Fully absorptive 3D IR spectroscopy using a dual mid-infrared pulse shaper

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This paper presents the implementation of 3D IR spectroscopy by adding a second pump beam to a two-beam 2D IR spectrometer. An independent mid-IR pulse shaper is used for each pump beam, which can be programmed to collect its corresponding dimension in either the frequency or time-domains. Due to the phase matching geometry employed here, absorptive 3D IR spectra are automatically obtained, since all four of the rephasing and non-rephasing signals necessary to generate absorptive spectra are collected simultaneously. Phase cycling is used to isolate the fifth-order from the third-order signals. The method is demonstrated on tungsten hexacarbonyl ($\text{W}(\text{CO})_6$) and dicarbonylacetylacetonato rhodium (I), for which the eigenstates are extracted up to the third excited state. Pulse shaping affords a high degree of control over 3D IR experiments by making possible mixed time- and frequency-domain experiments, fast data acquisition and straightforward implementation. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824638>]

I. INTRODUCTION

Infrared spectroscopy is a well-established technique for studying the structures and dynamics of molecular systems.^{1,2} In recent years, nonlinear infrared spectroscopies have been developed, such as 2D IR spectroscopy, in which it is possible to correlate vibrational frequencies.³ The diagonal and anti-diagonal widths of a 2D spectra yield information regarding the dynamics of the system, whereas cross peaks arise due to coupling of the vibrational modes. 2D IR spectroscopy also has improved spectral resolution over linear IR spectroscopy, such as FTIR spectroscopy, because it spreads the spectrum into a second dimension. Another very useful but not so commonly discussed advantage of 2D IR spectroscopy is that since the signal scales with the fourth power of transition dipole moment in 2D IR spectroscopy as compared to square of transition dipole moment in linear IR spectroscopy, weak and broad modes, like those of water, that often cause a large background in linear IR spectra are minimized in 2D IR spectra. Transition dipole moments in excitonic structures depend on the extent of delocalization of vibrational excitations and can be used to identify molecular structures.⁴

With 2D IR spectroscopy now well developed, attention is turning to 3D and higher correlations.^{5–9} Analogous to how peaks are spread into a plane in 2D IR spectroscopy; the planes will be spread over a cube in 3D IR spectra. A 3D spectrum can be generated in a number of different ways.^{10–16} Perhaps the easiest way is to scan all three time delays available in a 2D IR pulse sequence and calculate a Fourier transform.^{12,16} While such experiments are useful in fully characterizing third-order response function these “pseudo” 3D experiments do not probe higher lying eigenstates or higher order correlation functions.

There have been two fifth-order based implementations of the 3D IR experiments prior to this work that contain in-

formation beyond a third-order 2D IR experiment. Ding and Zanni used a fifth-order pulse sequence to generate 3D IR spectra by correlating two one-quantum coherences with a two-quantum coherence.¹⁰ Two-quantum coherences are useful because they provide the frequencies of overtone and combination bands that are used to calculate the couplings. However, the spectral resolution of those experiments was not optimal because only the rephasing spectra were generated. Absorptive spectra are often more useful because spectra generated solely from rephasing or non-rephasing data contain long range, dispersive components which increase spectral congestion and complicate interpretation.^{17,18} For those reasons, most 2D IR spectra are now reported with absorptive line shapes. Furthermore, absorptive spectra are more directly related to the frequency trajectories and line shape functions than rephasing and non-rephasing spectra.¹⁹ The first fully absorptive 3D IR spectra were collected by Garrett-Roe and Hamm.¹¹ They correlated one-quantum transitions along all three dimensions as a function of two waiting times in order to extract a three-point correlation function. Their data helped reveal evidence for heterogeneous structural dynamics in isotope substituted liquid water²⁰ and recently in ice.²¹ The method presented in this paper is conceptually the most similar to the one presented in Refs. 11, 20, and 21, namely, we present fifth-order based fully absorptive 3D IR spectroscopy.

The previous 3D IR experiments used variations on “box-car” phase matching geometries in order to collect their signals. In those geometries, the fifth-order signal is generated in a direction separate from all lower order signals and, thus, is background free. The drawback is that each pulse must be separately routed to the sample and time delayed, an independent local oscillator must also be used to heterodyne the emitted signal field, and each of the 3D IR spectra needed to create an absorptive signal must be independently measured, added, and phased. In this paper, we report a method for collecting 3D IR spectra using a three-beam phase matching

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geometry in which we add an additional pump beam to a standard two-beam 2D IR spectrometer. The new pump beam can be either a pair of femtosecond pulses or a frequency scanned picosecond pulse. In this phase matching geometry, the fifth-order signal is emitted in the same direction as the third-order 2D IR signal. Thus, 3D IR spectra are collected by modulating the 2D signal. Analogous to the way in which 2D IR spectra is collected in the pump-probe geometry so that both the rephasing and non-rephasing spectra are collected simultaneously to automatically give absorptive 2D spectra,^{22,23} in our beam geometry all of the fifth-order rephasing and non-rephasing spectra are collected simultaneously to generate an absorptive 3D IR spectrum. This beam geometry has the advantage that the pairs of pulses are phase stable. Drift of the relative phases between the pulses by even a fraction of the wavelength causes distorted line shapes, and so require passive or active phase stabilization of each laser pulses.²⁴⁻²⁷ With fixed phases, pulses can be indefinitely averaged, which is important for collecting large data sets such as for 3D IR spectroscopy.

