

WHAT ROLE CAN FOUR-WAVE MIXING TECHNIQUES PLAY IN COHERENT CONTROL?

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Abstract

The role of four-wave mixing (FWM) techniques in coherent control is considered from the point of view of some of the most important developments in this field over the past years, namely multiphoton excitation, pump-dump methods, interference between coherent pulses, chirped laser pulses, and optimal control. FWM techniques provide a powerful platform for combining coherently multiple laser pulses. We explore the effectiveness of these techniques in controlling chemical reactions. The phase relationship between the pulses is maintained by detecting the signal in a phase-matching direction. The results presented show control over the observed dynamics from ground and excited state populations. The FWM signal results from the polarization of the sample following three different electric field interactions. The virtual echo sequence is achieved by the interactions of the sample with three consecutive electric fields characterized by $\exp[i(\mathbf{kx}-\omega t)]$, $\exp[-i(\mathbf{kx}-\omega t)]$ and $\exp[i(\mathbf{kx}-\omega t)]$. This sequence allows control over the observed ground or excited state dynamics. With the photon echo pulse sequence, characterized by interactions with $\exp[-i(\mathbf{kx}-\omega t)]$, $\exp[i(\mathbf{kx}-\omega t)]$, and $\exp[i(\mathbf{kx}-\omega t)]$, we find that control of ground and excited state populations is not achieved. Differences between these two pulse sequences are shown experimentally and illustrated using wave packet simulations. Data obtained using the ‘mode suppression’ technique, in which the timing between the first and third laser pulses is fixed while the second pulse is scanned are presented. We show that this technique does not suppress the observed vibrational coherence from the ground or excited state but it yields an additional component to the signal that is independent of the vibrational coherence of the sample. Spectrally dispersed FWM is shown to be an ideal tool for studying intramolecular dynamics and this idea is applied to understanding the role of chirp in controlling molecule-laser interactions. All coherent control methods are affected by the rate of decoherence of the sample. Here we show how these rates are measured with FWM techniques. The measurements presented here illustrate how photon echo measurements yield the homogeneous relaxation rate while the virtual echo measurements yield the sum between homogeneous and inhomogeneous relaxation rates.

I. Introduction

The road to laser control of chemical reactions has been one of many important turns.^{1,2} The invention of the laser gave scientists the hope of controlling chemical reactions that went beyond photochemistry. One of the first paradigms was based on the monochromatic quality of the laser. This fostered the idea that chemical bonds could be selectively broken by multiple photon excitation MPE at a specific frequency determined by the vibrational frequency of the particular bond.³⁻⁷ It was soon discovered that the energy being deposited in one vibrational mode was quickly dissipated to other intramolecular chemical bonds by a process termed intramolecular vibrational redistribution (IVR).⁸⁻¹⁰ This realization meant that the MPE technique inevitably resulted in fission of the weakest bond. Therefore, the main use of MPE would be to deposit energy in selected molecules in a mixture, based on spectral absorption. Based on a thorough understanding of this method, bond selective fission would require excitation of a local mode in a molecular system with extremely slow IVR. This excitation would need to be followed by prompt bond fission achieved with UV excitation or a reactive collision. Vibrationally mediated chemistry was first proposed and demonstrated by Letokhov and coworkers.¹¹ Selective bond breaking of the OH or OD bonds in HOD was proposed by Imre and coworkers¹² and carried out experimentally by Crim and coworkers¹³ and Valentini and coworkers.¹⁴

With the realization that IVR prevented the accumulation of energy in a given chemical bond for periods longer than a picosecond, two different approaches to control chemical reactions were developed independently. One approach was based on the continuous and coherent excitation of two competing reactive pathways. This method dubbed coherent control (CC) is based on the constructive or destructive interference among the different photochemical pathways.^{15,16} This approach has yielded some very remarkable successes in controlling atomic ionization,¹⁷ controlling the outcome of chemical reactions,¹⁸ controlling the flow of current in semiconductors,¹⁹ and controlling directionality of photoelectron emission in the gas phase.²⁰ Although it is still too early to have a complete outline of the limitations of this technique, we can identify coherence relaxation as an important parameter for the efficiency of this technique. In general, coherence relaxation is slower for gas-phase samples, especially samples cooled by molecular beam expansion. On the other hand, the inhomogeneous and homogeneous broadening that accompanies condensed phase measurements makes this the most challenging environment for CC. To achieve coherent control in condensed phase, one must

ensure that the sample-laser interactions occur in a time scale that is faster than IVR and coherence relaxation.

