR pulse sequences. The red pulses represent $\mathbf{k}_1$ and $\mathbf{k}_2$, yellow represents $\mathbf{k}_3$, and blue, the UV phototrigger. Adapted from ref 13.

between the excitation and detection steps.[35] Such vibrational labeling (or *triggered exchange*) enables tracking chemical reactions from reactants to products using the inherent correlation of 2D spectra. Bredenbeck et al. have used this method to investigate the metal-to-ligand charge transfer in Re(CO)$_3$Cl(dmbpy).[35] In the electronic excited state, the two equatorial modes corresponding to symmetric and asymmetric stretching shift to higher frequency due to the shift of electron density from the metal to the dmbpy ligand. Previous transient-absorption experiments failed to clearly identify the proper peak assignments of the transient species[39] whereas, by observing the cross peaks in triggered-exchange 2DIR spectrum, the peak assignment was easily accomplished. This experiment gave convincing evidence that transient processes could be followed yielding a mapping of the vibrational eigenstates.

In contrast to the monometal carbonyl complexes, dimanganese decacarbonyl (DMDC) presents new challenges. Within the context of reaction dynamics probed with nonequilibrium 2DIR, DMDC is an attractive system since two different photoproducts, Mn(CO)$_5$ and Mn$_2$(CO)$_9$, can be generated depending on the choice of UV pump wavelength.[40−43] The ground state geometry is a staggered $D_{4d}$ symmetry with four IR active vibrations: 1983 cm$^{-1}$ (B$_2$), doubly degenerate 2014 cm$^{-1}$ (E), 2044 cm$^{-1}$ (B$_2$) [FTIR shown in Figure 3]. Thus, in the terminal carbonyl stretching region there are six Raman active

modes that are not observed in the IR spectrum.[44] Nevertheless, intramolecular relaxation channels certainly involve exchange of energy among both the dark and bright modes. Indeed, the bright vibrational modes are highly delocalized; the two B$_1$ modes involve motion of all 10 carbonyls, while the two E modes show substantial displacement of the eight equatorial carbonyls. This system therefore provides an excellent model of a complex with substantial interplay between IR and Raman modes, which will require explicit treatment in a comprehensive model of energy redistribution, dephasing and population relaxation and coherence transfer.

Experimental implementation of DMDC 2DIR spectra (pulse sequences shown in Figure 4) were first realized in the context of demonstrating a new mode of detecting nonlinear IR signals.[11] The Fourier transform 2DIR experimental setup is described in detail in ref 11. We have based our 2DIR spectrometer on a detection approach where the mid-IR signal ($\sim$2000 cm$^{-1}$) is translated to the visible ($\sim$14,500 cm$^{-1}$) by upconversion with the 800 nm ($\sim$12,500 cm$^{-1}$) light of the Ti:sapphire-based chirped-pulse amplification system.[10] In our implementation, both the signal and reference are upconverted with a single chirped pulse and the resulting visible light is sent into a standard 0.5 m spectrometer with 1200 grooves/mm grating and a 1340 × 100-pixel silicon CCD camera. The time-delay between the first two pump pulses is controlled using two pairs of ZnSe wedges (7.3° apex angle), yielding single spectra with 2.8 cm$^{-1}$ experimental resolution (12 ps maximum $t_1$). This method allows us to collect a full 2DIR spectrum in less than ten seconds of total data acquisition time. The addition of a 400 nm pulse, obtained by frequency doubling the 800 nm Ti:Sapphire output, allows the measurement of triggered-exchange and transient 2DIR spectra respectively.
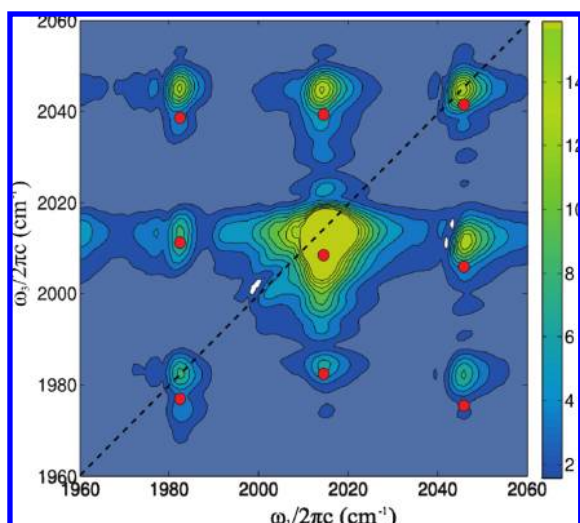
**FIGURE 5.** Absolute value rephasing 2DIR spectrum of 2.5 mM DMDC in *n*-hexane at $t_2 = 0$. The red dots represent the *ab initio* anharmonic transitions.