To generate this new pump beam, as well as the original beam, we use mid-IR pulse shaping. Pulse shaping is a very convenient method for collecting multidimensional spectra.²⁸⁻³¹ In fact, 3D spectra have been collected previously in the visible region of the spectrum using pulse shaping.^{12,14,15} First, when using pulse shaping, the spectra are automatically phased, which is otherwise a very complicated procedure for a 3D signal.¹¹ Second, there are no moving parts in our setup and since the shaper can change the pulse delays on a shot to shot basis, the data acquisition time is as rapid as possible. Third, phase cycling can be easily performed. One advantage of phase cycling is that it eliminates the need to chop the beams to remove background, thereby effectively increasing the repetition rate at which data are collected. Fourth, the shaper enables each dimension to be collected in either the time- or frequency-domains by programming without any additional alignment changes. The ability to choose between time- and frequency-domain data collection is particularly useful for 3D spectroscopy, because it can decrease data collection time and zoom-in on frequencies of interest. Most of the capabilities described above can be implemented in other ways with additional optics³² but with pulse shaping, these methods are simply a matter of computer programming.

We demonstrate our 3D IR approach on two metal-carbonyl compounds, $\text{W}(\text{CO})_6$ and dicarbonylacetylacetonato rhodium (I) (RDC). These compounds have very strong infrared absorption coefficients, long population and coherence times, and have mostly homogeneous dynamics, and so are often used as model systems in nonlinear IR spectroscopy.³³⁻⁵¹ $\text{W}(\text{CO})_6$ has a single carbonyl absorption band, while RDC has two coupled modes. 3D IR spectra are collected in both the time- and frequency-domains so as to understand the effects of pulse convolution. The accuracy of the phase cycling procedure is tested for suppressing background. The molecular eigenstates up to the 3rd-quantum states are determined and fit to an excitonic Hamiltonian. These experiments demonstrate the capabilities made possible by this 3D IR spectrometer and explore some of the features of

coupled systems in 3D IR spectra of molecular vibrational modes.

II. MATERIALS AND METHODS

Mid-infrared pulses with approximately 5 μJ energy, 185 cm^{-1} bandwidth, and centered at 5 μm are generated using a combined Ti:Sapphire system and a mid-infrared optical parametric amplifier (OPA) and has been described in Ref. 52. The mid-infrared pulses are split into a weak probe pulse (3%) and a strong pump pulse (97%). The pump pulse is then shaped by a modified dual acousto-optic modulator (AOM) pulse shaper, the details of which has been described in Ref. 53. Briefly, the dual AOM consists of two AOMs mounted on top of one another. A combination of a 90° periscope and 50/50 zinc selenide beam splitter generates two approximately equal (60% reflected, 40% transmitted) intensity input beams to the shaper setup. Both the beams are then frequency dispersed by a grating (150 grooves/mm, 5.4 μm blaze) set in a near Littrow configuration and collimated by a custom made CaF_2 lens ($f = 12.5$ cm) and subsequently shaped with a Ge AOM. Each AOM was controlled by a different arbitrary waveform generator (AWG) card that is triggered by the same electronic transistor-transistor logic (TTL) pulse from the regenerative amplifier, and hence are electronically synchronized. The beam from one shaper passes through a pair of ZnSe wedges in order to set the time-delays between the two pump beams. For each shaper, the relative timing between the two pump pulses are controlled by independently varying the carrier frequencies of the acoustic waves needed to shape the pulses. With the resolution of this shaper, delays of the order of ± 8 ps can be set. The pump pulses are focused onto the sample along with the probe pulse by a 90° parabolic mirror. The probe is frequency dispersed with a monochromator and detected with a 64 element mercury cadmium telluride (MCT) array. A schematic representation of the setup is shown in Fig. 1 along with the pulse sequence and time delays. The time delay between the two pump pulses and the probe pulse are controlled by a Newport automatic translation stage. The metal carbonyls, $\text{W}(\text{CO})_6$ and RDC, were purchased from Sigma Aldrich and used without further purification. The samples were dissolved in hexane to yield an OD of 0.4, which is in millimolar concentration range. Cascaded contributions do not significantly contribute to fifth-order spectra under these conditions.^{11,56,15}

III. PULSE SEQUENCE DESIGN

A. Phase cycling

In a fifth-order experiment there are five interactions of the sample with the laser pulses. The resulting polarization in the sample then emits an electric field in the phase matching direction⁵⁴ given by Eq. (1),

$$k_{\text{signal}} = \pm k_1 \mp k_1 \pm k_2 \mp k_2 + k_3, \quad (1)$$

where k_n are the wave vectors of the pulses. In our experiment, pulses with wave vectors k_1 are generated by one pulse shaper

FIG. 1. Schematic setup for fifth-order 3D IR experiment. OPA: optical parametric amplifier, BS: beamsplitter, TS: translation stage, PM: parabolic mirror, MCT: mercury cadmium telluride detector. Also shown is the pulse sequence along with the time delays. Pulses 1 and 2 are generated by shaper 1 and pulses 3 and 4 by shaper 2.

and k_2 by the other so that the fifth-order signal we seek is emitted in the same direction as our probe pulse k_3 .