The other approach to control chemical reactions circumventing IVR is founded on the use of ultrafast laser pulses. Conceptually, the laser-sample interactions take place in a time that is short compared to IVR. This concept was embodied in the theory of pump-dump.^{21,22} On the experimental front, Zewail, who had been active in the determination of IVR rates,²³ realized that shorter pulses would be critical for achieving control of chemical reactions.⁹ The development of lasers with femtosecond pulse duration made the pursuit of this work possible.²⁴⁻²⁷ Zewail's group quickly incorporated these techniques and dedicated their work to the study the ultrafast dynamics of chemical reactions in the gas phase.²⁸⁻³¹ Ultrafast lasers have been used to make important contributions to the study of chemical reactions in gases, liquids, solids and surfaces.²⁹⁻³²

The experimental observation of vibrational wave packet dynamics caused by impulsive excitation of multiple vibrational levels using femtosecond pulses indicated that pump-dump control could be used to achieve mode selective chemistry using ultrafast lasers, for a comprehensive review of wavepacket dynamics see Reference 2. This is true provided the timing between the laser pulses was carefully controlled. Most of the femtosecond pump-probe experiments can be considered control experiments even though the coherence between the laser pulses does not play a role in the observed signals. The timing between the laser pulses controls the species that is excited with the probe laser. Limitations to these types of experiments relate primarily to wave packet spreading and the lack of a well-defined phase between pump and probe pulses. Even for isolated molecules, wave packet spreading results from the anharmonicity of the potential energy surface. This limitation can be addressed with chirped laser pulses, whereby the laser chirp can be used to cause a focusing of the vibrational wave packet at a particular point in time and space.³³⁻³⁵ Single chirped laser pulses, in fact, have been used to control multiphoton excitation and chemical reactions.³⁶⁻⁴¹ The main limitation to the use of ultrafast, precisely-timed, chirped pulses has been our limited knowledge of the molecular Hamiltonian.

A new paradigm in control of chemical reactions was the proposition that an electric field exists such that a specific target can be optimally achieved.⁴² This approach to control depends on the search for the optimal laser pulse. The search, initially carried out by computer algorithms (for reviews see References 42,43 and

1) has reached experimental realization in recent years.⁴⁴⁻⁵⁰ Optimal control has the distinct advantage that the molecular Hamiltonian does not need to be known. The search is carried out by a number of statistical methods that operate on a trial and error basis. The solution is found by a number of iterations as the optimal field is found by convergence to a maximum attainment of the target. This iterative process without a priori knowledge implies that the technique can be applied to very complex systems. Interestingly enough, some of the theoretical work in the field of optimal control has sought that optimal solutions in many cases converge to combinations of a small number of pulses with a specific time delay and phase relationship, for example see References 51 and 52. This observation highlights the importance of every one of the methods that have been used to control chemical reactions: (a) multiphoton interactions, (b) short pulses, (c) pulse phase coherence, (d) timing between laser pulses, and (e) chirp.

The above combination of characteristics can be achieved by a setup combining collinear, phase-locked femtosecond laser pulses. Scherer *et al.* showed that phase locking provided control over the laser-molecule interaction in a collinear pump-probe arrangement.⁵³ Changing the phase of the laser pulses by π , the data from Scherer *et al.* showed control over the excited state wave packets of iodine.⁵³ The experimental realization of these measurements required active phase control over the two laser pulses in order to ensure a specific phase between the pulses in the interaction with the sample. This requirement makes the technique difficult. Bergmann and coworkers have developed a method for laser control of rovibrational population transfer based on stimulated Raman adiabatic passage (STIRAP). This technique uses two collinear pulses with different wavelengths that are partially overlapped in time such that the dump pulse precedes the pump pulse to achieve near 100% efficiency.⁵⁴ The combination of degenerate femtosecond laser pulses can be achieved using, four-wave mixing methods. These techniques, developed over the last three decades, are nonlinear optical processes based on the coherent combination of laser pulses without requiring active phase stabilization.⁵⁵⁻⁵⁹ Coherent AntiStokes Raman Scattering (CARS) measurements can be considered examples of control over excitation pathways, see for example the recent work of Schmitt *et al.*^{60,61} In some cases the emission of signal can be controlled in FWM experiments, this is achieved through the interference of different nonlinear four-wave mixing signals.⁶²

Our group has recognized nonlinear optical techniques, which use phase matching detection as a means to ensure coherence among a number of laser beams,

to be an ideal platform for the coherent combination of laser pulses. Our work on FWM has shown that pulse sequences can take advantage of the vibrational dynamics of the sample molecules for achieving control of the electronic and vibrational process with three degenerate laser pulses.^{63,64} Our work has yielded experimental observations as well as a theoretical understanding that shows that pulse sequences can be used to select among different Liouville pathways.^{64,65} More recently, we have shown that coherently combined chirped femtosecond pulses can be used to control intramolecular dynamics of the system and developed a technique for the characterization of these dynamics based on spectrally dispersed FWM.^{66,67} Realizing that coherent control can only be achieved while the system maintains its coherence, we have carried out coherence relaxation measurements that use some of the pulse sequences we have identified to provide information from ground or excited state coherence.

Gas-phase molecular iodine was chosen in this study for various reasons. (i) The visible $B \ ^3\Pi_{0+u} \leftrightarrow X \ ^1\Sigma_{0+g}$ transition has been well characterized by frequency^{68,69} and time domain spectroscopies.^{60,64,66,67,70-74} (ii) The B-X transition is resonant with the fundamental wavelength of our ultrafast laser system. (iii) The vibrational periods of both X and B states are longer than the duration of our laser pulses, allowing us to impulsively excite wave packets in each state. (iv) The vibrational periods of the X and B states are quite different making assignment of the signal relatively easy.