The 2DIR spectrum of 2.5 mM DMDC in cyclohexane solution at zero waiting time (Figure 5) reveals the nine prominent bands expected from the three-band linear spectrum. The diagonal to cross peak amplitude ratios are consistent with the known orientations of the four transition dipole moments taking into account the weighting due to the orientational correlation functions.[11,12] Using our rapid data acquisition method[11] we investigated the waiting-time dependence of the DMDC 2D spectrum. The most striking features in the data were pronounced coherent modulations of the cross peaks as shown in Figure 6.[12] Rephasing spectra were recorded at 100 fs waiting time intervals over roughly 20 ps, permitting direct Fourier transformation of the oscillatory cross peaks and a determination of their line widths. For the most well-resolved peak at $\omega_1 = 1983$ cm$^{-1}$, $\omega_3 = 2044$ cm$^{-1}$, the line width of the oscillation is measured to be 5 cm$^{-1}$. The spectral modulations are assigned to coherent excitation of distinct vibrational modes, and the observed frequency is given by the difference between the two states involved in the coherence. Previous 2D spectra have observed $t_2$ modulated quantum beats, though the spectra were not sampled in such a way as to permit direct Fourier transformation.[24] In the case of RDC, the modulations were clearly observed, but dispersed pump–probe measurements were used to observe the waiting-time dependence. Since the instantaneous frequency of the coherence is given by the difference of the instantaneous frequencies of the constituent energy levels, the correlation function of the frequency fluctuations of the coherence contains cross-correlations of the frequency fluctuations of the constituent levels. In the case that the frequency fluctuations are fully correlated, the coherence would not be observed to

decay at all, despite possibly arbitrary absolute fluctuations. In DMDC, we observe the line width to correspond roughly to those of the constituent levels, indicating uncorrelated fluctuations.

There are several peaks in the spectrum that are not consistent with the known three fundamental vibrational bands and the overtones and combination bands already discussed. Since DMDC has 10 carbonyl ligands, roughly 10% of the solute is Mn$_2$(CO)$_9$$^{13}$CO, and due to the highly coupled and delocalized nature of the eigenstates, the single isotope defect has an unintuitive effect on the 2D spectrum.[45] Assuming uniform distribution of the $^{13}$C, 8% of the total sample has the isotope substituted at an equatorial location, while 2% are substituted in the axial position. The two degenerate E-symmetry eigenstates (2014 cm$^{-1}$) are primarily composed of motion along the eight equatorial CO local modes, whereas the two B$_2$-symmetry modes involve motion of all 10 carbonyls. Using DFT calculations (see below) to predict isotope shifts (Figure 3) yielded spectral features that agree with experimental FTIR while corresponding to additional peaks measured in the 2DIR spectrum. In light of the significant contribution to the DMDC 2DIR spectrum, we also revisited previous work on RDC, finding evidence that similar isotopomer peaks were likely observed in chloroform solution. Since a coupled anharmonic model of RDC has been shown to reproduce the spectrum well,[18] we set one local CO mode frequency to $\omega_1^0(\mu_{^{12}C}/\mu_{^{13}C})^{1/2}$, keeping all bilinear coupling and anharmonicity terms identical to the original parameter set. Following diagonalization, the lowest energy transitions are 1983.7 and 2066.9 cm$^{-1}$. These transitions correspond to the very weak peaks observed in the FTIR spectrum of RDC in hexane and chloroform. Since $^{13}$C enrichment has traditionally been a common method in physical organic chemistry, the cumbersome task of enrichment may not be necessary, provided one is mindful to treat multiple isomers in theoretical analysis or modeling.