For ultrashort pulses the generated signal $E_{signal}^5(t_1, T_2, t_3, T_4, t_5)$ is proportional to sum of the rephasing $R_r^n(t_1, T_2, t_3, T_4, t_5)$ and non-rephasing $R_{nr}^n(t_1, T_2, t_3, T_4, t_5)$ response functions. Rephasing and non-rephasing terminology refers to whether the response functions have different or same sign of frequency along t_1 and t_3 times, respectively. The signal is then heterodyned with the local oscillator electric field ($E_{probe}^*(\omega_5)$), frequency dispersed by the spectrometer and subsequently detected in the frequency domain, which is mathematically equivalent to taking the real part of the complex Fourier transform along t_5 . Hence, the measured signal is a function of two indirect time domains and one direct frequency domain. The steps are mathematically expressed as follows:

$$E_{signal}^5(t_1, T_2, t_3, T_4, t_5) \approx \sum_n^{20} R_r^n(t_1, T_2, t_3, T_4, t_5) + \sum_n^{20} R_{nr}^n(t_1, T_2, t_3, T_4, t_5), \quad (2a)$$

$$S^5(t_1, T_2, t_3, T_4, \omega_5) \approx \text{Re}(E_{signal}^5(t_1, T_2, t_3, T_4, \omega_5) E_{probe}^*(\omega_5)). \quad (2b)$$

In addition to this signal, third-order signals are also emitted in the same phase matching direction, which are either from the interaction of the first two pump pulses and the probe, or the third and fourth pump pulses and the probe (we ignore all possible homodyne signals since they are much smaller). Since the third-order signals have different phase and intensity dependence from the fifth-order signal, we employ the following general four-frame phase cycling scheme to subtract off the third-order signals arising from all the

FIG. 2. Pulse sequences for the three different types of experiments reported in this work. The parameters t_1 (ω_1) and t_3 (ω_3) can be varied independently in the above sequences. (a) Time-domain scanning using double pulses, (b) mixed time- and frequency-domain data collection using double pulses from one shaper and frequency narrowed Gaussian pulses with another shaper, and (c) full frequency-domain data collection using frequency narrowed Gaussian pulses from both shapers.

rephasing and non-rephasing pathways which are collinear with the fifth-order signals

$$S = (S_I + S_{IV}) - (S_{II} + S_{III}). \quad (3)$$

S_N denotes the measured signal for frame N and S is the overall phase cycle. In the discussion that follows, we generate the 3D IR spectra using a number of different time- and frequency-domain pulse sequences. For each of these experiments we use a different pulse shape (double pulse or frequency narrowed Gaussian) from the two different shapers. Fig. 2 shows the types of pulse shapes employed and will be discussed in detail in Secs. III B and III C.

B. Time-domain data collection

One pulse sequence we use to collect the 3D IR data utilizes only femtosecond pulses. In this method, the 3D IR spectrum is generated by Fourier transforming the signal as a function of two indirect time-dimensions. The signal measured on the detector is given by

$$S = S^5(t_1, T_2, t_3, T_4, \omega_5) + S^3(t_1, T_2, \omega_5) + S^3(t_3, T_4, \omega_5) + |E_{probe}(\omega_5)|^2, \quad (4)$$

where the superscripts stand for the order of the signal and the last term is the local oscillator (probe beam) intensity. Since the phase of the fifth-order signal (Φ_{signal}^5) is given by the sum of the relative phases, i.e.,

$$\Phi_{signal}^5 = \Phi_{12} + \Phi_{34}, \quad (5)$$

whereas the third-order signals depend only on the relative phases of the double pulse, the phase cycle shown in Fig. 2(a) subtracts off the last three terms in Eq. (4). Table I illustrates the phase dependence of the different terms in the above equation.

TABLE I. Phase dependence of each of the terms in Eq. (4). The last row shows the phase cycle.

Frame	φ_{12}	φ_{34}	$S^5(t_1, T_2, t_3, T_4, \omega_5)$	$S^3(t_1, T_2, \omega_5)$	$S^3(t_3, T_4, \omega_5)$	$ E_{probe}(\omega_5) ^2$
I	0	0	-1	1	1	1
II	0	π	1	1	-1	1
III	π	0	1	-1	1	1
IV	π	π	-1	-1	-1	1
I+ IV-II-III	$-4S^5(t_1, T_2, t_3, T_4, \omega_5)$					

The signal is a sum of rephasing and non-rephasing signals and has all possible frequency combinations. A 2D Fourier transform of the above signal gives several possible combinations of absorptive and dispersive components, which end up in different quadrants of the frequency space. These quadrants are then flipped and added to generate a fully absorptive spectrum.^{18,55}

C. Mixed time-and-frequency and full frequency-domain data collection

Instead of collecting both indirect dimensions in the time-domain using femtosecond pulse pairs, one or both can be collected in the frequency-domain by scanning the center frequency of a narrow band pulse.²³ Equation (6a) represents one such possible mixed domain experiment where the first frequency dimension is collected in time domain with femtosecond pulses and the second frequency dimension is scanned in frequency domain. Equation (6b) shows the signal collected entirely in the frequency domain

$$S = S^5(t_1, T_2, \omega_3, T_4, \omega_5) + S^3(t_1, T_2, \omega_5) + S^3(\omega_3, T_4, \omega_5) + |E_{probe}(\omega_5)|^2, \quad (6a)$$

$$S = S^5(\omega_1, T_2, \omega_3, T_4, \omega_5) + S^3(\omega_1, T_2, \omega_5) + S^3(\omega_3, T_4, \omega_5) + |E_{probe}(\omega_5)|^2. \quad (6b)$$

Since the fifth-order signal depends on the electric fields of all the pump pulses, whereas the third-order signals depend only on the fields of two pump pulses, the pulse sequence shown in Figs. 2(b) and 2(c) can be used to isolate the fifth-order signal as shown in Tables II and III, respectively.