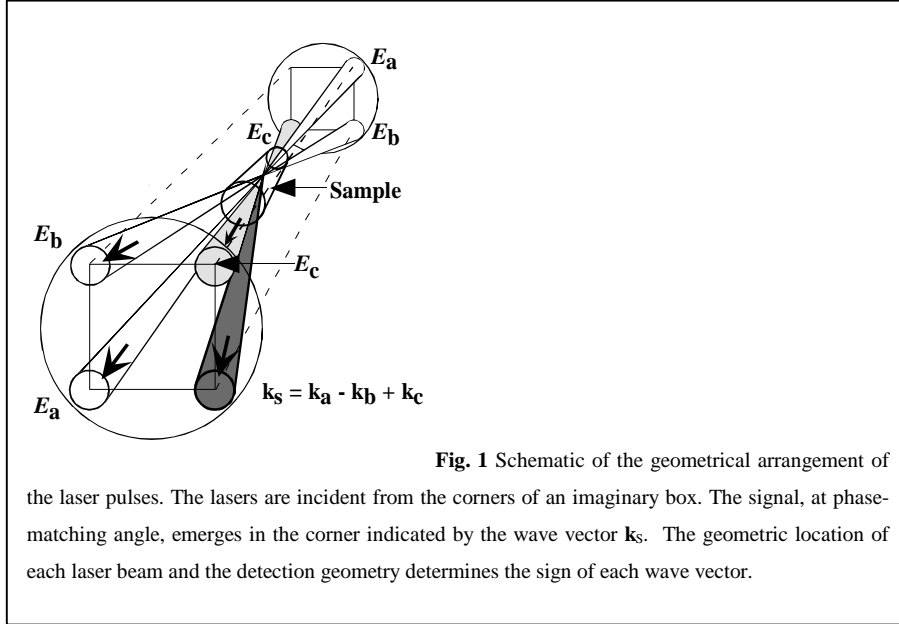
In this paper, we demonstrate how pulse sequences can be used to control the observation of ground or excited state vibrational dynamics in three-pulse FWM experiments. One of the reasons for the success of this technique arises from the realization that laser-molecule interactions can take place with two components of the electric field $\exp[-i(\mathbf{kx}-\omega t)]$ or $\exp[i(\mathbf{kx}-\omega t)]$. Which one interacts first with the molecule changes the nonlinear optical processes that can be observed and controlled. This dual interaction is typically explained in terms of *bra* and *ket* interactions. Here we show how this selection is done in the laboratory and illustrate with different pulse sequences the effects each interaction with the electric field has on the sample. We show that the FWM signal can be spectrally dispersed and that this additional dimension is of great importance in the characterization of intramolecular dynamics. We illustrate the effects of chirped pulse with spectrally dispersed FWM. Finally, as with most laser control methods, FWM based techniques are limited by the rate of coherence loss. We present measurement on the

rate of coherence loss using two methods in order to illustrate differences caused by inhomogeneous broadening.

II. Experimental

The experimental setup used for our measurements has been described earlier.^{66,75} The experiments were performed with home-built amplified CPM dye laser producing 65 fs pulses (transform-limited) centered around 620 nm. The bandwidth at FWHM is typically about 9 nm. At the output of the laser amplifier, the femtosecond pulses were compensated for linear chirp in a double-pass prism arrangement and had 350 μJ of average energy. After the compression, the beam was split by two successive beam splitters into three beams of approximately equal intensity attenuated down to $\sim 20 \mu\text{J}$ each. The three beams were combined in the usual FWM forward box geometry and focused by 500 mm lens in a quartz cell containing the iodine vapor (See Figure 1). The amount of iodine in the cell was such that the optical density reaches a maximum of 0.4 OD and is independent of temperature for $T > 80^\circ \text{C}$. The experiments presented here were carried out at 140°C . The coherence relaxation measurements were made in a different cell having excess iodine. The cell was heated evenly and the iodine vapor was in equilibrium with the temperature of the cell. Pulses in one of the beams (c or b, depending on the setup) were delayed with respect to the other two by a computer-controlled actuator (variable t delay), while the fixed delay (t_{nm} , where $n, m = a, b, \text{ or } c$) was manipulated by a manual translator (micrometer) by delaying the pulses from the second beam with respect to the fixed one. In all cases beam b was opposite to the signal (see Figure 1) and beam a was fixed in time. The fixed time delays were calibrated by autocorrelation with a computer-controlled delay.

The spatially filtered three-pulse FWM signal arising in the phase-matching direction $\mathbf{k}_S = \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c$ (see Figure 1) was collected by a spectrometer with wide spectral acceptance (2000 micron slits). For spectrally resolved transients, the slits were reduced to 250 micron. The transients were taken at 300-400 different time delays (about 200 shown) and averaged for 3-10 scans. At each time delay t , the signal was collected for 10 laser shots. Laser pulses with intensity outside one standard deviation were rejected. The accumulated intensity for each given time delay was stored and the final transients were divided by this set of intensities.



