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Invited Paper

Quantum coherence in nonlinear optical processes: theory and possible application to control of chemical reaction and quantum computation

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Abstract

Phase dependence in nonlinear optical processes reveals an intriguing interplay between the phase coherence of a short laser pulse and the laser-induced quantum wave-packet dynamics, which cannot be observed in the linear response regime. In this paper, the intra-pulse quantum coherence is demonstrated with three examples: molecular π pulses for total inversion of electron population, unexpected chirp dependence in multi-photon absorption yield, and active control of decoherence for quantum computation. These results demonstrate that quantum coherence is a unique method in the dynamic control of molecular systems, which cannot be achieved otherwise. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Chirping; Multi-photon absorption; Population inversion; Quantum control; Decoherence

1. Introduction

The primary result reported here is the study of intra-pulse coherence in non-linear optical processes, which has become a novel approach in quantum coherence control. The goal of quantum control is to design laser pulses to drive a quantum system toward a specific target by means of phase coherence. This approach achieves selectivity in a chemical reaction by quantum mechanical interference and therefore differs fundamentally from conventional photo-excitation based on intensity modulations and from traditional chemical and mechanical manipulations [1–5]. Much effort has been devoted to using pulse pairs and pulse sequences in creating and annihilating wave packets. In this paper, we explore quantum coherence within a single pulse with the following three examples.

2. Molecular "π pulse" for total inversion of electronic state population

The creation and control of designated molecular configurations with shaped laser fields has been an intriguing theoretical problem. One such highly non-equilibrium configuration is the total inversion of electronic population in a molecular system, which has many potential experimental applications to a variety of fields such as (i) the suppression of ground state interference in many types of excited electronic state spectroscopy, scattering and diffraction experiments, (ii) more effective impulsive photo-initiation of chemical and biochemical reactions as well as their quantum control, (iii) more effective pumping of molecular lasers, (iv) brighter short-pulse fluorescence microscopy of biological samples. In many biochemical and biophysical experiments, to avoid damaging the excited molecules or the delicate environment of living cells, one would like to achieve maximal electronic excitation or initiation of chemical reactions with minimum peak laser intensity. In two-level systems, such as atoms and spins (nuclear magnetic resonance), complete population inversion by resonant "π pulses" is a long-established solution. The parallel general solution for the electronic population of molecules, with their multiple rovibrational states, has not previously been found, although some theoretical progress has been made [6–8].

Recently, we have demonstrated that such a solution does exist for molecular systems and can be understood with simple physical models [9]. Our optimal recipe for

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molecular "π pulses" consists of three ingredients: (i) sufficiently broad bandwidth to include all significant rovibronic transition frequencies between the two electronic states, (ii) large positive frequency chirp, limited by the time period when dissipative effects becomes appreciable, and (iii) high laser intensity, limited by the threshold where multi-photon processes take place. The "magic" of the positive chirp can be explained by vibrational coherence in the femtosecond regime and by adiabatic passage in the picosecond regime. Furthermore, by using a chirped pulse, the peak intensity of the field can be lowered below the threshold of multi-photon ionization and other nonlinear effects.

To understand the magic of positive chirp, a classical-like wave packet picture is most convenient for describing the "coherence" between the evolution of the femtosecond light field and the superposition of vibrational states it creates on a given electronic state [10]. Vibrational wave packets propagate on the two electronic potential energy surfaces shown in Fig. 1, and amplitude is transfered between them when the vertical transition is resonant with the instantaneous frequency of the optical pulse. Thus, optimal electronic state inversion occurs when the evolution of light frequency is opposite to the evolution of resonant frequency due to wave packet motion, in the sense that the instantaneous peak photon energy is increasing with time (positive chirp, $c' > 0$) while $V_e - V_g$ for the molecular wave packet is decreasing. In addition, with a large frequency chirp rate, adiabatic inversion by frequency sweeping becomes evident as the broad bandwidth of the π pulse can lock all the transitions between the electronic states.

