# Fifth-order two-dimensional Raman spectra of CS<sub>2</sub> are dominated by third-order cascades

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We have demonstrated that fifth-order stimulated Raman spectra of the intermolecular modes in CS<sub>2</sub> are dominated by cascading third-order processes. Previous studies have successfully discriminated against a sequential cascading process, but did not account for parallel third-order cascades. All of our measured spectra were successfully simulated considering only cascades built directly from our measured third-order spectra. Using an appropriately chosen phase matching geometry we also measured the sequential cascade, which should exist with equal probability to the parallel cascade. When employing a phase matching geometry that provided substantial discrimination against all of the third-order cascades we were not able to measure any signal. We assign an upper limit for the true fifth-order signal of 2% of the cascaded signal. © 1999 American Institute of Physics. [S0021-9606(99)00131-2]

# I. INTRODUCTION

In recent years, significant effort has been focused on the development of higher order nonlinear optical spectroscopies, which involve multiple time and/or frequency variables, in an effort to probe microscopic details obscured by ensemble averaging inherent in linear spectroscopy.<sup>1–16</sup> The development of these techniques has exhibited many parallels with the extension of nuclear magnetic resonance (NMR) spectroscopy to multiple dimensions that began in the early 1970's.<sup>17,18</sup> Efforts to expand time-domain vibrational spectroscopy to higher dimensionality have, thus far, been dominated by Raman based techniques. This has followed directly from the fact that ultrafast laser technology has developed more rapidly in the visible and near-IR portion of the spectrum than at mid to far-IR wavelengths.

In time-domain nonresonant Raman spectroscopy of isotropic media, the third-order response is the lowest order nonzero response. The measured response is governed by the third-order susceptibility,  $\chi^3(\omega)$ , or equivalently in the timedomain by the third-order response function,  $R^{(3)}(\tau)$ .<sup>19</sup> Experimental examples include impulsive stimulated scattering (ISS),<sup>20</sup> optical Kerr effect (OKE), and optical heterodyne detected Raman induced Kerr effect spectroscopy (OHD-RIKES).<sup>21,22</sup> In these experiments, two light field interactions initially overlapped in time drive a vibrational coherence, the evolution of which is probed by a final Raman interaction occurring at some adjustable time later. There is a single time period under experimental control, and the measured response carries exactly the same information that is contained in an incoherent light scattering experiment involving a single-frequency variable.<sup>19</sup> Thus, the third-order time-domain nonresonant Raman experiment is considered a one-dimensional measurement that probes a macroscopic ensemble averaged response.

Fifth-order Raman spectroscopy, originally proposed by Tanimura and Mukamel, was initially directed towards investigating the relative contributions of homogeneous and

inhomogeneous line broadening.<sup>23</sup> The experiment involves preparation and probing steps that are very similar to those of the third-order Raman experiment. However, between the preparation of the initial vibrational coherence and the probing step, there is a second interaction with an additional pair of light fields that transfers the initial vibrational coherence to a second vibrational coherence. The second coherence is then probed in the final step. Thus, fifth-order time-domain Raman spectroscopy is a two-dimensional technique in that it has two controllable time periods, and the response is governed by the fifth-order response function,  $R^{(5)}(\tau_2, \tau_4)$ . Note that the two adjustable time variables are labeled  $\tau_2$  and  $\tau_4$ to remain consistent with our previous labeling.<sup>4</sup> The sequence of pulses and a representative ladder diagram for an  $R^{(5)}(\tau_2, \tau_4)$  response are shown in Figs. 1(a) and 1(b). The salient feature of these experiments is the direct transfer of the first vibrational coherence to the second vibrational coherence. For example, transferring an initial coherence to a second coherence of nearly equal frequency and opposite phase results in a rephasing process during the second time interval: this is analogous to spin echo<sup>17,18</sup> and photon echo<sup>24-26</sup> experiments, see Fig. 1(b). In this example, heterogeneous line broadening can then be removed via the rephasing events.

Following the initial-proposal, fifth-order time-domain Raman spectroscopy received considerable attention both theoretically<sup>12,27–32</sup> and experimentally.<sup>2–8,10,11,13,33</sup> The majority of the experimental efforts have involved probing the intermolecular modes of liquid CS<sub>2</sub>, a standard system in nonresonant Raman spectroscopy due to its very large polarizability and the wealth of available experimental results. It was quickly realized that, owing to the direct transfer of the first vibrational coherence to the second, the experiment offered substantially more information than had initially been considered. There is not only the ability to generate rephasing events in individual vibrational modes, but also the opportunity to directly probe the coupling between

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FIG. 1. (a) Diagram of the pulse sequence employed in these experiments and the labeling of the time variables. (b) Ladder diagram for one representative fifth-order Liouville pathway. The solid lines represent a ket side interaction and the dashed lines represent a bra side interaction. The wavy line is the emitted signal.

vibrations.<sup>2–4,10,11,27,28,31,32,34,35</sup> The existence of coupling between the Raman active vibrations is intrinsic to the generation of the fifth-order signal, making the experiment an exquisitely sensitive probe of these microscopic interactions. The fifth-order signal has the potential to identify the nature of the coupling and quantify the magnitude of the coupling between Raman active vibrations.