IV. RESULTS

A. Phase cycling accuracy

Since the third-order background is larger than the fifth-order signal by at least an order of magnitude even for metal

carbonyls, it is very important that the phase cycling is very accurate so as to attain good background subtraction. The phase cycling accuracy was tested as shown in Fig. 3 where we plot the third-order signal $S^3(\omega_1, \omega_5 = 1973)$ (blue trace) and the fifth-order signal $S^5(\omega_1, t_3 = 0, \omega_5 = 1973)$ (green trace) using the phase cycling scheme of Fig. 2(a). Also shown is the signal collected for the same fifth-order phase cycling scheme but with the beam from one of the shaper physically blocked to prevent fifth-order signal, leaving only the third-order signal that is not properly removed by the phase cycling scheme (black trace). We find that with our present phase cycling scheme, we have 0.3% residual third-order signal. Hence a fifth-order signal which is about 1%–10% of the third-order signal can be easily measured. Another interesting aspect that is revealed in this plot is the opposite phases of the third-order and fifth-order signals. Such phase relationship is expected from the extra factor of i^2 in the perturbative expansion of the density matrix⁵⁴ and agrees with previous observations.^{9,56}

B. W(CO)₆/hexane

W(CO)₆ has six CO stretching modes. However in a symmetric environment, it has only one triply degenerate IR active mode T_{1u} and thus can be considered to be a single oscillator system. It has a very large IR transition dipole moment (~ 1 D) and very long population and coherence lifetimes, which are ideally suited for testing fifth-order experiments. The 2D IR spectrum of W(CO)₆ is presented in Fig. 4(a). It has a pair of peaks separated by the anharmonic shift of the mode. The 2D line shapes reveal that the vibrational mode has largely homogenous dynamics in hexane, consistent with previous studies.^{23,33}

For the full time domain experiments reported in this paper, the t_1 and t_3 coherence times were scanned in steps of 50–4000 fs, which corresponds to a frequency resolution of 4 cm⁻¹ along the ω_1 and ω_3 axes. Delay times between the pulse pairs were set as follows: $T_2 = 0$ and $T_4 = 4.5$ ps for

TABLE II. Phase and intensity dependence of each term in Eq. (6a). I_3 is the normalized intensity of the frequency narrowed Gaussian pulse in Fig. 2(b). The last row shows the phase cycle.

Frame	φ_{12}	I_3	$S^5(t_1, T_2, \omega_3, T_4, \omega_5)$	$S^3(t_1, T_2, \omega_5)$	$S^3(\omega_3, T_4, \omega_5)$	$ E_{probe}(\omega_5) ^2$
I	0	1	-1	1	1	1
II	π	1	1	-1	1	1
III	0	0	0	1	0	1
IV	π	0	0	-1	0	1
I+ IV-II-III	$-2S^5(t_1, T_2, \omega_3, T_4, \omega_5)$					

TABLE III. Intensity dependence of each term in Eq. (6b). I_1 and I_2 are the normalized intensity of the frequency narrowed Gaussian pulses in Fig. 2(c). The last row shows the phase cycle.

Frame	I_1	I_2	$S^5(\omega_1, T_2, \omega_3, T_4, \omega_5)$	$S^3(\omega_1, T_2, \omega_5)$	$S^3(\omega_3, T_4, \omega_5)$	$ E_{probe}(\omega_5) ^2$
I	1	1	-1	1	1	1
II	0	1	0	0	1	1
III	1	0	0	1	0	1
IV	0	0	0	0	0	1
I+ IV-II-III	$-S^5(\omega_1, T_2, \omega_3, T_4, \omega_5)$					

$t_1 = t_3 = 0$. T_2 does not change with the coherence times (t_n), but T_4 was allowed to vary according to the equation $T_4 = 4.5 \cdot t_3$ because the mechanical delay stages are too slow to compensate for the t_3 delay change on a shot to shot basis.

A rotating wave frequency of 1850 cm^{-1} was used to sample the coherence times. The resulting spectral interferograms were Fourier transformed as was discussed earlier after applying a Hamming window function¹⁷ to force the free induction decay to zero (which reduces ringing in the spectra). All the spectra reported in this paper are the real parts of the complex signal, which give the fully absorptive 3D IR spectra.

3D IR spectra of $\text{W}(\text{CO})_6$ are shown in Fig. 5(a) drawn with isosurfaces at 20%, 40%, and 70% of the maximum intensity. Four lobes are observed. The color of the lobes represents the phases of the peaks, where red stands for positive and blue for negative. The volumes of the isosurface plots are proportional to the relative intensities of the peaks. The assignment of these features is the same as that previously reported for CO_2 .¹¹ When the first pulse interacts with the sample, it will create a coherence with the $\text{W}(\text{CO})_6$ fundamental, and so all the peaks lie at $\omega_{01} = 1983 \text{ cm}^{-1}$ along ω_1 . After the second pulse stops this coherence, the third pulse can either create another coherence with the fundamental or a coherence to the first overtone state (ω_{21}), and thus one gets two rows of peaks in the ω_3 plane at 1983 cm^{-1} and 1970 cm^{-1} . Besides these two frequencies, the fifth pulse can access the second overtone state at ω_{32} , so that peaks can appear at three frequencies along ω_5 at 1983 cm^{-1} , 1970 cm^{-1} , and 1955 cm^{-1} . The frequencies and assignment of the peaks are reported in Table IV.