III. Results and discussion

In Figure 2, we use a pulse sequence in which the first two fields, E_a and E_b , are delayed by 460 fs or 614 fs. Both pulses are followed by field E_c after a variable time delay t . In the virtual photon echo (VE) measurement the first applied electric field is E_a ; when t_{ab} is 460 fs (Figure 2a) ($460 \text{ fs} = 3/2 t_e$ where $t_e = 2\pi/\omega_e$ for I_2 in the B state), the dynamics show 307 fs oscillations, reflecting only the excited state contribution.^{63,64} When t_{ab} is 614 fs (Figure 2b) (twice the vibrational period of I_2 in the B state), the dynamics show 160 fs oscillations, reflecting predominately the ground state contribution.^{63,64,66,67} By changing the fixed time delay between fields E_a and E_b , the observation of excited or ground state dynamics of I_2 can be controlled.

In Figure 2c and 2d, transients are shown for a sequence in which the first interaction is with field E_b preceding field E_a . This setup is known as stimulated photon echo (PE).⁵⁹ In the photon echo configuration, when t_{ba} is 460 fs, the dynamics reflect an excited state contribution with 307 fs oscillations; no ground

state contribution is observed in this transient. When t_{ba} is 614 fs, the 307 fs oscillations still dominate; however, after two picoseconds, some 160 fs oscillations

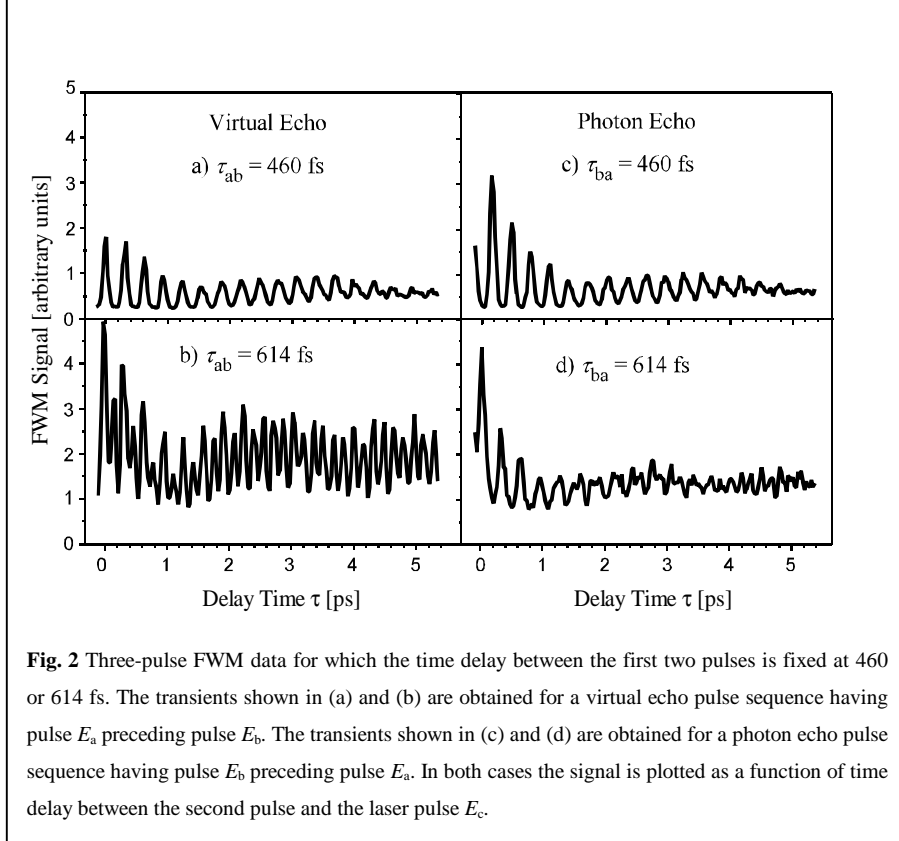
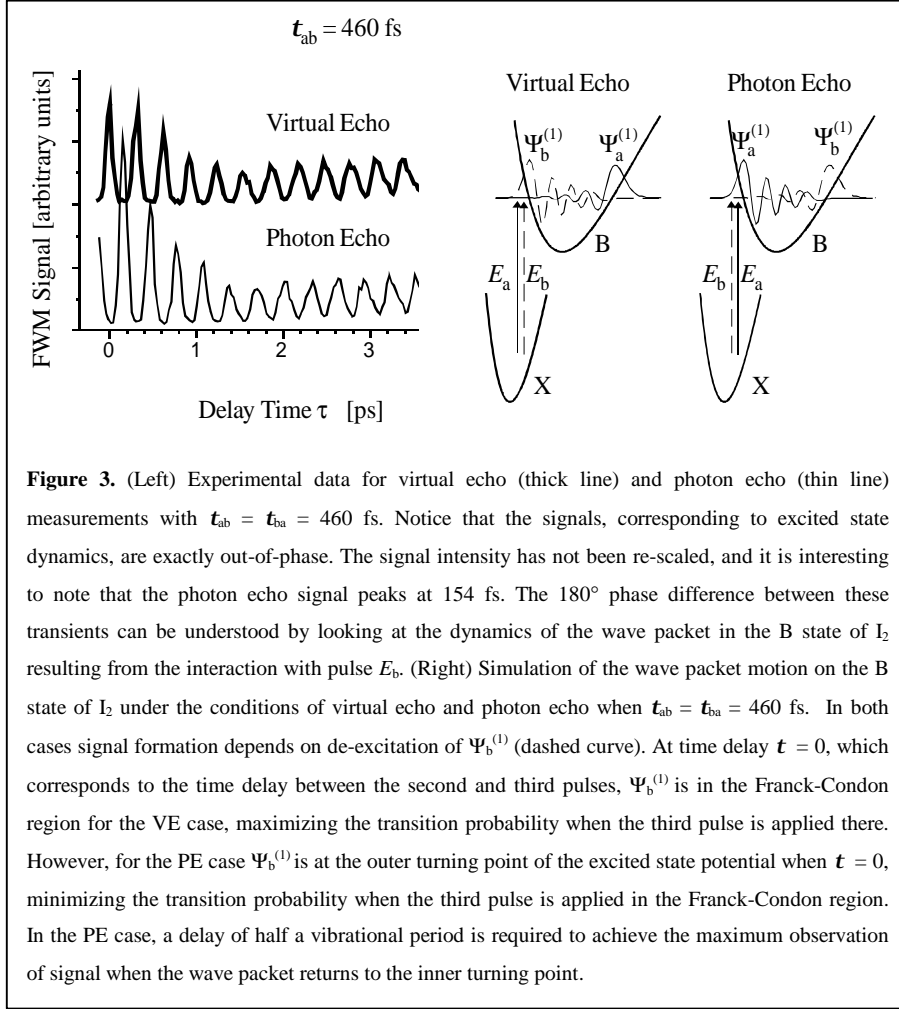


