Molecular “π Pulse” for Total Inversion of Electronic State Population

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Theoretical analysis leads us to the intriguing conclusion that nearly complete electronic population inversion of molecules can be achieved with intense positively chirped broadband laser pulses, as a combined result of vibrational coherence and adiabatic inversion. Strong field quantum calculations demonstrate inversion probabilities of up to 99%. The results are robust with respect to changes in light field parameters as well as to thermal and condensed phase conditions, are supported by experimental evidence, and have many potential applications in chemistry, biochemistry, biology, and physics. [S0031-9007(97)05267-8]

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Optimal inversion of the electronic population of a molecular system [1–7] is an intriguing theoretical problem 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 photoinitiation 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, and (v) induced transparency. In particular, for many biochemical and biophysical experiments, one would like to achieve maximal electronic excitation or initiation of chemical reactions without damaging the excited molecules or the delicate environment of living cells. In atoms [8] and in some spin systems (nuclear magnetic resonance), where two level approximations are reasonable, complete population inversion by pulses of electromagnetic radiation, where the entire population of one state is transferred to another state, is a long-established technique. The parallel solution for the electronic population of molecules, with their multiple rovibrational states, has not previously been found, although several theoretical calculations have been made [9–12]. In this Letter, we demonstrate that such a solution does exist for molecular systems and can be understood with simple physical models. We show that this solution is robust with respect to variation of the parameters of the “pulses” as well as robust to the effects of temperature and of intermolecular interactions. Finally, we point to recent experimental evidence supporting these conclusions.

For atoms and quasi-two-level systems, a resonant π pulse has a bandwidth broader than the transition line but narrow enough as to avoid overlap with neighboring absorption lines. A parallel argument for molecular systems suggests that the bandwidth of a possible molecular π pulse should be on the same order as the width of the corresponding molecular absorption spectrum, which is approximately 10^2 to 10^3 cm^{-1} at room temperature. According to the uncertainty principle, the duration of such a pulse is a few femtoseconds. A two-level-system interacting with a resonant pulse exhibits Rabi oscillations, with the Rabi frequency given by $\Omega_0 = E_0\mu/\hbar$, E_0 being the peak field strength and μ being the transition dipole moment [8]. Complete inversion takes place when the pulse satisfies a constant area condition $\Omega_0\tau = \pi$, with τ being the pulse duration. However, multiple rovibrational optical transitions and multiple coupling strengths in real molecular systems make it impossible to define a single π pulse which is in resonance with all transitions and which simultaneously satisfies the area condition for each transition. Therefore, π pulses based on two-level models are unlikely to achieve complete electronic population inversion for molecular systems. Furthermore, for a typical value of transition dipole moment, the intensity for such a molecular π pulse would be on the order of 10^{12}–10^{14} W/cm^2. In this intensity range, the deviation from the two electronic state model may become observable and hence population inversion may be complicated by other competitive processes such as multiphoton excitation and ionization. One way to avoid such high intensity is to make use of chirped pulses (in which the frequency of the light varies with time), which significantly reduce the field strength by increasing the pulse duration while maintaining the same power spectrum. In fact, with the introduction of linear chirp, there are two interesting mechanisms, unexpected from zero chirp (transform-limited) pulses, which prove crucial for the success of molecular π pulses.

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. Vibrational wave packets propagate on the two electronic potential energy surfaces shown in Fig. 1, and amplitude is transferred between them when the vertical transition is resonant with the instantaneous frequency of the optical pulse. The instantaneous frequency of the optical pulse is determined by the chirp, with a positively chirped pulse having low frequencies followed by high frequencies (as shown in Fig. 1) and a negatively

