Population and coherence control by three-pulse four-wave mixing

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Control of coherence and population transfer between the ground and excited states is reported using three-pulse four-wave mixing. The inherent vibrational dynamics of the system are utilized in timing the pulse sequence that controls the excitation process. A slight alteration in the pulse sequence timing causes a change in the observed signal from coherent vibration in the ground state to coherent vibration in the excited state. This control is demonstrated experimentally for molecular iodine. The theoretical basis for these experiments is discussed in terms of the density matrix for a multilevel system. © 1999 American Institute of Physics.

The probability of exciting a molecular system from the ground, |g⟩, to the excited state, |e⟩, by applying an electric field E is written quantum mechanically as

\[ P_{ge} = \langle e| \mu \cdot E | g \rangle^2 = \langle e| \mu \cdot E | g \rangle \langle g| \mu \cdot E^* | e \rangle, \] (1)

where \( \mu \) is the transition dipole moment that couples both states. Population inversion is not usually achieved because of the competition between the rates of absorption and stimulated emission. Control of the population transfer can be achieved if the two electric fields involved in the transition probability in Eq. (1) are different and are correlated in time or in phase. The three-pulse four-wave mixing (FWM) technique allows one to combine three nonphase-locked electric fields in a phase-matching geometry. The first two fields cause the population transfer and the third field probes the system. The specific timing between the pulses can be used to control the values of diagonal (population) and off-diagonal (vibrational coherence) matrix elements after the interaction with the first two electric fields. In this Communication, we briefly describe the three-pulse FWM technique and demonstrate on molecular iodine that pulse sequences can be designed to control the transition probability between two electronic states of a molecule.

It has long been recognized that in order to optimize the transfer of population between two states sophisticated electric fields are required.1–4 One can create such electric fields by a combination of phase and amplitude masks,5–7 or one can combine phase-locked laser pulses to achieve the desired field. Scherer et al.8 showed that when two phase-locked laser pulses were combined in phase the excited state dynamics of molecular iodine could be observed as fluorescence enhancement; however, when they were combined out of phase, the signal is observed as fluorescence depletion. Coherent control of chemical reactions depends on the relative phase of two different laser pulses that interact with the sample. The relative phase of the pulses can be used to control the population transfer from the ground to two different excited states.9–11 A different approach to controlling population transfer12 and enhancing reaction yields13,14 uses chirped laser pulses. Recent experiments in our group using chirped femtosecond three-pulse FWM have demonstrated that laser chirp can be used to control coherence transfer between the ground and excited states of I2.15

The theoretical foundation for three-pulse FWM is based on the time evolution of the density matrix in Hilbert space.16 Formulas are derived for a multilevel system with ground and excited electronic states with vibrational levels. Ultrafast transform-limited pulses are assumed with a bandwidth that exceeds the vibrational spacing in the ground and excited states. Electric field interactions are treated within the perturbation limit. A more detailed description of this theory will be published elsewhere.17,18 Initially, the density matrix, \( \rho^{(0)} \), contains the populations of the vibrational levels of the ground state with \( \Sigma \rho^{(0)}_{gg} = 1 \), while the population of each vibrational level in the excited state is taken as \( \rho^{(0)}_{ee} = 0 \). Here, the index \( g \) corresponds to the ground state vibrational quantum number, \( v^g \), and the index \( e \) corresponds to the excited state vibrational quantum number \( v^e \). In our calculation, we assume that the ground state vibrational levels are equally populated. This assumption is justified for a high temperature Boltzmann distribution. Different initial vibrational population distributions yield similar results.15,17 After the first interaction with the electric field, the density matrix evolves into a coherence between the ground and excited states where all the diagonal terms are zero and no net population transfer has occurred. The interaction with a second electric field completes the population transfer [Eq. (1)] without electronic coherence between the \( |g⟩ \) and \( |e⟩ \) states.


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Pulse Sequence

Double-sided Feynman Diagrams

(a) Excited State Dynamics

(b) Ground State Dynamics

FIG. 1. Pulse sequence and double-sided Feynman diagrams corresponding to the three-pulse FWM measurements. The diagrams show the observation of (a) excited state dynamics and (b) ground state dynamics. In this pulse sequence, the first two electric fields are separated in time by \( \tau_{ab} \). The third beam is scanned in time with time delay \( \tau \). The diagrams on the left correspond to the virtual echo signal in the direction \( \mathbf{k}_a = \mathbf{k}_b - \mathbf{k}_c + \mathbf{k}_r \); the diagrams on the right correspond to the echo signal in the direction \( \mathbf{k}_r = -\mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c \). In our experimental setup, we detect signal only in the \( \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c \) direction.

In general, an odd number of interactions with the electric fields will produce a coherence state, which is also a time-dependent polarization of the molecules. An even number of interactions will produce a population state that is characterized by the population of the vibrational levels in each electronic state (the diagonal terms) and the vibrational coherence within each electronic state (the off-diagonal terms in the diagonal blocks).

The changes in the density matrix after each interaction with an electric field involve different processes that can be followed using double-sided Feynman diagrams. For further information about these diagrams and their applications to four-wave mixing processes, the reader is referred to Refs. 16, 17, and 19–21. A wavy arrow symbolizes each electric field interaction and time progresses from the bottom to the top. The arrows pointing towards (away from) the center represent the photon annihilation (creation) operator; absorption or emission of a photon requires two electric field interactions. The diagrams in Fig. 1(a) show absorption of a photon and transfer of population to the excited state, while the diagrams in Fig. 1(b) show that the population remains in the ground state. The third pulse forms a polarization which emits radiation in the phase-matching direction \( \mathbf{k}_r = \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c \). The density matrix of the system depends on the sum of all the processes described by the four diagrams in Fig. 1. For calculating the density matrix (population and coherence) after two pulses, all diagrams must be used. Because we detect in the \( \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c \) direction, only the virtual echo processes are needed for calculating the emitted light after the third pulse. Furthermore, by proper selection of \( \tau_{ab} \), the time delay between the first two electric fields, we obtain a signal predominately from the excited or the ground state (i.e., \( V_{\text{Echo}} \) or \( V_{\text{Echo}}^\prime \)).