Although there appeared to be some limited agreement between theoretical predictions and the experimentally measured spectra, a number of discrepancies remained, even at a qualitative level of comparison. The most obvious difference between theory and experiment is the high degree of asymmetry in the experimental response along the two adjustable time delays. In previously reported experimental investigations,  $^{4,8,10}$  the response along the first delay,  $\tau_2$  , appears to peak at  $\tau_2 = 0$  with a rapid initial decay that evolves into a single exponential decay at long times, consistent with the reorientational relaxation identified in third-order experiments.<sup>21,22</sup> At early times along the second time delay,  $au_4$ , the response rises to a maximum near 180 fs, consistent with the early time response in the third-order experiments. These early time dynamics are typically associated with inertial and interaction induced responses. However, at long times in  $\tau_4$  the response decays far more rapidly than along  $\tau_2$ : reorientational relaxation appears to be missing from the response along  $\tau_4$ .

The deficiencies in the agreement between simulation and experiment have warranted reconsideration of the origin of the experimentally measured response. One of the greatest difficulties in measuring the true  $R^{(5)}(\tau_2, \tau_4)$  response is avoiding contamination from cascading third-order processes. These processes generate signals in the same phase matched direction and with the same overall dependence on the laser fluence as the true  $R^{(5)}(\tau_2, \tau_4)$  response. However,



FIG. 2. Representative ladder diagrams for the possible cascading pathways (a) sequential and (b) parallel.

even though the cascades generate the final signal in the same phase-matched direction, the phase matching conditions for the intermediate steps in the cascades may be significantly different than the true  $R^{(5)}(\tau_2, \tau_4)$  response. As a result, the phase matching, as well as the relative magnitudes of both the cascaded and true responses, will dictate the relative contribution from each of the possible processes to the measured signal. The cascading lower order signals contain no more information than the individual lower order signals aside from the ability to directly measure the interferences between different  $R^{(3)}(\tau)$  tensoral responses.<sup>36</sup> Cascading lower order processes have been seen in a number of different experiments.<sup>37–39</sup> In both frequency-resolved<sup>9</sup> and time-resolved<sup>40,41</sup> fifth-order coherent anti-Stokes Raman spectroscopy (CARS) measurements, the authors concluded that the observed signals were dominated by cascading thirdorder processes.

There are two types of third-order cascades that can lead to an overall fifth-order signal. The two types of cascades are shown in Figs. 2(a) and 2(b), and we refer to them as sequential and parallel. Previous fifth-order stimulated Raman investigations of the intermolecular motions in CS2 and CS<sub>2</sub>/benzene binary mixtures have taken the sequential cascade into consideration.<sup>4,8,11,42</sup> However, the parallel cascade, shown in Fig. 2(b), was not included in the analysis of the intermolecular fifth-order spectra. In this manuscript, we demonstrate that the parallel cascade is the dominant contributor to the previously reported fifth-order nonresonant Raman studies of intermolecular modes, and we place an upper limit on the ratio of the signal from cascaded processes to the true  $R^{(5)}(\tau_2, \tau_4)$  response. We note here that throughout this manuscript we refer to the measured response as  $R^{(5)}$ in reference to the overall dependence of the observed signal on the incoming laser fields. This includes both the true  $R^{(5)}(\tau_2, \tau_4)$ , governed by the fifth-order response function, and the cascaded responses, governed by two third-order response functions.

#### **II. EXPERIMENT**

# A. Experimental setup

The experimental apparatus has been described in detail previously.<sup>4</sup> Briefly, 1 nJ, 28 fs [Gaussian, full width at half maximum (FWHM)] pulses centered at 800 nm are generated in a standard titanium sapphire oscillator.<sup>43</sup> The pulses are regeneratively amplified resulting in 40  $\mu$ J, 47–65 fs (Gaussian, FWHM) pulses at 3.8 kHz.<sup>44</sup> The output is split into five beams of nearly equal intensity that are focused into a 1.0 mm long sample of  $CS_2$  by a 2 in. diameter, 30 cm focal length singlet quartz lens. Pulse widths were determined by autocorrelations between pairs of each of the five beams using a 0.2 mm BBO crystal in place of the sample. The polarization of each beam was individually adjustable by a  $\lambda/2$  plate. A power attenuator consisting of a cube polarizer and  $\lambda/2$  plate was used to adjust the total power at the sample to 2.5–5.5  $\mu$ J/pulse. Mechanical stages (Newport) provided the two adjustable time delays with resolutions of 0.67 fs along  $\tau_2$  and 6.7 fs along  $\tau_4$ . For 2D fifth-order spectra, the stages were swept in such a fashion as to collect surfaces as a function of the two time delays between the laser pulses directly,  $\tau_2$  and  $\tau_4$ . The skewing of the data in quadrant II with respect to  $\tau_2$  and  $\tau_4$ , which was present in the previously reported spectra taken by sweeping the true stage delays, is avoided via this mode of collection.<sup>4</sup> The signal was collected by imaging onto a silicon diode (Thorlabs DET-1). Beam one was mechanically chopped at one half the frequency of the laser, and the data were collected by a lock-in amplifier synchronized to the mechanical chopper. The output of the lock-in amplifier was sent to a personal computer used for storing the data.