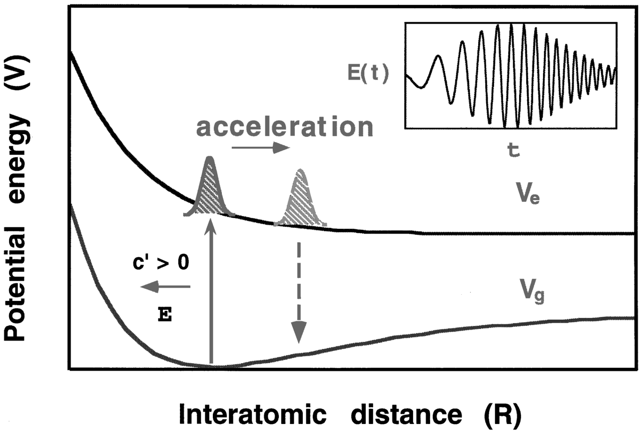

FIG. 1. Illustration of wave packet motion induced by a femtosecond pulse and its coupling to the chirped laser field. Optimal electronic state inversion occurs when the evolution of light frequency is opposite to the evolution of resonant frequency due to wave packet motion, in the sense that the instantaneous peak photon energy is increasing with time (positive chirp, $c' > 0$) while $V_e - V_g$ for the molecular wave packet is decreasing. The inset is a schematic positively chirped electric field.

chirped pulse having high frequencies before low. In the Franck-Condon region, the ground state potential energy surface is relatively flat, while the excited state surface is sloped, resulting in an initially excited wave packet which gains momentum and accelerates downward such that its resonant frequency $V_e - V_g$ decreases with time. This time-dependent transition energy, which results from the multilevel nature of the molecular system and has no analog in the theory of two-level systems, couples to the time-dependent light pulse frequency and their interaction determines the effectiveness of population transfer to the excited state. For the case of a positively chirped pulse, by the time the Rabi oscillation starts to cycle the excited electronic population back to the ground surface, the pulse has become off resonant with the moving wave packet it created and can only pump more amplitude up to the excited state. In contrast, a negative chirp (where the photon energy decreases with time) can follow the motion of the wave packet and hence cycle the excited electronic population back to the ground surface. This wave packet picture has been used by Ruhman and Kosloff [13] to explain intrapulse pump-dump mechanics and by Cerullo, Bardeen, Wang, and Shank [14] to explain the chirp dependence of dye fluorescence. A positively chirped pulse discriminates against the pump-dump sequence of photon interactions which occurs for both transform limited pulses and negatively chirped pulses.

Though the above argument is based on vibrational coherence, positive chirp is effective for electronic state inversion in any molecular system, including rotational and vibrational wave packets, gas phase and condensed phase samples, and even dissipative systems. In fact, by virtue of a simple four-level model [15], we can demonstrate a universal principle: As long as the eigenenergy spectrum is bounded from below and the initial configuration is a thermal distribution on the ground electronic surface, a positively chirped pulse is always more efficient for population inversion than zero chirp (transformed-limited) or negatively chirped pulses.

In addition to the positive chirp effect, adiabatic inversion due to chirp also becomes substantial in the picosecond regime. When the frequency sweep is much lower than any other time scale, molecular systems respond to the frequency sweep as an adiabatic parameter rather than a dynamical variable. Thus, for adiabatic inversion, the frequency sweep should be accomplished over a sufficiently long duration, ideally in the picosecond regime, in order to lock the adiabatic electronic states. Further, if the frequency sweeps from below the lowest transition frequency of the absorption spectrum to above the highest frequency of the absorption spectrum, adiabatic passage can switch the electronic states, giving rise to complete electronic population inversion [8]. A diabatic population inversion has been demonstrated for a subset of eigenstates on the ground electronic surface [3–5]. Here, we predict that chirped pulses with broader bandwidths than used before can invert essentially the complete electronic population. Since the adiabatic effect is independent of the sign of the chirp, the combination of the positive chirp effect and the adiabatic frequency sweeping effect makes intense positively chirped pulses with broad bandwidth the optimal choice for molecular "π pulses."

To verify our proposal and to test the feasibility of such pulses under thermal and condensed phase conditions, we present example numerical results of strong field quantum calculations for the $X(\Sigma^+) \rightarrow A(\Sigma^+)$ transition [16] of LiH, results which have been confirmed by calculations on other molecules. The wave functions are expanded as $\Sigma_{JM} R_J Y_{JM}$, where Y_{JM} are spherical harmonics and R_J are the associated radial functions. Rotational and vibrational effects including the rovibrational coupling are taken into full consideration and are treated exactly by nonperturbative quantum mechanics. The set of radial wave functions labeled with J is propagated with a small time step of less than 0.1 fs through the Fourier transform method [17].