Fig. 2 Three-pulse FWM data for which the time delay between the first two pulses is fixed at 460 or 614 fs. The transients shown in (a) and (b) are obtained for a virtual echo pulse sequence having pulse E_a preceding pulse E_b . The transients shown in (c) and (d) are obtained for a photon echo pulse sequence having pulse E_b preceding pulse E_a . In both cases the signal is plotted as a function of time delay between the second pulse and the laser pulse E_c .

can be seen. Fourier transforms of these two photon echo transients confirm that for $t_{ba} = 614$ fs, there is ground state contribution absent when $t_{ba} = 460$ fs (FFT not shown). The signal contribution due to rotational dynamics (slow 2 ps modulation) that is clearly observed in the virtual echo transients is much smaller in the PE transients. In both cases, VE and PE, the value of the time delay t_{ab}/t_{ba} selects the Liouville pathways that yield to the dynamics of the ground or excited state. Note that this selection is much more efficient for the virtual echo setup.



In Figure 3, enlargements of the virtual echo and photon echo transients for $t_{ab} = t_{ba} = 460$ fs are shown. It is clear that the two transients are exactly out-of-phase with each other; when one is at a maximum, the other is at a minimum. In both cases, field E_c with $\exp[i(\mathbf{k}_c \cdot \mathbf{x} - \omega t)]$ must interact with the wave packet formed in the excited state by field E_b with $\exp[-i(\mathbf{k}_b \cdot \mathbf{x} - \omega t)]$ producing the de-excitation of the wave packet $\Psi_b^{(1)}$. In Figure 3 (right), schematics based on calculated wave packets of the excitation process after the first two electric fields are shown. The wave packet resulting from excitation by field E_a is shown as a solid line; the wave packet

resulting from excitation by field E_b is shown as a dashed line. In the virtual echo case, field E_b interacts with the system secondly with $t_{ab} = 460$ fs. At $t = 0$ fs (time delay for field E_c with respect to the second pulse), the dashed wave packet is at the inner turning point of the potential where the transition probability is maximized. Therefore the interaction results in a maximum signal. However, in the photon echo, field E_b interacts first with the system (still with $t_{ba} = 460$ fs) and at $t = 0$ fs, the wave packet is at the outer turning point of the potential with negligible transition probability upon interaction with field E_c . After half a vibrational period, the wave packet returns to the inner turning point, where the transition probability is maximized and the interaction with E_c produces a maximum signal. Therefore, the signals for photon echo and virtual echo are exactly out-of-phase. This is true in the particular case chosen where both PE and VE signals contain only excited state contributions. Pshenichnikov *et al.* have observed that an optical setup that interferes the electric fields resulting from the VE and PE signals leads, in some cases, to the complete loss of signal due to destructive interference.⁶² Here we show that the excited state vibrational coherence is exactly out of phase.