The qualitative descriptions of the peak assignment above can be rigorously described in the formalism of Feynman pathways.^{10,11,15} There are over 40 Feynman diagrams that contribute to these peaks for a single oscillator. As an ex-

ample, we show one possible pathway that gives rise to the peak B (Fig. 6). Each arrow represents an interaction of radiation field with sample and generates either a coherence state or a population state. Coherence states oscillate at the corresponding frequencies along the respective times. On Fourier transformation this gives rise to a peak at the corresponding frequencies. All the peaks in the 3D IR spectra of $\text{W}(\text{CO})_6$ can be similarly assigned to one or more Feynman pathways. We note that there is a peak expected at $\omega_1 = \omega_{01}$, $\omega_3 = \omega_{21}$, and $\omega_5 = \omega_{01}$ theoretically which is absent in the full time-domain and mixed time- and frequency-domain spectra but is present in the full frequency-domain spectra (Fig. 8(b) peak at $\omega_1/2\pi = 1983 \text{ cm}^{-1}$, $\omega_3/2\pi = 1970 \text{ cm}^{-1}$).

We also collected spectra of $\text{W}(\text{CO})_6$ in which the ω_3 -axis was collected in the frequency domain, as shown in Fig. 7(a). To generate this spectrum, frequency narrowed Gaussian pump beams were used with 5 cm^{-1} full width half maxima (FWHM) scanned in steps of 2.5 cm^{-1} . The t_1 time delays were scanned in steps of 50 fs up to 2000 fs, which corresponds to a frequency resolution of 8 cm^{-1} . The narrowband Gaussian pulses lead to broad ($\sim 2 \text{ ps}$) pulse in the time domain. Consequently, the T_2 and T_4 delay times were set to 2 ps to avoid pulse overlap effects. The Hamming window was used along the time-domain dimension, for the same reasons as above and the data was Fourier transformed along the t_1 dimension to obtain the fully absorptive 3D IR spectra. The line shapes of the two-dimensional cuts of the above 3D spectra (Fig. 7(b)) have an asymmetric nature because of the difference in frequency resolution of the two axes. Even though we use a narrowband Gaussian pulse to scan ω_3 axis, it does not lead to significant distortion or broadening as has been shown before.²³ Consequently, the resolution along the ω_1 axis is about 3 times less than that along the ω_3 axis. Scanning t_1 to longer delay times is expected to improve the resolution along that axis significantly, thereby leading to much more symmetric shapes.

FIG. 3. Demonstration of phase cycling accuracy: 5th order signal: green, 3rd order signal: blue, and 10*background: black.

FIG. 4. 2D IR spectra of (a) $\text{W}(\text{CO})_6$ (b) RDC.

FIG. 5. (a) Full 3D IR spectra with slices at the (b) fundamental, (c) first overtone, and (d) second overtone frequencies along the ω_5 axis.

TABLE IV. Peaks in the 3D IR spectrum with frequencies and the assignments.

Labels	Peak frequencies presented as ($\omega_1, \omega_3, \omega_5$) cm ⁻¹	Designations
A	1983, 1983, 1983	($\omega_{01}, \omega_{01}, \omega_{01}$)
B	1983, 1983, 1970	($\omega_{01}, \omega_{01}, \omega_{21}$)
C	1983, 1970, 1970	($\omega_{01}, \omega_{21}, \omega_{21}$)
D	1983, 1970, 1955	($\omega_{21}, \omega_{21}, \omega_{32}$)

FIG. 6. Feynman pathways for peak B showing the frequencies at the three different coherence times t_1 , t_3 , and t_5 .

FIG. 7. (a) Mixed time- and frequency-domain 3D IR with slices at the (b) fundamental, (c) first overtone, and (d) second overtone frequencies along the ω_5 axis.

FIG. 8. (a) Full frequency-domain 3D IR with slices at the (b) fundamental, (c) first overtone, and (d) second overtone frequencies along the ω_5 axis.

Although acquiring the free induction decays in time-domain is increasingly becoming the method of choice for most nonlinear infrared spectroscopic techniques, there are certain advantages in being able to collect the data in frequency-domain. With our dual shaper we can scan the frequencies of the two shapers independently. Consequently, it can be used to zoom in on particular frequency combinations, like those of cross peaks. Such ability will be useful for interpreting complicated spectra. As a proof of principle, we collected data where both axes were scanned in the frequency domain (Fig. 8). Frequency narrowed Gaussian pulses with the same bandwidth as the preceding experiments were used. Unlike the spectra collected using mixed time-and-frequency domain, this spectrum is symmetrical because both axes have the same frequency resolution and line shapes. Furthermore, there is a weak peak that can be seen in the slice spectra at $\omega_5 = 1983$ cm⁻¹ and also in the 3D spectrum at lower iso-surface values (not shown). As alluded to earlier this is expected from Feynman pathways but was absent in the full time-domain and mixed time-frequency domain experiments. We hypothesize that this is due to non-perturbative saturation effects^{33,57} arising from the extremely high transition dipole moment of W(CO)₆. The fact that this peak is present in the full frequency-domain experiment suggests that those effects can be minimized with narrowband weak pulses. In principle it is possible to do 3D IR experiments at lower pump intensity to minimize such effects, while still retaining enough power to generate fifth-order signal, but we have not pursued that in this work. It is interesting to note that this peak was also unexpectedly weak in the 3D IR spectra of water and ice,^{20,21} suggesting that its intensity may be especially dependent on vibrational dynamics.