The experiments were preformed at room temperature. Carbon disulfide, 99.9%, was used as received from Aldrich Chemical Co.

# **B.** Phase matching

The phase matching geometries employed in these experiments are shown in Fig. 3. Table I lists the crossing angles in the sample for each of the five beams accounting for both the air/sample cell and sample cell/CS<sub>2</sub> interfaces. The signals were collected along the phase-matched direction  $k_1 - k_2 - k_3 + k_4 + k_5$ . In addition to the overall fifthorder phase-matched direction, we are also concerned with the intermediate steps involved in both the sequential and parallel cascade processes. There are two possible intermediate steps for the sequential cascade, along  $k_2 - k_1 + k_3$  and  $k_1 - k_2 + k_4$ , and there are two possible intermediate steps for the parallel cascade along  $k_1 - k_2 + k_5$  and  $-k_3 + k_4$  $+k_5$ . The overall signal intensity will be weighted by the degree of phase matching. The degree of phase matching can be expressed as sinc( $\Delta k l/2$ ), where  $\Delta k$  represents the difference between the incoming wave vectors and the signal wave vector and l is the path length.<sup>19</sup>

Although our sample cell has a path length of 1 mm, the actual path length is determined by the crossing of the in-



FIG. 3. Circles are the crossing volumes of the incoming beams as a function of position in the sample for the experimental phase matching geometries employed. The solid lines are Gaussian fits to these distributions. The FWHM of the Gaussian fits are reported as the effective path length in Table II. (Inserts) The experimental phase matching geometries. The circles are the incoming fields. The diamonds are the positions of the sequential cascade intermediates and the squares are the positions of the parallel cascade intermediates. The direction of the overall fifth-order signals are shown as the open circles containing an "s." The angles for the different geometries are displayed in Table I and the sinc( $\Delta k l/2$ ) values for the different phasematched signals and intermediates are displayed in Table II.

coming beams in the sample. To estimate the effective path length as determined by the beam crossing, we have calculated the overlap volume of all five beams as a function of position in the sample. Our beams had diameters of 3 mm at the focusing lens. The crossing volume was weighted by a Gaussian transverse beam amplitude profile with a FWHM of 40% of the beam diameter. Both the weighted crossing volumes as a function of position in the sample and a Gaussian fit to the distributions are shown in Fig. 3. We assign the FWHM of the Gaussian fit to the crossing volume distributions as the effective path length. The resulting effective path lengths are listed in Table II for each of the phase matching geometries employed along with the resulting values of the phase matching conditions for the overall fifth-order process and the possible third-order cascade intermediates. The positions of the cascade intermediates are shown in Fig. 3.

Third-order measurements were collected in the phase

TABLE I. Angles in the sample for each of the five beams in the phase matching geometries shown in Fig. 3. All values are given in degrees. Theta ( $\theta$ ) is the azimuthal angle measured counterclockwise from the positive *x* axis and phi ( $\varphi$ ) is the elevation from the *z* (propagation) axis.

Phase matching geometry	Beam 1		Beam 2		Beam 3		Beam 4		Beam 5	
	θ	φ	θ	$\varphi$	θ	$\varphi$	θ	φ	θ	φ
3(a)	150.5	2.4	112.5	1.9	67.5	1.9	29.5	2.4	-90.0	1.8
3(b)	123.5	1.6	163.5	0.4	80.9	2.1	35.1	2.1	-90.0	1.8
3(c)	-15.3	1.8	-158.2	1.7	-138.9	0.8	-40.2	1.0	168.4	2.5

matching geometry shown in Fig. 3(a) along  $k_2 - k_1 + k_5$  with beams 3 and 4 blocked.

#### **III. RESULTS**

# A. Third order

Figure 4 shows the third-order homodyne response,  $|R^{(3)}|^2$ , for CS<sub>2</sub> at room temperature and three combinations of the field polarizations,  $R^{(3)}_{zzzz}(\tau)$ ,  $R^{(3)}_{yzyz}(\tau)$ , and  $R^{(3)}_{zyyz}(\tau)$ . Here, and throughout the rest of this paper, we adopt the labeling convention for the polarization indices in which the time ordering of the interacting fields reads from right to left. Our spectra agree well with the numerous previous measurements on this system.<sup>20–22,33</sup> All of the third-order spectra contain a pulse width limited electronic response centered at the time origin. The nuclear response shows an inertial component at early times with the signal rising to a maximum around 180 fs. This is followed at long times by a single exponential decay with a time constant of 0.8 ps that is associated with reorganizational relaxation. The relative weighting of the electronic and nuclear responses varies significantly for the different polarization combinations. The polarization dependence of the third-order response will be presented and discussed in greater detail elsewhere.<sup>36</sup> The third-order responses are presented here for use in simulations of cascaded third-order signals, which will be compared with the measured fifth-order spectra.