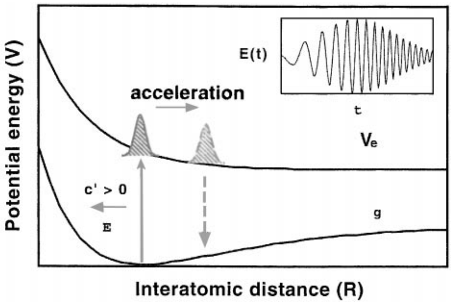

Fig. 1. Illustration of wave packet motion induced by a femtosecond pulse and its coupling to the chirped laser field. The inset is a schematic positively chirped electric field.

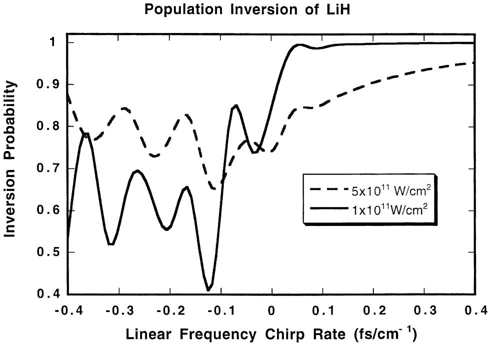

Fig. 2. Plot of the inversion probability of LiH as a function of linear frequency chirp rate for a fixed power spectrum with $P_0 = 100$ mJ/cm^2 ($I_0 = 5 \times 10^{11}$ W/cm^2) and $P_0 = 10$ mJ/cm^2, ($I_0 = 5 \times 10^{10}$ W/cm^2). The peak intensity is labeled for the $\pm 4 \times 10^{-5}$/cm^2 linear frequency chirp rate and increases as the chirp rate decreases.

Numerical results for a displaced oscillator, LiH and other molecules indicate that essentially complete electronic inversion of molecules can indeed be achieved by introducing positive frequency chirp in intense ultrafast laser pulses [9]. In Fig. 2, the inversion probability for LiH molecules is plotted as a function of linear frequency chirp rate c' for two values of peak intensity. The initial state for Fig. 2 is assumed to be the ground vibrational, rotational, and electronic state, that is, $v = M = J = 0$. As can be seen, the positive chirp consistently leads to high inversion probabilities, with complete inversion of over 99% for the higher-intensity curve. As expected, there is an overall increase of inversion probability with the absolute value of the chirp on both the negative and positive sides because of the adiabatic frequency sweeping effect and a sharp increase as one moves away from zero chirp toward the positive side because of the positive chirp effect. The valleys and peaks on the negative half of the plot are the result of the intra-pulse pump–dump mechanism and the vibrational oscillation on the excited electronic surface. Furthermore, such electronic population inversion is robust with respect to variations of the pulse parameters and with respect to thermal and condensed phase conditions including initial thermal distributions of rotational and vibrational levels and electronic dephasing.

In order to demonstrate complete inversion, the span of the laser pulse spectrum must be comparable to that of the absorption spectrum, but even if the laser pulse spectrum is not as broad as the absorption, the use of positively chirped pulses can still enhance the electronic state inversion. The recent condensed phase experimental results [11] on dye molecules and on the feedback quantum control of electronic state population transfer [12] demonstrate that such transfer can be enhanced by as much as factor of two using high-intensity, wide bandwidth, positively chirped pulses.

3. Chirp effects in multi-photon processes: time-delayed three-level model

This part of work is motivated by a three-photon absorption experiment in molecular iodine carried out in the Wilson group [13]. For a fixed power spectrum, the chirp increases the pulse duration and hence decreases the peak intensity. Since the multi-photon absorption yield depends on peak intensity, one would expect that the fluorescence from the three-photon absorption should reach a maximum at zero chirp. Surprisingly, the experimental result shows enhancements of as much as a factor of three for chirped pulses with respect to transform-limited zero chirp pulses. Theoretical analysis [14] reveals three possible intra-pulse mechanisms involved in the multi-photon processes:

3.1. *Sequential resonance effect*

The sign of the chirp leads to a frequency ordering that is in resonance first with the transition from the ground state to the intermediate state, and then in resonance with the transition from the intermediate state to the final state. (see Fig. 3) This resonance sequence within the same pulse helps build up transient population in the intermediate state and thus enhance the overall population transfer. The sequential resonance effect has been first predicted for atomic systems and is now used to explain the three-fold enhancement for the positive chirp in the iodine experiment.