The electric field of the light is described by a Gaussian functional form

$$E(t) = E_0 \exp\left[-\frac{t^2}{2\tau^2} - i\omega_0 t - ic\frac{t^2}{2}\right], \qquad (1)$$

where E_0, ω_0, τ, and c are the amplitude, carrier frequency, pulse duration, and linear temporal chirp rate, respectively. The Fourier transform of this field is given by

$$\tilde{E}(\omega) = \tilde{E}_0 \exp\left[-\frac{(\omega - \omega_0)^2}{2\Gamma^2} - ic'\frac{(\omega - \omega_0)^2}{2}\right], \quad (2)$$

where Γ is the bandwidth and c' is the linear frequency chirp rate [18]. We use a carrier frequency of

$\omega_0 = 29\,027\ \mathrm{cm}^{-1}$ and a bandwidth of $\Gamma = 1000\ \mathrm{cm}^{-1}$, which, in the transform limit (zero chirp), corresponds to $\tau = 5$ fs, or equivalently a pulse FWHM of $2\sqrt{\ln 2}\tau = 8.3$ fs. To match the experimental conditions, c' is varied for a fixed power spectrum. For the given bandwidth Γ, by chirping the pulse, we increase the pulse duration according to $\tau^2 = 1/\Gamma^2 + \Gamma^2 c'^2$, change the temporal linear chirp rate by $c = c'\Gamma^2/\tau^2$, and decrease the peak intensity, because the integrated intensity $P_0 = \tau E_0^2$ is a conversed quantity. For example, when $c' = \pm 4 \times 10^{-5}/\mathrm{cm}^{-2}$, the $\tau = 5$ fs transform-limited pulse is stretched to a chirped $\tau = 200$ fs pulse and accordingly, the peak intensity is reduced by a factor of 40.

The resulting inversion probability for LiH molecules is plotted as a function of linear frequency chirp rate c' in Fig. 2 for two values of peak intensity. The inversion probability is the probability for the initially ground electronic state system to be on the excited electronic state after the pulse. The initial state for Fig. 2 is assumed to be the ground vibrational, rotational, and electronic state, that is, $\nu = M = J = 0$. As can be seen, the positive chirp consistently leads to high inversion probabilities, with complete inversion of over 99% for the higher intensity curve. For comparison, the inversion probabilities for the transform-limited $\tau = 5$ fs pulses are 61% and 53% for the two curves. 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 intrapulse pump-dump mechanism and the vibrational oscillation on the excited electronic surface. Simulations demonstrate that the large inversion probability is robust with respect to variations of molecular "π pulse" parameters such as the amount of positive chirp c' (see the upper curve in Fig. 2) and pulse intensity $|\tilde{E}(\omega)|^2$ (above a sufficiently high value), as well as moderate variations of carrier frequency ω_0 and bandwidth Γ.

The inversion is also robust with respect to thermal and condensed phase conditions. In Fig. 3(a), the inversion probability is given as a function of temperature. At each temperature, the probability is averaged over the relevant initial vibrational ($\nu = 0, 1$) and rotational ($0 \le J \le 10, M \le J$) quantum numbers on the ground electronic surface, and weighted by the Boltzmann distribution function. The inversion probability for the $M = J$ initial state for linearly polarized light is relatively small in comparison with other initial states but does not effect the overall inversion probability which is an average over M and J quantum numbers. Although there is a noticeable probability decrease with temperature, nearly complete inversion with a probability above 99% is maintained up to 500 K. It is clear from our analysis that, as the absorption bandwidth increases with temperature, one should broaden the pulse spectrum accordingly, to sustain the high inversion probability.

Electronic dephasing, which represents the random fluctuations of electronic transition frequencies, has a short time scale of tens to hundreds of femtoseconds in dense environments, and hence is capable of undermining the phase modulation induced by the chirp. In Fig. 3(b), the inversion probability for LiH with the initial quantum number $\nu = J = M = 0$ is plotted as a function of electronic dephasing time T_2. Here, a stochastic phase