### B. Fifth order

Figures 5(a) and 5(b) present contour plots of the complete homodyne detected,  $|R^{(5)}|^2$ , 2D fifth-order spectra for two of the most commonly measured polarization combinations,  $R_{zzzzzz}^{(5)}(\tau_2, \tau_4)$  and  $R_{zzzyyz}^{(5)}(\tau_2, \tau_4)$ . The spectra in Fig. 5 were taken using the phase matching geometry in Fig. 3(a). The  $R_{zzzzz}^{(5)}(\tau_2, \tau_4)$  spectrum is nearly identical to that previously reported<sup>4</sup> and the  $R_{zzzyyz}^{(5)}(\tau_2, \tau_4)$  surface is in good agreement with the slices measured by Steffen *et al.* and Tominaga and Yoshihara.<sup>8,10</sup> Due to the symmetry of phase matching geometry 3(a), quadrants I and II are related by a pulse pair interchange between pulses 1 and 4 and pulses 2 and 3. For both of the polarizations shown, this pulse pair interchange which tensor element is measured, and as a result quadrant II is simply a mirror image of quadrant I.

Away from the two time axes both surfaces show similar behavior. Along  $\tau_2$  the signals decay rapidly from a maximum at  $\tau_2 = 0$  and evolve into a single exponential decay at long times with the same time constant,  $t_c \sim 0.8$  ps, that is associated with reoganizational relaxation in the third-order measurements. Along  $\tau_4$ , the response at early times rises to a maximum at  $\tau_4 \sim 180$  fs, which is similar to the inertial behavior seen in the third-order measurements. The signal then decays much more rapidly,  $t_c \sim 0.25$  ps, than along  $\tau_2$ . In the  $R_{zzzzz}^{(5)}(\tau_2, \tau_4)$  spectrum there is a prominent ridge on the  $\tau_4 = 0$  axis that is pulse width limited in  $\tau_4$  and shows nearly identical time-dependent behavior to the  $R_{zzz}^{(3)}(\tau)$  response along  $\tau_2$ . This ridge also exists in the  $R_{zzzyyz}^{(5)}$  $\times(\tau_2,\tau_4)$  spectrum; however, the relative intensity is significantly reduced, and the behavior along  $\tau_2$  is more similar to  $R_{zvvz}^{(3)}(\tau)$ . There also appears to be a ridge on the  $\tau_2 = 0$ axis in both spectra. This ridge is more prominent in the  $R_{zzzyyz}^{(5)}(\tau_2, \tau_4)$  spectrum, and in both cases the behavior along  $\tau_4$  appears to mirror the decay along  $\tau_4$  away from the axis. The  $R_{zzzzz}^{(5)}(\tau_2, \tau_4)$  spectrum shows a strong peak at the time origin that is pulse width limited in both time dimensions. This feature does appear in the  $R_{zzzyyz}^{(5)}(\tau_2, \tau_4)$  spec-

TABLE II. Degree of wave vector matching for the overall fifth-order response and the cascade intermediates,  $sinc(\Delta kl/2)$ . The beam geometries are shown in Fig. 3. The effective path lengths, *l*, are the FWHM of the Gaussian fits to the crossing volume distributions shown in Fig. 3.

		sinc( $\Delta k l/2$ ) for geometries shown in Fig. 3.				
	-	3(a)	3(b)	3(c)		
Overall fifth-order signal	$k_1 - k_2 - k_3 + k_4 - k_5$	0.89	0.46	0.88		
Sequential	$k_2 - k_1 + k_3$	-0.20	0.96	-0.09		
intermediates	$k_1 - k_2 + k_4$	-0.19	0.96	-0.09		
Parallel intermediates	$k_1 - k_2 + k_5$	0.75	-0.09	-0.15		
	$-k_3+k_4+k_5$	0.75	-0.14	-0.15		
Effective path length (mi	0.61	0.73	0.73			



FIG. 4. Homodyne detected third-order spectra for CS<sub>2</sub> at room temperature. There are three combinations of the field polarizations shown:  $R_{zzzz}^{(3)}$  no marker (solid line only),  $R_{yzyz}^{(3)}$  "+," and  $R_{zyyz}^{(3)}$  "\*." The  $R_{zzzz}^{(3)}$  spectrum has been scaled by a factor of 0.67.

trum, but it has a much lower intensity as compared with the rest of the response.

Figure 6 shows the  $R_{zzzzz}^{(5)}(\tau_2, \tau_4)$  spectrum taken in phase matching geometry 3(b). Although the signal intensity is comparable to that in the  $R_{zzzzzz}^{(5)}(\tau_2, \tau_4)$  spectrum taken in phase matching geometry 3(a), there is a clear change in the 2D response. The overall response now appears symmetric about the two time variables with a time-dependent response



FIG. 5. Contour plots of the 2D fifth-order spectra collected using phase matching geometry 3(a) for CS<sub>2</sub> at room temperature. Two different combinations of the incoming beam polarizations are shown: (a)  $R_{zzzzzz}^{(5)}$ , (b)  $R_{zzzyzz}^{(5)}$ . Parallel cascades dominate the signals of both spectra.