We also study the photochemistry of DMDC by transient-2DIR spectroscopy, where the Mn–Mn bond is cleaved by 400 nm excitation and the reaction is followed by a standard 2DIR measurement: "UV-pump–2DIR-probe". The Mn(CO)$_5$ photoproducts show a single absorption band near 1982 cm$^{-1}$, assigned to a doubly degenerate E mode (Figure 7). This band is initially broad due to the excess excitation energy populating the low-frequency modes in the molecule, and becomes narrower as the waiting time between the UV and first IR pulse, $\tau$, is increased. Spectral narrowing results from vibrational cooling.[43] Transient-2DIR spectroscopy also provides a direct measurement of the vibrational lifetime of the photoproducts as a function of $\tau$ serving as a useful experi-
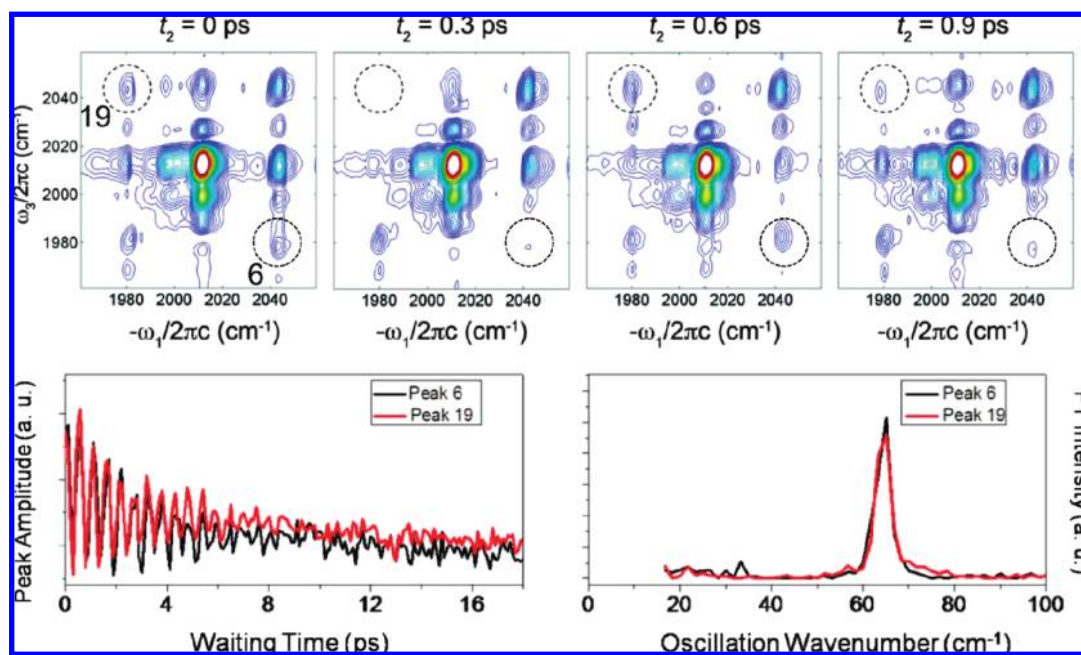
**FIGURE 6.** (top) 2DIR spectra showing cross peak oscillations. (bottom) Peak volumes and their respective power spectra. Adapted from ref 12.
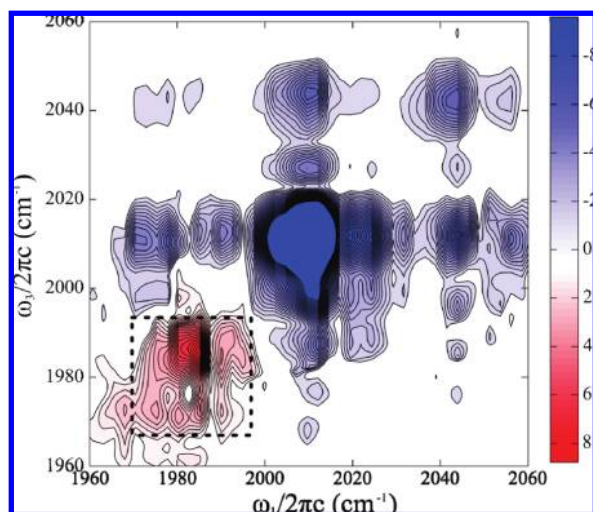