3.2. *Time-delay resonance effect*

Within the same laser pulse, there is a time delay between the first and the second photons, as shown in Fig. 3. During this time delay, the vibrational wave packet created by the first photon gains momentum and moves towards the resonance window. The optimal chirp stretches the pulse duration to match the delay-time necessary for the wave packet to reach the resonance window. In contrast, the shortest pulse with zero chirp does not provide enough delay time for the wave packet motion; therefore, the peak intensity at zero chirp does not lead to the maximum yield, as one would expect.

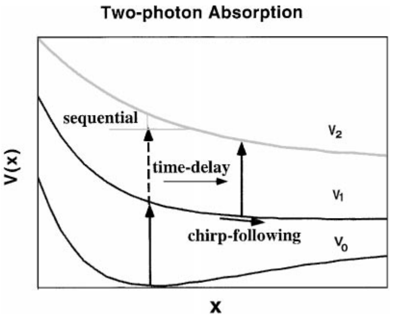

Fig. 3. A schematic diagram of a two-photon process where a molecule in the ground state |0⟩ is excited by a nearly resonant electric field to a final electronic state |2⟩ via an intermediate state 1⟩. The three intra-pulse dynamical mechanisms, i.e., sequential-resonance, time-delay, and chirp following, are illustrated from top to bottom.

3.3. *Chirp-following resonance effect*

Since the transition frequency is defined for the instantaneous position of the wave packet, the wave packet motion in Fig. 3 introduces time dependence in its resonance frequency. The optimal laser chirp follows the change in the transition frequency so that the population transfer to the final state can be most efficient [15,16]. Since the resonant frequency decreases with time, a negative chirp is usually preferred to maximize the chirp-following effect.

To capture the basic physics of multi-photon processes, one should take into account the wave packet motion on the intermediate state. This consideration leads to a simple time-delayed three-level model, where the vibrational wave packet created by the first photon gains momentum and moves to a new position for the second excitation. Then, the second transition frequency in the three-level model is no longer a constant but is a function of the delay time. With this simple modification, two-photon yield (or three-photon yield) can be obtained in a closed-form expression [14]

$$N_2 = \frac{P^2}{\Gamma\tau}|C(\Delta)|^2 \tag{1}$$

with $C(\Delta)$ explicitly given as

$$C(\Delta) = \int_0^\infty \mathrm{d}s \exp\left[-\gamma^2\frac{s^2}{4} - \frac{(\Delta-\alpha s^2)^2}{4\gamma^2} + \mathrm{i}(\Delta-\alpha s^2)\frac{s}{2}\right], \tag{2}$$

where $\gamma^2 = 1/\tau^2 + \mathrm{i}c$, P is the integrated intensity, τ is the pulse duration, Γ is the bandwidth, c is the linear chirp, s is the delay time, and Δ is the off-resonance detuning.

With this expression, two-photon yield is plotted in Fig. 4 as a function of linear chirp rate for a given power spectrum. Depending on the off-resonance detuning, the chirp-dependence of two-photon yield is the combined result of the three mechanisms. For a resonant pulse, the peak at the negative chirp is the result of the intra-pulse chirp following effect. With a small detuning, two peaks on each side of zero chirp are the result of the intra-pulse time-delay effect. As the detuning further increases, the intra-pulse sequential resonance effect starts to dominate and the higher peak moves to the positive side. This last curve corresponds to the iodine experiment. These results agree with our physical pictures and help to understand multi-photon experiments in molecular systems.