FIG. 6. Contour plot of the 2D fifth-order spectra collected using phase matching geometry 3(b) for CS<sub>2</sub> at room temperature for  $R_{zzzzzz}^{(5)}$ . Sequential cascades dominate the signal.

along each of the two dimensions that is very similar to the one-dimensional  $R_{zzzz}^{(3)}(\tau)$  response. Now there is an inertial rise with a maximum at ~180 fs and a decay at long times with a time constant of ~0.8 ps along both  $\tau_2$  and  $\tau_4$ . The ridges along the time axes have also become more symmetric. They are both pulse width limited in one time dimension and have the  $R_{zzzz}^{(3)}(\tau)$  time dependence along the other time dimension. The ridge along  $\tau_4$  at  $\tau_2=0$  has a greater intensity than the ridge at  $\tau_4=0$  along  $\tau_2$ . This is the result of the ridge at  $\tau_2=0$  having contributions from both quadrants I and II within the autocorrelation width of the pulses. There is also a strong peak at the time origin that is pulse width limited in both time dimensions.

Phase matching geometry 3(c) was derived to provide a high degree of discrimination against all four of the cascading pathways. Even though the overall fifth-order process is well phase matched in geometry 3(c), we were unable to measure any significant signal in this phase matching geometry. Based on the signal levels found for the spectra in Figs. 5 and 7, we are able to place an upper limit on the signal from phase matching geometry 3(c) at 2% of the signals collected in phase matching geometries 3(a) and 3(b).



FIG. 7. Simulation of the 2D response, Eq. (1d), for the case of nonlinear polarizability coupling, Eq. (3), and in the isotropic limit. A sum of the three brownian oscillators reported in Ref. 33 was used to model the time dependences.

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#### **IV. DISCUSSION**

#### A. Fifth-order response

The true fifth-order response,  $R_{nmlkji}^{(5)}(\tau_2, \tau_4)$ , can be expressed as the sum of three hyperpolarizability interactions, Eqs. (1a)–(1c), and a three-point polarizability correlation function, which describes the two-dimensional response, Eq. (1d).<sup>27</sup> As discussed

$$R_{nmlkji}^{(5)}(\tau_2,\tau_4) \propto \langle \xi_{nmlkji} \rangle \delta(\tau_2) \, \delta(\tau_2 + \tau_4) \tag{1a}$$

$$+\frac{i}{4\hbar}\langle [\alpha_{nm}(\tau_4), \gamma_{lkji}(0)]\rangle \delta(\tau_2)$$
(1b)

$$+\frac{i}{2\hbar}\langle [\gamma_{nmlk}(\tau_2), \alpha_{ji}(0)]\rangle \delta(\tau_4)$$
(1c)

$$-\frac{1}{4\hbar^2} \langle [[\alpha_{nm}(\tau_2 + \tau_4), \alpha_{lk}(\tau_2)], \alpha_{ji}(0)] \rangle$$
(1d)

previously, the 2D response, Eq. (1d) can be expressed in terms of the coordinates via a Taylor expansion of the polarizability operator.<sup>12,31,33</sup> The assumption of a linear dependence of the polarizability on the coordinates leads to a zero value for the three-point correlation function in Eq. (1d). This demonstrates the intrinsic dependence of the fifth-order signal on the microscopic coupling in the system. Two types of coupling have been identified that can generate the fifthorder signal, anharmonicity in the vibrational potential, AN, and nonlinearity in the dependence of the polarizability on the vibrational coordinate, NP.<sup>5,12,23</sup> The individual responses based on AN and NP coupling can be expressed in terms of single time, two-point correlation functions, Eqs. (2) and (3).<sup>12,31</sup>

$$R^{(5),AN} \propto g^{(3)} \alpha^{(1)} \alpha^{(1)} \alpha^{(1)} \int_0^\infty d\tau C(\tau_4 - \tau) C(\tau) C(\tau_2 - \tau),$$
(2)

$$R_{nmlkji}^{(5),\text{NP}} \propto \alpha_{nm}^{(2)} \alpha_{kl}^{(1)} \alpha_{ji}^{(1)} C_{nmlk}(\tau_4) \cdot C_{lkji}(\tau_2 + \tau_4) + \alpha_{nm}^{(1)} \alpha_{kl}^{(2)} \alpha_{ji}^{(1)} C_{nmlk}(\tau_4) C_{lkji}(\tau_2).$$
(3)

In Eqs. (2) and (3),  $\alpha^{(n)}(t)$  is the *n*th derivative of the polarizability with respect to the coordinate(s), and  $g^{(3)}$  is the third derivative of the ground state potential with respect to coordinates.

Using a fit to the third-order response consisting of three brownian oscillators as the basis set of two-point correlation functions, Tokmakoff *et al.* simulated the intrinsic heterodyne response for both the AN and NP coupling cases.<sup>33</sup> They demonstrated that anharmonic coupling was not consistent with the measured fifth-order observable. In particular, the rise of the signal in the AN simulations was far too slow along  $\tau_4$ . Simulations based on NP coupling were more successful in generating the measured response. The simulations were for the heterodyne detected cross-term  $R^{(3)}(\tau_4)R^{(5)}(\tau_2,\tau_4)$ , and although the NP coupling expression for  $R^{(5)}$  in Eq. (3) is asymmetric in the two time variables, the  $R^{(3)}$  term also provided significant asymmetry in the total response allowing for good agreement with the strongly asymmetric measured spectra. Figure 7 shows a simulated room temperature homodyne response,  $|R^{(5)}(\tau_2, \tau_4)|^2$ , for the NP coupling case using the three brownian oscillators in Ref. 33. As noted by Hahn *et al.*, the required assumption of a set ratio between  $\alpha^{(1)}$  and  $\alpha^{(2)}$  for all of the modes considered when using the NP coupling expression in a sum over multiple modes is often not justified.<sup>45</sup> Using instantaneous normal mode simulations (INM), Murry *et al.* have demonstrated that this assumption is clearly not appropriate for the intermolecular motions in  $CS_2$ .<sup>46</sup> Therefore, we only simulate the fully coupled, or isotropic, limiting case where the response is described by a single mode represented by a sum of the three brownian oscillators.