**FIGURE 7.** Transient-2DIR spectrum of DMDC in cyclohexane with 400 nm excitation at $\tau = 80$ ps and $t_2 = 2$ ps. Red contours (boxed) represent absorption due to the $Mn(CO)_5$ photoproducts, and blue contours (unboxed) represent bleaches due to depletion of $Mn_2(CO)_{10}$.

mental approach to measuring temperature-dependent vibrational energy transfer. A full characterization of the photochemistry of DMDC and other systems can be achieved using this powerful new technique.

## III. Theoretical Modeling of 2DIR Spectra

Extracting the wealth of information contained in a 2DIR spectrum often requires molecularly detailed theoretical modeling. However, accurate modeling of two-dimensional spectra

is significantly more challenging than that of one-dimensional IR spectra, and represents an ongoing challenge to currently available techniques. Multiple approaches have been applied to the modeling of 2DIR spectra which range from empirical fitting of the parameters of the underlying vibrational Hamiltonian to computing the spectra via electronic structure methods. Herein we outline some of the most commonly used theoretical approaches to modeling 2DIR within the context of metal carbonyls and report the results of recently obtained *ab initio* calculations pertaining to DMDC.

**Empirical and Semiempirical Modeling.** The simplest method for obtaining molecular information from 2DIR spectra is to fit the experimentally measured spectra to a parametrized model. The basic fitting parameters within this approach are the individual CO transition frequencies, couplings, and dipole moments and the normal-mode dephasing and population relaxation rate constants. For example, Tokmakoff and co-workers[18,22] have provided a self-consistent interpretation of their polarization-controlled absolute-value rephasing and absorptive 2DIR spectra of RDC using such an approach. To this end, they have employed a model vibrational Hamiltonian including only the two local CO stretches and assumed that the expansion of the vibrational potential surface in powers of those modes coordinates can be truncated at third order. By fitting this model to the experimental spectra, the authors were able to evaluate the angle between the two carbonyls and the strength of the coupling between them. A simulated 2DIR spectrum of RDC using the

experimental parameters is shown in Figure 2. The spectrum was computed using SPECTRON, which is a package for computing optical response functions and nonlinear signals starting from the eigenvalues of the molecular Hamiltonian and the associated transition dipole moments.[46] While this approach is very useful and inherently intuitive for small systems like RDC, it becomes impractical in the case of larger metal−carbonyl complexes such as DMDC. This is because one would need ∼210 Hamiltonian parameters in order to perform similar fitting in the case of DMDC.

*Ab Initio* **Methods.** The calculation of 2DIR spectra from first principles offers several key advantages. First, experimental peak positions can serve as benchmarks for modern electronic structure methods beyond the harmonic approximation. Standard electronic structure packages include efficient modules for computing second-order force constants and higher order (anharmonic) force constants can be computed via finite difference methods.[47,48] Once the force constants are known, writing the matrix that represents the vibrational Hamiltonian in terms of the harmonic basis is straightforward. The energy levels and corresponding stationary states can be obtained by diagonalizing this matrix, and then used in order to obtain the transition frequencies and dipole moments. In this context, it should be pointed out that despite the fact that often the errors in harmonic frequencies are of the same order of the anharmonic shifts (∼10−100 cm$^{-1}$), one can still predict the latter accurately since the corresponding errors are expected to cancel out.[49] Consequently, the anharmonic shifts may be reliable even if the harmonic frequencies are not. The main limitation of this method, however, is that, due to its intrinsic high computational expense, its application is currently limited to systems that involve a small number of vibrational modes. For example, this method has been successfully applied to RDC by Moran and co-workers,[50] where the anharmonic vibrational potential surface in terms of the two carbonyl coordinates was expanded up to fourth order using DFT. One important conclusion from this study is that the fourth-order force constants affect the spectra significantly, despite the fact that the spectra can be fitted to a model Hamiltonian that only accounts to anharmonicity up to third order.[18,22] This observation underscores the importance of going beyond empirical models. Hayashi and Mukamel[51] have also applied the same approach, in order to estimate the signature of hydrogen atom transfer in malonaldehyde on the corresponding 2DIR spectra. Similarly, Dreyer has recently reported calculated 2DIR spectra which were obtained via *ab initio* techniques for the widely studied hydrogen-bonded acetic acid dimer[52] and 7-azaindole dimer.[53] Finally, it should be