C. RDC/hexane

The experiments on W(CO)₆ were performed in order to compare the time- and frequency-domain methods by which the spectra could be collected and confirm the peak pattern for a single oscillator spectrum.¹¹ In this section, we present spectra collected on RDC using the time-domain approach in order to explore the peak patterns associated with a coupled

FIG. 9. 3D IR spectra of RDC with (a) parallel and (b) perpendicular polarizations.

vibrational system. RDC has two IR active carbonyl stretching modes at 2015 cm^{-1} and 2084 cm^{-1} , which are the asymmetric (A) and symmetric (S) stretch modes, respectively.^{46,49} Figure 4(b) shows the 2D IR spectra of RDC and is in agreement to previously reported spectra. It consists of a pair of diagonal peaks 1, 2 and 1', 2' at the fundamental and first overtone, respectively. The coupling between the modes is manifested by the cross peaks 3, 4 and 3', 4', which are separated by the off-diagonal anharmonicity. The peaks 5, 5' and 6, 6' arise from relaxation assisted pathways like coherence and/or population transfer.

The 3D spectra were collected at relative polarizations of the pump and probe pulses set parallel $[0,0,0,0,0]$ and perpendicular $[\pi/2,\pi/2,\pi/2,\pi/2,0]$, where $[\theta_1, \theta_1, \theta_2, \theta_2, \theta_3]$ represents the polarization ordering of the electric fields in the experiment, θ_1, θ_2 being the polarizations of the two pump pulses and θ_3 is the polarization of the probe pulse.

The 3D IR spectra of RDC exhibit both “diagonal” peaks and “cross peaks” (Fig. 9). Each of the absorption bands in RDC produces a diagonal peak pattern analogous to that of $\text{W}(\text{CO})_6$. The cross peaks can potentially arise in six different quadrants. The cross peaks are much stronger for the 3D IR spectrum collected with perpendicular than parallel polarization because of differential scaling of the Feynman pathways leading to the diagonal and cross peaks, and has been worked out for general fifth-order pulse sequence.⁵⁸ In order to extract the eigenstates from the spectra we take six slices perpendicular to the ω_5 axis. Each of those slices have diago-

nal peaks, cross peaks, and possible population and coherence transfer peaks and can be further split into two or more peaks based on whether it is a fundamental, first or second overtone. To simplify the description here, we instead label the peaks in two projections of the 3D spectra ($S^5(\omega_1, \omega_3, \omega_5)$) along the ω_1, ω_5 plane and the ω_3, ω_5 planes as defined by the following equations:

$$S^5(\omega_1, \omega_5) = \int S^5(\omega_1, \omega_3, \omega_5) d\omega_3, \quad (7a)$$

$$S^5(\omega_3, \omega_5) = \int S^5(\omega_1, \omega_3, \omega_5) d\omega_1. \quad (7b)$$

Because of the slice-projection theorem of Fourier analysis, these spectra are formally analogous to the corresponding slices in the time domain, i.e.,

$$S^5(\omega_1, \omega_5) \equiv S^5(\omega_1, t_3 = 0, \omega_5), \quad (8a)$$

$$S^5(\omega_3, \omega_5) \equiv S^5(\omega_3, t_1 = 0, \omega_5). \quad (8b)$$

Hence, these spectra can be understood in terms of response functions with either the t_1 or the t_3 coherence times set to zero. Shown in Fig. 10 are the projections on these two planes. In Fig. 10(a), the peaks arise in two lines along ω_1 , which correspond, to the two fundamental stretching frequencies of RDC (2015 cm^{-1} for A and 2084 cm^{-1} for S). The peaks are labeled A–F for one mode and A'–F' for the other mode. In Fig. 10(b), the same peaks arise in four rows along ω_3 . Those correspond to the fundamental and first overtone frequencies of the two modes. Fig. 11 shows the Feynman diagram pathways for two such peaks. We can extract all the normal mode frequencies from the above spectra. Table V lists the frequencies of each of these peaks for one mode, with similar

FIG. 10. Projections of the 3D spectra for perpendicular polarization along (a) ω_1, ω_5 and (b) ω_3, ω_5 planes.

FIG. 11. Feynman pathways for peaks C and F.

TABLE V. Frequencies and assignments for peaks labeled A–H for RDC projection spectra.

Peak	Frequency (ω_1, ω_5) cm^{-1}	Designation	Frequency (ω_3, ω_5) cm^{-1}	Designation
A	(2084, 2084)	(ω_s, ω_s)	(2084, 2084)	(ω_s, ω_s)
B	(2084, 2070)	$(\omega_s, \omega_s - \Delta_s)$	(2084, 2070), (2070, 2070)	$(\omega_s, \omega_s - \Delta_s), (\omega_s - \Delta_s, \omega_s - \Delta_s)$
C	(2084, 2052)	$(\omega_s, \omega_s - \Delta_s - \Delta_{2s})$	(2070, 2052)	$(\omega_s - \Delta_s, \omega_s - \Delta_s - \Delta_{2s})$
D	(2084, 2015)	(ω_s, ω_a)	(2084, 2015)	(ω_s, ω_a)
E	(2084, 1985)	$(\omega_s, \omega_a - \Delta_{as})$	(2084, 1985), (2070, 1985)	$(\omega_s, \omega_a - \Delta_{as}), (\omega_s - \Delta_s, \omega_a - \Delta_{as})$
F	(2084, 1967)	$(\omega_s, \omega_a - \Delta_{2sa} + \Delta_s)$	(2070, 1985)	$(\omega_s - \Delta_s, \omega_a - \Delta_{2sa} + \Delta_s)$
G	(2084, 1997)	$(\omega_s, \omega_a - \Delta_a)$	(2084, 1997), (2070, 1997)	$(\omega_s, \omega_a - \Delta_a), (\omega_s - \Delta_s, \omega_a - \Delta_a)$
H	(2015, 2052)	$(\omega_a, \omega_s - \Delta_s - \Delta_{2s})$	(2000, 2052)	$(\omega_a - \Delta_a, \omega_s - \Delta_s - \Delta_{2s})$

assignments for the other mode. Peak G and H arise from population and/or coherence transfer and will be discussed later.