Shank and coworkers introduced a technique aimed at suppressing the contribution of vibrational coherence to photon echo signals.^{76,77} In this technique the time delay between the first and third pulse is fixed and the second beam is scanned. The goal of this method was to achieve accurate relaxation rate measurements in liquids by minimizing the observation of vibrational dynamics. The extent of apparent suppression has been shown to be proportional to the extent of inhomogeneous broadening in the sample.⁷⁸ Here we present this type of mode suppression measurement on a gas phase sample. Mode suppression should take place when the time delay between pulses E_b and E_a are in phase with the vibrational motion in the sample, here 614 fs, and mode suppression should not take place when the time delay t_{ba} is out of phase, here 460 fs.^{76,77} Beam E_c is scanned between time zero, where pulse E_b is fixed, and positive times, see Figure 4. The data for 460 fs, mode suppression is OFF, shows pronounced 307 fs vibrations corresponding to the excited state. Notice that the data shows no background or ground state contributions. The data for 614 fs, mode suppression is ON, shows a considerable background signal as well as ground and excited state vibrational dynamics. Our data indicates that the background of the ‘mode suppressed’ signal corresponds to a contribution that is independent of vibrational motion. However, excited and ground state vibrations are not suppressed in the gas phase where the contributions of inhomogeneous broadening are small. Note that with mode suppression we do not achieve control of ground or excited state excitation as we do

using the virtual echo setup,^{63,64,79} compare the results presented in Figures 2 and 4.

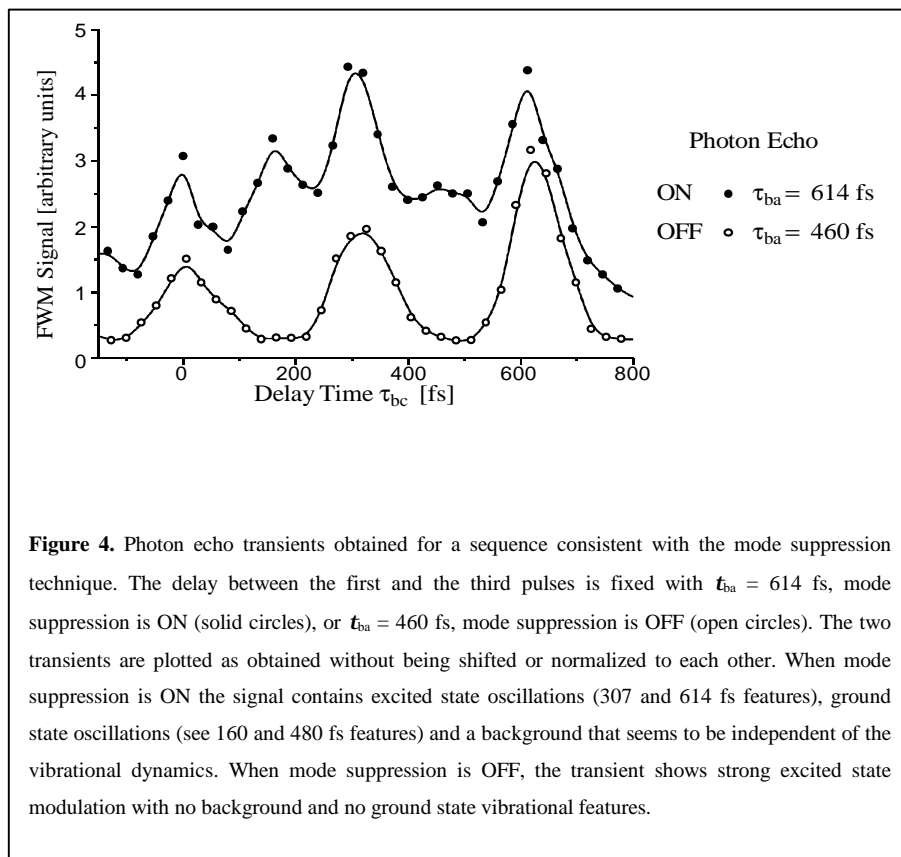


Figure 4. Photon echo transients obtained for a sequence consistent with the mode suppression technique. The delay between the first and the third pulses is fixed with $t_{ba} = 614$ fs, mode suppression is ON (solid circles), or $t_{ba} = 460$ fs, mode suppression is OFF (open circles). The two transients are plotted as obtained without being shifted or normalized to each other. When mode suppression is ON the signal contains excited state oscillations (307 and 614 fs features), ground state oscillations (see 160 and 480 fs features) and a background that seems to be independent of the vibrational dynamics. When mode suppression is OFF, the transient shows strong excited state modulation with no background and no ground state vibrational features.

All the transients presented so far are plots of the spectrally integrated signal as a function of time. The FWM emission contains valuable spectral information.^{66,67,80} Figure 5 shows spectrally dispersed data obtained as a function of t for a VE setup. When transform-limited pulses were applied with (a) $t_{ab} = 460$ fs, the spectrally dispersed signal can be assigned to the dynamics of the excited state with an oscillation period of $t_e = 307$ fs corresponding to vibrational levels $v' = 6-11$. No evidence of ground state dynamics is evident in this transient. In order to explore the role of the pulse chirp in the control of the molecular dynamics, experimental data for VE setup with $t_{ab} = 460$ fs was obtained when beams E_a and E_b are equally chirped, $f^2 = +3300$ fs² (see Figure 5b). From these