**TABLE 1.** *Ab Initio* Harmonic and Anharmonic Fundamental Frequencies (in cm$^{-1}$) for DMDC

| mode (symmetry) | experimental frequency | harmonic ($\omega$) | anharmonic ($\nu$) |
|---|---|---|---|
| 1-E$_3$ | 1981[a] | 1972.5 | 1912.2 |
| 2-E$_3$ | 1981[a] | 1972.5 | 1909.9 |
| 3-B$_2$ | 1983[b] | 1980.6 | 1964.1 |
| 4-A$_1$ | 1997[a] | 1990.7 | 1985.5 |
| 5-E$_1$ | 2014[b] | 2004.8 | 1939.6 |
| 6-E$_1$ | 2014[b] | 2004.9 | 1937.4 |
| 7-E$_2$ | 2024[a] | 2005.6 | 1960.3 |
| 8-E$_2$ | 2024[a] | 2008.6 | 1921.4 |
| 9-B$_2$ | 2044[b] | 2035.6 | 1993.6 |
| 10-A$_1$ | 2116[a] | 2097.0 | 2039.4 |

[a] The experimental frequencies are obtained from Raman in light petroleum (from ref 58). [b] The experimental frequencies are obtained from FTIR in *n*-hexane (this work).

noted that the dephasing and population relaxation rate constants are treated phenomenologically. To the best of our knowledge, an extension of this approach to include a first principles treatment of the population and dephasing rates has not been reported.

**Vibrational Perturbation Theory (VPT2).** The main advantages of VPT2 over the approach described in the previous section lie in its favorable scaling with the number of modes and relative ease of implementation.[54−56] This makes VPT2 the method of choice for molecules with a large number of modes. In this approach, the transition frequencies are computed within the framework of second-order perturbation theory, and transition dipole moments based on the harmonic states. As an example, we report new results obtained by using VPT2 in order to elucidate the origin of the anharmonic shifts observed in DMDC. To this end, we have employed DFT, using the Becke−Perdew (BP86) functional with a standard 6-31G(d) basis on C and O atoms, and LANL2DZ pseudopotential basis on the metal atoms. This particular functional/basis combination was chosen because it was found to satisfactorily reproduce the harmonic frequencies for the IR active modes as well as the transition dipole moments (see Figure 3). A very tight geometry optimization is imperative for obtaining reliable force constants. All geometry optimizations and Cartesian second derivative matrices were computed using the Q-Chem 3.1 package of programs.[57]

The computed harmonic frequencies were found to be red-shifted relative to the experimental values by 3−19 cm$^{-1}$, in reasonable agreement with the experimental values (see Table 1). The corresponding anharmonic fundamental frequencies are red-shifted relative to the harmonic ones by 16−86 cm$^{-1}$ and are well below the experimental values. Although the anharmonic shifts are consistent with the experimental ones in terms of their order of magnitude, sign and trends, they are significantly smaller than the experimental values (see Fig-