Comparison between our homodyne spectra and the NP coupling simulation in Fig. 7 clearly shows a number of qualitative discrepancies. Compared to the data in Fig. 5(a), which peaks at  $\tau_2=0$  along  $\tau_2$ , the simulation peaks away from zero along  $\tau_2$  and decays too slowly along  $\tau_4$ . Compared to the data in Fig. 6, the simulation decays too rapidly along  $\tau_4$ . Although only the isotropic limiting case has been examined, consideration of multiple modes as the basis correlation functions for the NP coupling simulation would not improve agreement with experiment: as long as the NP coupling is considered time independent, the basic symmetry of the response will remain the same even though the actual time dependence of the experimental response might change.<sup>33</sup>

## B. Third-order cascades

There are two types of third-order cascades that can lead to an overall fifth-order signal. Ladder diagrams for the two types of cascades are shown in Figs. 2(a) and 2(b), and we have labeled them sequential and parallel. A sequential cascade involves the emission of a photon from the first vibrational coherence that then participates in driving a vibrational coherence on a different chromophore. Previous fifthorder investigations of the intermolecular motions in CS<sub>2</sub> and CS<sub>2</sub>/benzene binary mixtures have addressed this type of cascade directly.<sup>4,8,11,35,42</sup> The phase matching geometries in these experiments were designed with the express purpose of poorly phase matching the first step in the sequential cascade in an effort to discriminate against the sequential cascade signal. This discrimination appears to have been quite successful: a sequential cascade will generate a response that is completely symmetric in both of the time variables; however, it has been the distinct asymmetry of the experimentally observed spectra that makes the data so difficult to explain.

The ladder diagram for the parallel cascade is shown in Fig. 2(b) and begins with the preparation of vibrational coherences on separate chromophores as a result of interactions with the first and second pairs of laser fields. The probing interaction on one of the chromophores then results in a field that is involved in a probing interaction on the other chromophore. This type of cascade was not previously considered in the intermolecular fifth-order spectroscopic studies and thus was not considered in the design of the phase matching geometries used in these studies.<sup>48,10</sup> However, the

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FIG. 8. Contour plots of the simulated homodyne 2D cascaded spectra for phase matching geometry 3(a). The spectra were calculated from Eqs. (4) and (5) directly using the third-order spectra in Fig. 4 as the third-order responses and weighting everything by the appropriate phase matching values shown in Table II. Two combinations of the incoming fields are shown (a)  $R_{zzzyzz}^{(5)}$ , (b)  $R_{zzyyz}^{(5)}$ .

parallel cascade was very recently investigated and implicated as the major contributor to the signal in fifth-order CARS experiments.<sup>40,41</sup> As shown in Eq. (5), a parallel cascade results in an asymmetric signal about the two time variables.

The cascaded responses are expressed in terms of the third-order responses in Eqs. (4) and (5).

$$R_{nmlkji,\text{sequential}}^{(3)^{2}} = R_{\text{seq}}^{(5)}(\tau_{2},\tau_{4}) = R_{\sigma kji}^{(3)}(\tau_{2})R_{nml\sigma}^{(3)}(\tau_{4}) + R_{\sigma kji}^{(3)}(\tau_{4})R_{nml\sigma}^{(3)}(\tau_{2}), \quad (4)$$

$$R_{nmlkji,\text{parallel}}^{(3)^{2}} = R_{\text{par}}^{(5)}(\tau_{2},\tau_{4}) = R_{\sigma m j i}^{(3)}(\tau_{2}+\tau_{4})R_{n\sigma l k}^{(3)}(\tau_{4}) + R_{\sigma m l k}^{(3)}(\tau_{4})R_{n\sigma j i}^{(3)}(\tau_{2}+\tau_{4}).$$
(5)

In addition, there are terms that arise from the interchange symmetry with respect to i/j and k/l. These terms are not exactly equal in all cases; for example, note the difference between the measured  $|R_{zyzy}^{(3)}(\tau)|^2$  and  $|R_{zyyz}^{(3)}(\tau)|^2$  responses in Fig. 4. The homodyne cascaded signal is proportional to  $|R_{seq}^{(5)}(\tau_2, \tau_4) + R_{par}^{(5)}(\tau_2, \tau_4)|^2$ . For a given phase matching geometry, the intermediate third-order responses must be weighted by their individual phase matching values, and the overall process will have the same phase matching condition as the true  $R^{(5)}$ . All of the phase matching values for the geometries employed here are displayed in Table II. Figure 8 shows the simulated homodyne cascade signals for phase matching geometry 3(a) for both of the combinations of field polarizations measured in Fig. 5. The simulated cascade for phase matching geometry 3(b) is shown in Fig. 9 for the all