In the normal mode basis, we have two one-quantum eigenstates which are either A or S and have fundamental frequencies of ω_a and ω_s , respectively. There are three two-quantum states which have energies of $\omega_{2a} = 2\omega_a - \Delta_a$, $\omega_{2s} = 2\omega_s - \Delta_s$, $\omega_{as} = \omega_a + \omega_s - \Delta_{as}$, and stand for the two overtone states and the combination band, respectively. The three-quantum states are the 2nd overtones ($\omega_{3a} = 3\omega_a - 2\Delta_a - \Delta_{2a}$, $\omega_{3s} = 3\omega_s - 2\Delta_s - \Delta_{2s}$) and two combination bands ($\omega_{2as} = 2\omega_a + \omega_s - \Delta_{2as}$, $\omega_{2sa} = \omega_a + 2\omega_s - \Delta_{2sa}$). Overall, there are 10 eigenstates that are accessed by the fifth-order experiment. In this notation the Δ_a (Δ_s) and Δ_{2a} (Δ_{2s}) stands for first and second diagonal anharmonicity and Δ_{as} , Δ_{2as} , Δ_{2sa} are the 2Q and 3Q off-diagonal anharmonicity, respectively, defined as

$$\Delta_{2a} = \omega_{2aa} - \omega_{3a2a}, \quad (9a)$$

$$\Delta_{2as} = 2\omega_a + \omega_s - \omega_{2as}, \quad (9b)$$

where the ω_{2aa} and ω_{3a2a} are the frequencies between the first overtone and the first excited state and the coherence between the second overtone and the first overtone, respectively. There is an analogous set of equations for the symmetric mode. Fig. 12 illustrates the measured eigenstates for $\text{W}(\text{CO})_6$ and

State	$\text{W}(\text{CO})_6$ Energy	State	RDC Energy
$ 3\rangle$	5908 cm^{-1}	$ 3S\rangle$	6206 cm^{-1}
		$ A+2S\rangle$	6121 cm^{-1}
		$ 2A+S\rangle$	6045 cm^{-1}
		$ 3A\rangle$	5998 cm^{-1}
$ 2\rangle$	3953 cm^{-1}		
$ 1\rangle$	1983 cm^{-1}	$ 2S\rangle$	4154 cm^{-1}
		$ A+S\rangle$	4071 cm^{-1}
		$ 2A\rangle$	4015 cm^{-1}
$ 0\rangle$	0 cm^{-1}	$ S\rangle$	2084 cm^{-1}
		$ A\rangle$	2015 cm^{-1}
		$ 0\rangle$	0 cm^{-1}

FIG. 12. Normal modes for $\text{W}(\text{CO})_6$ and RDC.

RDC. Except for two third overtone states that will be discussed later, the values are in close agreement to reported values.⁴⁸

V. DISCUSSION

To extract the local mode parameters from our experiment we fit the experimental eigenstates to that obtained from the following Hamiltonian:

$$H = \hbar\omega b_1^\dagger b_1 + \hbar\omega b_2^\dagger b_2 + \beta_{12}(b_1^\dagger b_2 + b_2^\dagger b_1) - \frac{\Delta}{2}b_1^\dagger b_1^\dagger b_1 b_1 - \frac{\Delta}{2}b_2^\dagger b_2^\dagger b_2 b_2, \quad (10)$$

where ω and Δ are the local mode frequency and anharmonic shift, respectively. Only bilinear coupling terms β_{12} between the two modes are included in the fits. b_1 ($b_1^\dagger$) and b_2 ($b_2^\dagger$) are the harmonic oscillator annihilation (creation) operators of the two modes. Because of the symmetric nature of the molecule, we assume the same local mode frequency and anharmonic shift for both the modes. When such a Hamiltonian is expressed in the local mode basis, it breaks down in block diagonal form and can be diagonalized iteratively to fit to the measured eigenstates, which are the normal modes. We see that we get a reasonable fit (within $\pm 2 \text{ cm}^{-1}$) which is within our experimental accuracy ($\pm 3 \text{ cm}^{-1}$). The local mode parameters extracted from the peaks are shown in Table VI. Inclusion of higher order (biquadratic) coupling terms in the Hamiltonian does not improve the fit (not shown). It is important to point out that local mode parameters can also be extracted from 2D IR (column V). As we can see that the local mode parameters extracted from the 2D IR works quite well up to the second overtone, but breaks down for third overtone (error $> 3 \text{ cm}^{-1}$) (column VI) which illustrates the necessity of including the higher overtones in the fit.