**TABLE 2.** Anharmonic Shifts ($\Delta = 2\omega_{0-a} - \omega_{a-2a}$) Obtained Including Only a Subset of the Modes/Force Constants in the Perturbation Treatment[a]

| | all modes | | CO modes | IR active CO modes | |
|---|---|---|---|---|---|
| mode | 3rd and 4th order | 3rd order only | 3rd and 4th order | 3rd and 4th order | 2DIR expt |
| 1 | 5.2 | 10.2 | 4.3 | | |
| 2 | 5.3 | 10.2 | 4.3 | | |
| 3 | 6.5 | 12.8 | 5.4 | −6.3 | 11 |
| 4 | 9.7 | 19.1 | 8.0 | | |
| 5 | 5.5 | 10.3 | 4.5 | −4.7 | 13 |
| 6 | 5.5 | 10.3 | 4.5 | −4.7 | 13 |
| 7 | 3.9 | 7.4 | 3.0 | | |
| 8 | 4.6 | 7.6 | 3.7 | | |
| 9 | 3.2 | 5.3 | 2.5 | −2.1 | 15 |
| 10 | 3.4 | 5.0 | 2.6 | | |

[a] The first two columns show the perturbation including all 60 modes in the molecule with 3rd and 4th order force constants, and 3rd order only. The third and fourth columns show the anharmonic coefficients obtained by including only the carbonyl modes and only the IR active carbonyl modes.

ure 5 and Table 2, column 6). This comparison in fact underscores the strengths and weaknesses of modeling 2DIR spectra based on *ab initio* calculations. Specifically, although one cannot expect quantitative agreement with experiment in light of the very small size of the spectral shifts, orders of magnitudes and general trends are generally reproduced. As a result, *ab initio* calculations can be used to illuminate the otherwise obscure mechanistic origins underlying the experimentally observed shifts.

To this end, we have repeated the calculation of the anharmonic shifts for various reduced models that account for different subsets of the modes and force constants. Truncating the Hamiltonian at third order yields anharmonicities that are about two times larger than those obtained using the full Hamiltonian. Although the anharmonicities are a closer match to experimental values, these changes suggest that fourth order terms contribute significantly to the shifts. This result is also consistent with a similar conclusion reported by Moran and co-workers[50] on RDC. Next, we consider a reduced model that only includes the ten carbonyl stretch modes (see column 3 of Table 2). The values of the anharmonic shifts are observed to be rather insensitive to this reduction, which implies that coupling between the CO stretches and the other vibrational modes in DMDC are rather small. Finally, we consider a reduced model that only includes the four photoactive carbonyl modes (see column 4 of Table 2). Although the magnitudes of the anharmonic shifts in this case are similar to those obtained by including all carbonyl modes, they have the opposite signs and are therefore qualitatively wrong. These results underscore the importance of explicitly accounting for the strong coupling between the bright and dark carbonyl stretch modes in the case of DMDC, rather than including them as weakly coupled bath modes.

## IV. Outlook

Rich spectral features and narrow line widths make metal carbonyls ideal model systems for study via 2DIR spectroscopy. Thus far most of the 2DIR work on metal carbonyls has utilized the molecules as test systems to aid in the development 2DIR spectroscopy rather than using 2DIR to learn about the molecules. Metal carbonyls, however, have useful catalytic and photochemical applications, including dye-sensitized solar cells, metalloenzymes, and model compounds.[28] By combining the time resolution and structural sensitivity of 2DIR, future experiments are poised to provide exciting new insights into classic problems in chemical physics such as geminate rebinding, cage effects and orientational relaxation. Despite the wealth of experimental results reported thus far, much remains to be extracted from the data. In particular, these systems provide challenging model systems for testing *ab initio* methods, as well as motivation for extending current theoretical methods for modeling spectra into unexplored domains. For example, at the present time, most attempts at modeling 2DIR spectra of metal carbonyl complexes have been based on treating dephasing and population relaxation in terms of empirically determined rate constants, within the framework of Redfield theory. However, features in the recently obtained experimental 2DIR spectra of DMDC strongly suggest that this model may be too restrictive in the sense that it does not account for strong coupling to the dark carbonyl modes (if assumed to be part of the bath), coherence-transfer, coupling between populations and coherences, and solvent effects. Additionally, new tools are needed to model triggered 2DIR experiments in systems such as DMDC undergoing photochemically induced nonequilibrium processes during the measurement. Finally, metal carbonyl complexes provide an ideal setting for further theory development and for enhancing the power and versatility of 2DIR spectroscopy.

## BIOGRAPHICAL INFORMATION

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