FIG. 9. Contour plot of the simulated homodyne 2D cascaded spectra for phase matching geometry 3(b). The spectrum was calculated from Eqs. (4) and (5) directly using the third-order spectrum in Fig. 4 as the third-order response and weighting everything by the appropriate phase matching values shown in Table II.  $R_{zzzzzz}^{(5)}$  is shown.

parallel case. In the simulations, the third-order responses are taken directly as the square root of the third-order homodyne spectra. For the two polarization combinations considered, potential interferences between the individual third-order responses in the overall cascaded process are not evident. This is consistent with the positive tensor values for both the electronic and nuclear portions of all involved third-order responses:  $R_{zzzz}^{(3)}(\tau)$ ,  $R_{yzyz}^{(3)}(\tau)$ , and  $R_{zyyz}^{(3)}(\tau)$ .<sup>47</sup> We have also added an additional Gaussian weighted ridge along the  $\tau_2 = 0$  axis to simulate the counting of both quadrants I and II that can occur within the autocorrelation width of the pulse.

There is not only excellent qualitative agreement between the simulated third-order cascaded spectra and our measured spectra, but also significant quantitative agreement. Figure 10 shows slices from the simulated and experimental spectra for phase matching geometry 3(a) that demonstrate the agreement in the time-dependent behavior along both dimensions. Phase matching geometry 3(b) exhibits a similar degree of quantitative agreement. In addition to the time-dependent behavior, the relative magnitudes of the signals for the two polarization combinations considered in Figs. 5 and 8 are also in good quantitative agreement across the entire 2D spectrum.

# C. Relative magnitudes of the cascaded and true fifth-order signals

From the third-order cascade simulations and the change in shape of the measured response with different phase matching conditions, it is clear that the measured fifth-order spectrum is dominated by cascading third-order signals. Based on (1) the degree of disagreement with the simulated true fifth-order response, Sec. IV A, (2) the excellent agreement with simulated third-order cascaded spectra, and (3) our inability to measure any significant signal in phase matching geometry 3(c), which strongly discriminates



FIG. 10. Comparison of slices from the spectra shown in Figs. 5 and 8. The solid lines are from the measured spectra, Fig. 5, and the dashed lines are from the simulated cascades, Fig. 8. The spectra shown on the left are slices along  $\tau_2$  for  $\tau_4 = 150$  and 250 fs. The spectra shown on the right are slices along  $\tau_4$  for  $\tau_2 = 300$  and 500 fs.

against all the cascaded pathways, we assign a lower limit of 50 for the ratio of the homodyne detected third-order cascade to the true fifth-order signals.

Other experimental investigations are also completely consistent with signals originating from cascaded third-order processes. For the experimental conditions used by Steffen et al., we calculate an effective path length of  $\sim 0.9$  mm and find a sinc( $\Delta k l/2$ ) value of ~0.6 for each of the parallel cascade intermediates while both of the sequential cascade intermediates are very poorly phase matched,  $sinc(\Delta k l/2)$ < 0.1.<sup>10</sup> As a result, we would predict that parallel cascades dominate the signals, just as in our results for phase matching geometry 3(a). This is consistent with the agreement between the results of Steffen et al. and Fig. 5(b).<sup>10,11,13,35</sup> We note that although phase matching geometry 3(c) was derived from the phase matching geometry employed by Steffen et al., our small changes in beam positions and modest increases in the incoming beam angles resulted in a reasonably large decrease in the phase matching for the parallel cascade intermediates. For the experimental setup employed

by Tominaga and Yoshihara, we calculate an effective path length of 0.5 mm and find that the sequential cascade intermediate  $k_2 - k_1 + k_3$ , and parallel cascade intermediate  $k_1$  $-k_2+k_5$ , are almost perfectly phase matched, sinc( $\Delta kl/2$ )  $=0.99.^{5}$  The other two cascade intermediates are poorly phase matched, sinc( $\Delta k l/2$ )~0.1. In this case, we would predict spectra that have equal contributions from sequential and parallel cascades. An equally weighted sum of the two different types of cascades will have the same time dependence along  $\tau_2$  as that of either cascade alone, which is the time dependence of the third-order signal. However, the time dependence along  $\tau_4$  will have a decay that is faster than that along  $au_2$  but slower than the  $au_4$  decay for spectra dominated by the parallel cascades. This is consistent with the data of Tominaga *et al.*, which appear to have a  $\tau_4$  decay that lies between that of our parallel cascade dominated spectra, Fig. 5(b), and the third-order decay shown in Fig. 4.<sup>5,8</sup> Thus, we believe that the signals reported by Tominaga and Yoshihara<sup>5,6,8,42</sup> and Steffen *et al.*,<sup>10,11,13,35</sup> as well as by Tokmakoff *et al.*,<sup>4,33</sup> arise predominantly from cascades.