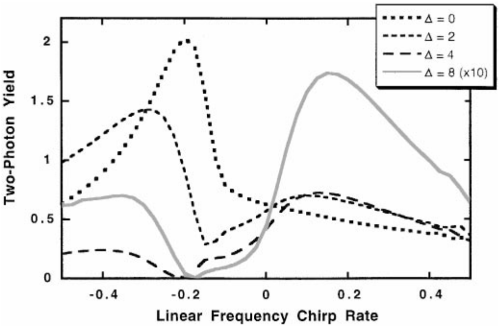

Fig. 4. A plot of the two-photon yield evaluated from Eqs. (1) and (2) as a function of the linear frequency chirp rate c' for $\Gamma = 5$, $\alpha = 1$ and $P^2/\gamma = 1$. The four curves corresponds to a resonant electric field ($\Delta = 0$), a near-resonant electric field ($\Delta = 2$), an off-resonant electric field ($\Delta = 4$), and a far-off-resonant electric field ($\Delta = 8$), respectively.

4. Control of decoherence with tailored laser fields

The coupling of a quantum system to the fluctuating environments leads to irreversible lose of the phase information (i.e., coherence) of the system, which is known as dephasing or decoherence. The rate of decoherence can be measured with photon echo and other related techniques. A more challenging problem is to design strategies to preserve the phase information against dissipation. Maintaining coherence becomes a practical issue for implementing quantum computation and quantum communication, which exploit the phase coherence of quantum systems [17,18]. A possible approach is to reduce dissipation by introducing strong coupling to a coherence source [19]. Here, we explore the possibility of controlling decoherence with strong light–matter interactions, which transfer the coherence of the laser field to the coherence of the quantum system.

To quantitatively measure the degree of decoherence and its suppression, we can analyze the change of dissipative eigen-structures as the result of the coupling to the laser field. Formally, dissipative quantum dynamics follows Liouville equations, $\dot{\rho} = \mathscr{L}\rho$, with ρ being the density matrix. The Liouville operator $\mathscr{L}$ is generally non-Hermitian and has a set of complex eigenvalues, where the imaginary part ω is the oscillation frequency and the real part γ is the decay rate [20]. The coupling to an intense laser field changes the eigen-structure of the system such that $\omega(E)$ becomes the Rabi oscillation frequency and $\gamma(E)$ becomes the decoherence rate. Numerical calculations of two-state systems show that the $\gamma(E)$ decreases monotonically with the field strength E, thus supporting the proposal of optical control of decoherence [21].

To further exploit the phase coherence of laser fields, let us consider the two-state system in Fig. 5. Here, the condensed phase environment introduces a random phase, which carries opposite signs on the ground and excited wave functions. When the Rabi oscillation is faster than the correlation time scale of phase fluctuations, the random phases on the two states cancel out and thus the decoherence can be avoided. During the Rabi oscillations, the wave-packet on the excited state relaxes to the lower-frequency region, and the wave packet on the ground state relaxes to the higher-frequency region. Thus, the optimal laser field to control decoherence consists of alternating frequency components, which match the change in the resonant frequency. This idea is currently being tested and the preliminary results agree with the analysis [21].

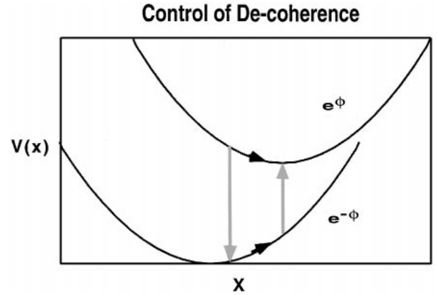

Fig. 5. A schematic diagram for the suppression of decoherence with strong laser field. To effectively control decoherence, the laser frequency can be modulated to match the change in the transient transition frequency.

5. Summary

To conclude, (i) nearly complete electronic population inversion of molecular systems can be achieved with intense positively chirped broadband laser pulses. (ii) A time-delayed three-level model can be used to identify and characterize three intra-pulse dynamical mechanisms in the three-photon iodine experiment. (iii) Control of decoherence, crucial for the realization of quantum computation and communication, is suggested by using tailored intense laser fields. Together, these examples provide not only interpretation and predication for nonlinear optical experiments but also new possibilities to control chemical reactions and quantum decoherence by single-field phase modulation.

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