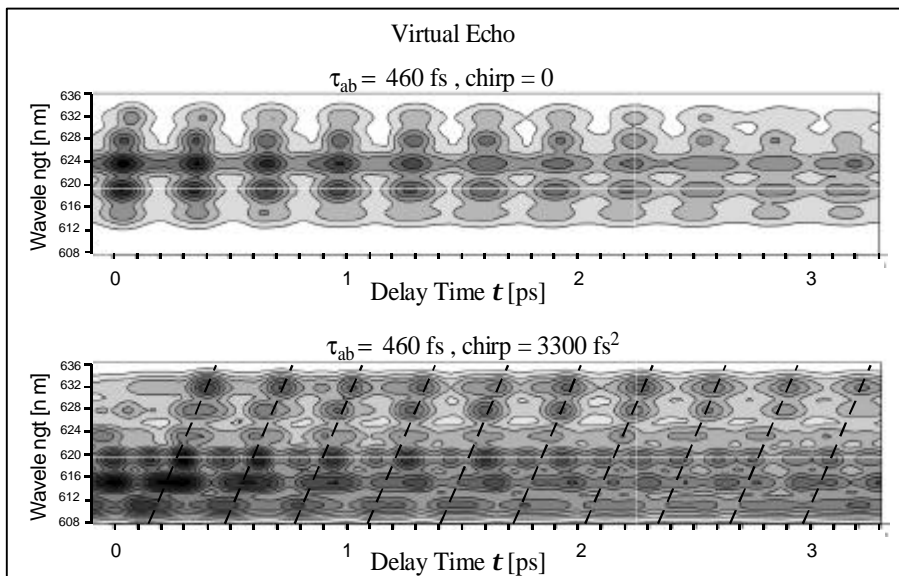
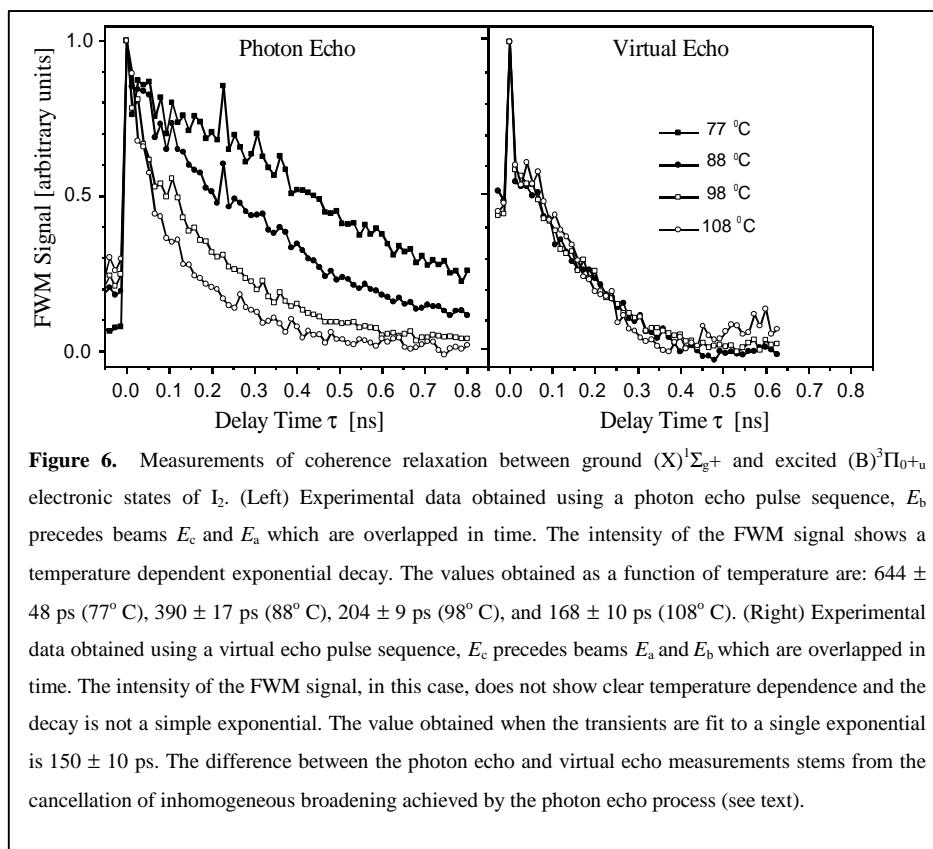


Figure 5. Spectrally dispersed data obtained for three-pulse FWM with a virtual echo sequence. (Top) Experimental data obtained with $t_{ab} = 460$ fs and transform-limited pulses. The first 3.3 ps of the spectrally dispersed data are presented as a contour plot. The data show primarily excited state vibrational dynamics (307 fs period). (Bottom) Same as above but the laser pulses were chirped with $\mathcal{F}^2 = 3300$ fs². The data show a mixture of ground and excited state vibrational coherence. Dashed lines corresponding to the magnitude of the linear chirp are drawn to indicate that the observed vibrational dynamics are chirped. The observation of the different phases as a function of wavelength would be lost in spectrally integrated FWM measurements.

data, it is clear that chirp pulses add a new contribution from the ground state dynamics. Near the 620 nm region of the spectrum, the mixing of both states dynamics is evident, whereas for longer wavelength the excited state dynamics prevails. Notice that the vibrational dynamics observed at redder wavelengths (632 nm) are advanced in time compared to those at bluer wavelengths (611 nm). This time delay is caused by the positive linear chirp in the laser pulses, which corresponds to ~ 300 fs in the 28 nm spectral range. Dashed lines with the calculated chirp rate are drawn in figure 5 and are shown to be in very good agreement with the experimental observation. The clear observation of a linearly chirped vibrational wave packet, as shown in figure 5, can not be obtained from spectrally integrated transients. Future experiments are planned with oppositely chirped pulses

and with different sign and magnitude of chirp for each pulse. For the measurements presented here the three beams were equally chirped in magnitude and sign.