The Hamiltonian used in this fit assumes that the carbonyl local modes are completely uncoupled from all the other vibrational modes in the molecule. Since carbonyl bands are spectrally separated from other vibrational modes, such a description is valid unless there is an accidental resonance such as a Fermi resonance. Fermi resonances lead to trilinear coupling, which are related to cubic terms in the Taylor expansion of the potential energy surface in terms of the vibrational coordinates. The accuracy of the fits obtained suggests that such resonances are either very weak or nonexistent in RDC.

While it is relatively easy to obtain a good fit for the frequencies of the modes, it is much harder to explain the

TABLE VI. Measured and fitted eigenstates and the local mode parameters.

Eigenstate label	Experimentally determined eigenstates (cm ⁻¹)	Local mode parameters extracted from fits to 3D IR (cm ⁻¹)	Fits to eigenstates from local mode parameters in column III (cm ⁻¹)	Local mode parameters from 2D eigenstates only (cm ⁻¹)	Fits to eigenstates from local mode parameters in column V (last four values are extrapolated) (cm ⁻¹)
A⟩	2015	$E = 2044, \Delta_a = \Delta_b = 28.68, \beta_{12} = 30.03$	2014	$E = 2049, \Delta_a = \Delta_b = 27.69, \beta_{12} = 34.15$	2015
S⟩	2084		2082		2083
2A⟩	4015		4015		4015
A + S⟩	4071		4071		4071
2S⟩	4154		4152		4154
3A⟩	5998		6000		5998
2A + S⟩	6045		6044		6041
2S + A⟩	6121		6119		6118
3S⟩	6206		6210		6212

relative intensities of the peaks. Harmonic scaling laws are often used to relate the transition dipole moments of coherences, i.e., $\mu_{21} = \sqrt{2}\mu_{01}$ and $\mu_{32} = \sqrt{3}\mu_{01}$. It is observed that the peak intensities significantly deviate from harmonic scaling laws even after taking bandwidth into consideration. Such effects most likely originate from non-perturbative saturation effects in metal carbonyls since they have extremely high transition dipole moments. In coupled oscillator spectra, presence of relaxation assisted peaks further affects the relative peak intensities.

In addition to peaks that originate from the non-dynamical fifth-order interactions, there are also peaks which arise from population and coherence transfer effects.⁴⁷ Such peaks have been observed and characterized in 2D IR spectra of RDC and other systems. In 3D IR spectra, such peaks are more pronounced because of a higher possibility of coherence and population transfer in two coherence or population times as opposed to one, as has been pointed out for two-quantum 2D IR spectroscopy.⁵⁸ Furthermore, higher vibrational levels are expected to have faster coherence transfer lifetimes. Fig. 13 shows two such possible Feynman diagrams that describe peak G, with similar diagrams for peak H. Peaks G and H can be created by either population or coherence transfer but requires at least one of the two. Additional 3D IR experiments with varying population time delays would be needed to distinguish between the two processes. Understanding vibrational coherence transfer and vibrational population transfer is important both in understanding vibrational

spectroscopy in condensed phases and in elucidating chemical reaction mechanisms. Although it is possible to study such processes using 2D IR spectroscopy, ambiguities that exist in peak assignments can be alleviated by 3D IR spectroscopy. For instance, the peaks 6 and 6' in the 2D spectra (Fig. 4(b)) are not overtones but are caused by coherence or population transfer which we know because the real overtone peaks appear at C and C' in the 3D spectra.

VI. CONCLUSION

In conclusion, fully absorptive 3D IR spectroscopy is implemented with a dual acousto-optic shaper. By adding a second shaped pulse to the 2D IR spectrometer, we add another dimension to measure absorptive 3D IR spectra without complicated alignments. Use of mid-IR pulse shaping enables automatic phasing, ease of implementation and high degree of control over 3D experiment. We explore data collection in the time- and frequency-domains. We extract the eigenstates of a single mode oscillator and a coupled oscillator up to the third excited state. With a third dimension, assignment of relaxation assisted peaks is less ambiguous and we identify several such peaks.

Three-dimensional IR spectroscopy will have several unique capabilities over 2D IR spectroscopy.⁵⁹ With 3D IR spectroscopy it is possible to measure three point frequency fluctuation correlation functions, arising out of non-Gaussian dynamics.⁶⁰ Trilinear coupling terms between three modes arising out of cubic anharmonicities will exhibit cross peaks in 3D IR that cannot be observed in 2D IR spectra.¹⁷ Judicious choice of narrowband and broadband pulse sequences like the ones demonstrated in this paper can enable one to isolate 3D spectra of just the cross peaks leading to simplifications of congested spectra. These capabilities will increase the scope and applicability of infrared spectroscopy. Of course it takes longer to collect a 3D than 2D IR spectrum both because a larger number of data points must be collected and because the signal strength is smaller, which could limit its utility in monitoring kinetically evolving samples like protein aggregation.⁶¹ However, one could still collect 2D planes

FIG. 13. Feynman diagrams for peak G due to population or coherence transfer (dashed line) in T_4 .

through the 3D IR spectra without collecting the entire data set, by either using a mixed time/frequency pulse sequence or by holding constant one time delay, as is often done in NMR. For samples at equilibrium in which averaging is not difficult, we believe that experiments like these will become routine in pulse shaping spectrometers since the laser beams are passively phase stable, spectra are automatically phased and absorptive line shapes obtained, as demonstrated here. It should also be possible to collect 3D IR spectra using a single pulse shaper to create all four pump pulses like has recently been done in visible spectroscopy.^{14,15} The data presented here will help to facilitate this development by providing a well-characterized 3D IR spectrum as a reference.

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