The density matrix elements after two electric field interactions contain a dependence on \( \tau_{ab} \) and this parameter can be used to control the transition probability from the ground to the excited state. After the second pulse is applied, the population transfer between the ground and excited states is given by

\[
\sum_e \rho_{ee}^{(2)} - \sum_g \rho_{gg}^{(2)} \\
\approx \cos \left( \frac{\omega_e \tau_{ab}}{2} \right) \cos \left( \frac{\omega_g \tau_{ab}}{2} \right) \cos (\omega \tau_{ab} - (\mathbf{k}_g - \mathbf{k}_b) \mathbf{r}),
\]

(2)

where \( \omega_e \) and \( \omega_g \) are the vibrational frequencies of the ground and excited states, respectively, \( \omega \) is the laser carrier frequency, and \( \mathbf{r} \) is the spatial coordinate in the sample. After the third pulse is applied at time \( \tau_{ab} + \tau \), the signal is a sum of two contributions, one from molecules that remained in the ground state following two interactions with the electric fields,

\[
S_g \propto \sum_{e,g,e',g'} \left| \tilde{\rho}_{gg}^{(2)} - \bar{\rho}_{gg'}^{(2)} \right|^2 \\
\propto (1 + \cos(\omega_e \tau_{ab}))(1 + \cos(\omega_g \tau)),
\]

(3a)

and the other from molecules in the excited state,

\[
S_e \propto \sum_{e',g,e''} \left| \tilde{\rho}_{ee'}^{(2)} + \bar{\rho}_{ee''}^{(2)} \right|^2 \\
\propto (1 + \cos(\omega_e \tau_{ab}))(1 + \cos(\omega_e \tau)),
\]

(3b)

where \( \bar{\rho}^{(2)} \) indicates only the terms of \( \rho^{(2)} \) that satisfy the phase-matching condition \( \mathbf{k}_a = \mathbf{k}_b + \mathbf{k}_c \). The matrix elements \( \rho_{gg}^{(2)} \) and \( \rho_{ee}^{(2)} \) describe the vibrational coherence in the ground and the excited states, respectively. Note that the signal amplitude depends on both the population and coherence elements as seen in Eqs. (3). If we define \( \tau_r = 2 \pi / \omega_e \) (and \( \tau_g = 2 \pi / \omega_g \)), at a time delay \( \tau_{ab} = \tau_r (n + 1/2) \), the signal for the ground state goes to zero. When \( \tau_{ab} = \tau_g n \), the signal for the ground state reaches a maximum. Similarly \( \tau_{ab} = \tau_g (n + 1/2) \) and \( \tau_{ab} = \tau_g n \) correspond to the minimum and maximum signals from the excited state, respectively. Maximum control can be achieved for values of \( \tau_{ab} \) that maximize one.
The most prominent peak is centered at 208.3 cm⁻¹ corresponding to ground state vibrational dynamics. A smaller peak centered at 107.7 cm⁻¹ corresponding to the rotational motion of the ground state. Note that the data in the range of 0–30 cm⁻¹ are magnified 15 times.

The experimental data presented here show that the time delay between the first two pulses in a three-pulse FWM experiment can be used to control the population transfer between ground and excited states. We have used this technique in order to study the vibrational dephasing in the ground and excited states of iodine as a function of temperature and pressure. By changing \( \tau_{ab} \), we were able to obtain both separate values from the same setup. \(^{25}\) The ability to transfer populations between different states is the chief tenet of the pump-dump control theory of Rice and Tannor. \(^{26,27}\) With three-pulse FWM we have shown that this control can be achieved with great efficiency. This technique can be used-
ful to study ultrafast dynamics involved in chemical reactions where one may want to follow processes that occur in the excited or the ground state exclusively.

Experimental control using multiple laser pulse excitation has been explored by a number of groups. While some of these experiments have been carried out without phase-locked pulses or phase-matching conditions, the most striking control over the excitation process is observed for phase-matched or phase-locked setups. Scherer et al. measured this effect by observing a change in the total fluorescence of I$_2$. Warren and Zewail used collinear phase-locked pulses to observe photon echos in I$_2$. Pshenichnikov et al. used a phase-locked FWM arrangement where the virtual echo and conventional echo processes interfere constructively or destructively. Time-delayed pulses can be combined to achieve population inversion by adiabatic passage. From Eq. (2), one can see that the population transfer is modulated by an electronic term with control parameters $\omega_\tau \tau_{ab}$ and a spatial condition $(k_g - k_b) \mathbf{r}$. The amplitude is further governed by the vibrational motion of both electronic states with control parameters $\omega_v \tau_{ab}$ and $\omega_g \tau_{ab}$. Our measurements use the vibrational time scale, which is independent of phase locking, to achieve the control.

In summary, we have demonstrated that pulse sequences can be found for three-pulse FWM experiments to optimize population and coherence transfer between two electronic states. In particular, we showed that for $\tau_{ab} = 460$ fs only excited state dynamics are observed, while for $\tau_{ab} = 614$ fs primarily ground state dynamics are observed. We plan to expand these types of experiments to systems where it will be possible to control the outcome of chemical reactions.

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