Coherent control by definition depends on the rate of coherence loss in the sample. Therefore, measurements of the rate of coherence loss are of great importance. Since the first observation of photon echoes in molecules,⁵⁵ the technique has been heralded for the fact that inhomogeneous contributions to the relaxation rate cancel. This property has been utilized in numerous measurements primarily in condensed-phase samples.⁸¹ Here we illustrate photon echo and virtual echo measurements for gas-phase iodine. The results, shown in Figure 6,



demonstrate the temperature dependence of both methods. The reduced temperature dependence of the virtual echo measurements results from the overwhelming inhomogeneous contribution to the observed relaxation rates.

Measurements with the virtual echo pulse sequence are dominated by inhomogeneous broadening. Contributions to inhomogeneous broadening in this sample arise primarily from Doppler effects as well as from the Boltzmann distribution of initial rotational and vibrational states that are excited by the broadband ultrafast laser pulses. The photon echo data show clear temperature dependence and yields the homogeneous rate of decoherence in the sample. It is interesting to note that one can extrapolate to room temperature where the coherence in the sample lasts for several nanoseconds. These long coherence times may be useful for performing nonlinear optical operations related to quantum computing.

IV. Conclusions

In this paper, we explore the role of FWM methods in studying laser control of chemical reactions. The number of ultrafast pulses, the timing between them (sequence), their phase, and chirp are shown to be effective control parameters on the molecular system. All of these parameters play a role in the search for optimal laser fields for control. Here we demonstrate that FWM techniques are very useful in coherently combining a discrete number of laser pulses. This allows us to learn about the role of one or more control parameters in controlling a process. From our experiments, we obtain a set of conditions that achieves a particular target in terms of parameters that can be related to the Hamiltonian of the system being controlled. Theoretical as well as some experimental studies in optimal control have found that the optimal fields in many cases correspond to two or three pulses with a particular phase relationship and chirp.

One of the clearest applications of FWM methods to coherent control is their usefulness in measuring coherence relaxation. In recent years, ultrafast FWM methods have focused on measuring the rate of coherence loss in condensed phase. Here we show how the methods work for gas-phase samples and make a comparison between photon echo and virtual echo type measurements. The main difference is that for photon echo measurements the inhomogeneous broadening cancels giving a more accurate homogeneous coherence relaxation time. Our data can be used to extrapolate a homogeneous coherence time for iodine in the nanosecond scale, giving the possibility of performing a very large number of coherent interactions with this gas-phase sample at room temperature.

Degenerate FWM methods are shown here to be very useful in the characterization of intramolecular dynamics. Our measurements show the dynamics of the wave packet prepared by the first two laser pulses. When the pulses are transform limited and the delay between them is 460 fs, only excited state dynamics are observed. However, when the laser pulses are chirped, the observed dynamics are quite different. The results obtained from spectrally dispersed FWM show how the phase of different components of the wave packet are advanced or delayed. Lozovoy *et al.*⁶⁶ have shown that with two pulses that are equally chirped (sign and magnitude) the coherence of the wave packet can be controlled but not the population transfer. To affect the population transfer between two different states, the two pulses should have the same chirp magnitude but opposite signs.⁶⁶

In this paper, we illustrate differences between photon echo and virtual echo phenomena. We show that the signals have opposite phase. The distinction between these phenomena is of great importance for non-collinear excitation. Our results show control of the molecular system within the framework of phase-matching detection. This implies that only the subset of molecules forming a transient grating in the sample is controlled and yields the coherent signal observed. To achieve control over all molecules in the laser path, one must combine the lasers collinearly using phase-locking techniques.⁵³ Measuring changes in the overall population must then be done with a phase incoherent method. We show that with the virtual echo setup controlling the time between the first two pulses allows to control the observation of ground or excited state dynamics. This type of control is not available with the photon echo setup. Shank's and Wiersma's group have used the timing between the first and third pulses to suppress the contribution of vibrational coherence in the measurement of coherence relaxation of molecules in condensed phase.⁷⁶⁻⁷⁸ Mode suppression methods are shown here to add a component to the signal that is independent of vibrational coherence to the signal. However, in our data we do not observe the suppression of ground or excited state dynamics. Our finding is consistent with the observation of Wiersma indicating that mode suppression depends on large inhomogeneous broadening. Presumably, under large inhomogeneous broadening the vibrational coherence is lost leaving only the signal that is independent of the coherence.

In summary, we have shown that degenerate FWM methods can be used to measure coherence life times and to characterize the intramolecular dynamics of the system that is being controlled. We have shown the effect of chirp in controlling the vibrational coherence of the system. We have shown that the sequence in which

pulses are coherently combined can lead to control of the dynamics that are observed. With these observations, we conclude that FWM methods can play an important role in coherent control of chemical reactions.

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