For comparison of the third-order cascade processes with the nonlinear polarizability coupling model, we express the third-order response functions as a linear expansion of the polarizability operator in terms of the coordinate, Eq. (6). Higher order nonlinear contributions to  $R^{(3)}(\tau)$  are assumed to be negligible. For this discussion, we consider the case where the incoming fields are all parallel, and the tensoral indices are dropped.

$$R^{(3)}(\tau) \propto \alpha^{(1)} \alpha^{(1)} C(\tau).$$
(6)

As discussed in Sec. IV A, only the isotropic case is considered. Using Eq. (6) for  $R^{(3)}(\tau)$ , comparison of Eqs. (3), (4), and (5) shows that the ratio of the cascaded third-order process to the NP coupling case for the true fifth-order response can be expressed in terms of the ratio of the first and second derivatives of the polarizability with respect to the coordinate:

$$\frac{R_{\text{cascade}}^{(5)}}{R_{\text{NP}}^{(5)}} \propto \frac{[\alpha^{(1)}]^4}{[\alpha^{(1)}]^2 \alpha^{(2)}} = \frac{[\alpha^{(1)}]^2}{\alpha^{(2)}}.$$
(7)

Using INM simulations, Murry *et al.* have calculated the relative ratios of  $\alpha^{(1)}$  and  $\alpha^{(2)}$  for 5000 intermolecular modes in CS<sub>2</sub>.<sup>46</sup> Although their results show this ratio to be somewhat randomly distributed amongst the 5000 modes, the majority of the modes have a ratio of  $\alpha^{(1)}/\alpha^{(2)} > 100$ . This result implies that for the homodyne measurement, where the signal is proportional to  $|R^{(5)}|^2$ , the cascaded signal will be  $10^2 - 10^4$  times larger than the fifth-order signal from NP coupling. This is a value well above our lower limit for this ratio of 50.

For intermolecular modes, Fourkas and Keyes have suggested that a cancellation among the continuous distribution of frequencies for the anharmonic coupling will result in a much lower contribution to the fifth-order response than NP coupling.<sup>48</sup> However, using *ab inito* calculations Hahn *et al.* have found that for the intramolecular modes in CHCl<sub>3</sub>, the AN coupling is one to ten times larger than the NP coupling.<sup>45</sup> They also report values for the ratio in Eq. (7), and for some modes the ratio of Eq. (7) approaches unity. This would suggest that the AN coupling contribution to the true fifth-order response in these intramolecular modes may be as large or larger than the cascaded contribution. Using typical values and the expression provided in Ref. 9, Ulness et al. estimated that the time-resolved sequential CARS process was one to ten times larger than the true fifth-order CARS process.<sup>40</sup> Both of these estimates suggest that for intramolecular modes, the AN coupling may result in signals that are comparable to the cascaded processes. We note that there are features in the fifth-order nonresonant spectra of  $CCl_4$  and  $CHCl_3$  obtained by Tokmakoff *et al.*<sup>2</sup> that cannot be explained by cascaded processes alone.

An additional parameter that is typically considered when comparing cascades to the true fifth-order response is the number density, or concentration, dependence. The concentration dependence has been cited as evidence that the measured spectra were from the true fifth-order response for both intramolecular and intermolecular modes.<sup>8,42,49,50</sup> For the intramolecular modes, where the chromophores are well defined and the polarizability can be considered molecularly additive, this type of analysis is straightforward. However, this type of analysis is not applicable to the case of intermolecular modes. The typical approach taken when attempting to vary the concentration of intermolecular modes is the use of binary mixtures. When one considers the many body nature of the intermolecular modes and the complexity of binary mixtures, it is not directly evident that there is any proportionality between the ill-defined concept of concentration for intermolecular modes and the binary mixture fraction. An additional complication in the use of binary mixtures comes from the significant changes in the polarizability weighted density of states as a function of binary mixture fraction. In other words, the intermolecular spectrum is changing with binary mixture fraction. These types of effects are clearly evident in third order measurements of CS<sub>2</sub> in binary mixtures.<sup>21</sup> As a result, a binary mixture dependence of the signal intensity cannot be used to make an assignment of the origin of a given intermolecular spectral feature.

#### **V. CONCLUSION**

We have experimentally demonstrated that the signals in fifth-order stimulated Raman measurements of the intermolecular modes in CS<sub>2</sub> are dominated by cascading third-order processes. We were able to generate nearly perfect matches to the measured 2D spectra using simulations based on cascades of our directly measured third-order signals. In addition, we were unable to measure any signal when using a phase matching geometry designed to discriminate against the cascaded process while maintaining good phase matching for the overall fifth-order response. The results show that the previous measurements are predominantly the result of a parallel cascade process that had not been previously considered in intermolecular studies. Using an appropriately designed phase matching geometry, the sequential cascade process, which should occur with an equal intensity to the parallel cascade, was also measured. We place an upper limit on the ratio of the cascaded to true fifth-order contribution to the homodyne signal of 2% of the cascaded signal. This upper limit is consistent with an analysis of the ratio based on nonlinear polarizability coupling as the origin of the true fifth-order signal. The ratio suggests that for CS<sub>2</sub> even the most cleverly designed phase matching geometry may not be capable of providing sufficient discrimination against the cascaded processes when finite beam diameters are considered. One possible solution, albeit quite challenging experimentally, may be a heterodyne measurement where the phase of the local oscillator is adjusted to select the true fifth-order signal, which should be phase shifted from the cascaded signals by  $\pi/2$ . This solution, along with a detailed derivation of the cascaded responses for both fifth- and seventh-order stimulated Raman experiments, will be presented in Ref. 51.

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