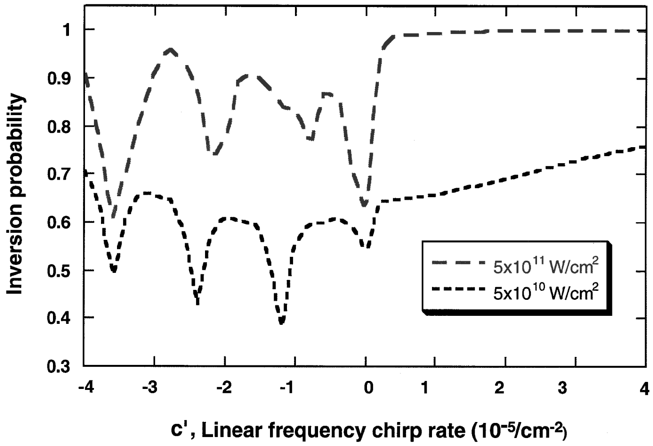

FIG. 2. Plot of the inversion probability of LiH as a function of linear frequency chirp rate for a fixed power spectrum with $P_0 = 100\ \mathrm{mJ/cm}^2$ ($I_0 = 5 \times 10^{11}\ \mathrm{W/cm}^2$) and $P_0 = 10\ \mathrm{mJ/cm}^2$, ($I_0 = 5 \times 10^{10}\ \mathrm{W/cm}^2$). The peak intensity is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

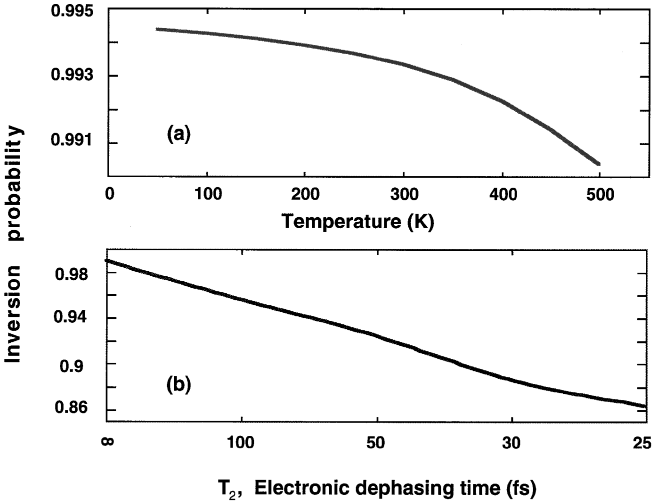

FIG. 3. (a) Plot of LiH inversion probability as a function of temperature, for $\tau = 100$ fs, $c' = 2 \times 10^{-5}/\mathrm{cm}^2$, $P_0 = 8\ \mathrm{mJ/cm}^2$ ($I_0 = 8 \times 10^{11}\ W/\mathrm{cm}^2$). (b) Plot of LiH inversion probability as a function of electronic dephasing time T_2 for $\tau = 50$ fs, $c' = 1 \times 10^{-5}/\mathrm{cm}^2$, $P_0 = 10\ \mathrm{mJ/cm}^2$ ($I_0 = 2 \times 10^{12}\ \mathrm{W/cm}^2$).

sampling [15] is built into the numerical algorithm so that electron decoherence can be reproduced on the density matrix level. As can be seen from Fig. 3(b), no large loss of excited state population is observed until the dephasing time T_2 becomes smaller than the pulse duration τ. This result suggests that population inversion should be accomplished before electronic phase coherence is lost. Energy relaxation on the excited electronic state generally gives rise to an irreversible loss of the energy of the excited wave packet (e.g., the Stokes shift in dye molecules [14], which further enhances the positive chirp effect in the inversion process. Other dissipative effects, such as electronic population relaxation and rotational reorientation, take place on longer time scales than the pulse duration considered here, and hence have no significant effects on electronic population inversion.

In conclusion, the optimal recipe for molecule "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 multiphoton 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. Numerical results for 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. The numerical examples demonstrate that the positive chirp effect is robust with respect to variations of the pulse parameters and with respect to thermal and condensed pulse 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 equal to or greater than that of the absorption spectrum, which can be on the order of 1000 cm^{-1}. The main experimental challenge is to achieve such a broad pulse spectrum, although intense 5 fs FWHM ($\Gamma = 1670\ \text{cm}^{-1}$) pulses have recently been demonstrated [19]. The intensity requirements are not prohibitive, since it is straightforward to achieve intensities of $10^{12}\ \text{W/cm}^2$ with microjoule energy pulses by focusing the beam. 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 of Cerullo, Bardeen, Wang, and Shank [14] on dye molecules and of Bardeen, Yakovlev, Wilson, Carpenter, Weber, and Warren [20] on the feedback quantum control of electronic state population transfer demonstrate that such transfer can be enhanced by as much as a factor of two using high intensity, wide bandwidth, positively chirped pulses.

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