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Using time-dependent rate equations to describe chirped pulse excitation in condensed phases

Christopher J. Bardeen [a,*], Jianshu Cao [b], Frank L.H. Brown [c], Kent R. Wilson [c]

[a] Box 20-6, CLSL, Department of Chemistry, University of Illinois, 600 S. Mathews Ave., Urbana, IL 61801, USA
[b] Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA
[c] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0339, USA

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Abstract

A time-dependent rate equation formalism is developed to describe high-intensity excitation of molecules in condensed phases using broadband laser pulses. When electronic and vibrational dephasing rates are fast relative to the pulse dynamics, the generalized optical Bloch equations can be written as a set of coupled rate equations with coefficients that depend on the time-dependent overlap of the pulse spectrum with the molecular lineshape. These rate equations are shown to reproduce qualitatively the effects observed experimentally in recent quantum control experiments using high-intensity, chirped femtosecond pulsed excitation. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Advances in both the theoretical understanding of light-driven quantum molecular dynamics and the experimental ability to create and shape light fields has resulted in the field known as 'quantum control' [1]. Recent experiments have involved the use of chirped pulses [2–7], in which the phase structure of an ultrashort pulse is modified in order to control the sample. Chirping the pulse delays some of its frequency components with respect to others. A positively chirped pulse has low frequencies leading and high frequencies trailing, while a negatively chirped pulse has the opposite frequency ordering. For a zero chirp or transform-limited pulse, all the frequencies arrive at the same time. Note that we can modify the phase structure of the laser pulse, and thus its temporal properties, without changing the pulse energy or the power spectrum. Recently, the techniques of quantum control have been applied to large molecules in condensed phases [8–10] and even proteins [11]. The analysis of such chirped pulse experiments is the subject of this Letter.

With systems like atoms or small molecules in the gas phase, we can achieve selectivity by controlling the quantum interferences among amplitudes of a few quantum states [1]. This is truly *quantum* control, since such interferences are purely the result of quantum mechanics and cannot be understood from a classical treatment. We consider here the opposite limit of fast electronic and vibrational dephasing, where such quantum coherences decay very rapidly. Our approach is similar in spirit to a more sophisticated treatment by Fainberg [12] which describes high-power chirped pulse excitation in terms of mov-

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[*] Corresponding author. E-mail: bardeen@scs.uiuc.edu

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ing wavepackets, but instead describes these experiments in terms of eigenstates and rate equations. The rate equations are similar to those used to analyze steady-state experiments [13], except that they take the pulsed nature of the excitation into account via time-dependent rate coefficients. These time-dependent rates may be evaluated in terms of the overlap of the Wigner representation of the laser pulse with the molecular absorption and emission spectra, all experimentally measurable quantities. Multiple levels and coherence effects due to nonzero dephasing times can be incorporated in a straightforward manner. Example calculations on 4-level systems demonstrate various effects recently observed in high-power chirped pulse excitation of molecules in solution.

2. Theory

We begin with the 4-level system illustrated in Fig. 1, where transitions occur between levels $|0\rangle$ and $|3\rangle$ and levels $|1\rangle$ and $|2\rangle$. For the sake of clarity, we neglect levels $|1\rangle$ and $|2\rangle$ for the time being and consider only levels $|0\rangle$ and $|3\rangle$. This 2-level system is described by the following optical Bloch equations:

$$\dot{\rho}_{00}(t) = \frac{-1}{T_1}(\rho_{00}-1) + \frac{i}{\hbar}\left[\mu^* E^*(t)\rho_{03} - \mu E(t)\rho_{03}^*\right], \tag{1}$$

$$\dot{\rho}_{33}(t) = \frac{-1}{T_1}\rho_{33} + \frac{i}{\hbar}\left[\mu E(t)\rho_{03}^* - \mu^* E^*(t)\rho_{03}\right], \tag{2}$$

$$\dot{\rho}_{03}(t) = -\left(i\Delta + \frac{-1}{T_2}\right)\rho_{03} + \frac{i}{\hbar}\mu E(t)(\rho_{33}-\rho_{00}), \tag{3}$$

where T_2 is the dephasing time, T_1 is the population lifetime in level $|3\rangle$ before it relaxes to level $|0\rangle$, Δ is the detuning of the laser carrier frequency from the resonance frequency, $\Delta = (\varepsilon_3 - \varepsilon_0 - \hbar\omega_{\mathrm{laser}})/\hbar$, μ is the transition dipole moment, and $E(t)$ is the electric field in the rotating wave approximation (i.e., the full $\varepsilon(t) = E(t)\exp(-i\omega t) + E^*(t)\exp(+i\omega t)$). Assuming μ to be real and constant (the Condon approximation), we integrate to solve the equation for the off-diagonal matrix element to obtain

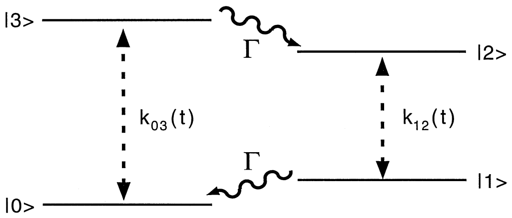

Fig. 1. The 4-level system used in the calculations in this Letter, with the time-dependent transistion rates derived in the text and the relaxation rate Γ, which represents the Stokes shift.

$$\rho_{03}(t) = \frac{-i\mu}{\hbar}\int_{-\infty}^{\infty} dt' \exp\left[-\left(i\Delta + \frac{1}{T_2}\right)(t-t')\right] \times E(t')\left[\rho_{33}(t') - \rho_{00}(t')\right], \tag{4}$$

and make use of the identity [14]

$$E^*(t')E(t'') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega'\, W\left(\frac{t'+t''}{2}, \omega'\right) \times \exp\left[i\omega'(t'-t'')\right], \tag{5}$$

where $W(t,\omega)$ is the Wigner transform of $E(t)$,

$$W(t,\omega) = \int_{-\infty}^{\infty} d\tau\, E^*\left(t - \frac{\tau}{2}\right) E\left(t + \frac{\tau}{2}\right)\exp[i\omega\tau]. \tag{6}$$

The Wigner transform is a particularly useful representation of the electric field, since it can be obtained experimentally [15] and provides a conceptual picture of the laser pulse structure jointly in time and frequency space. Substituting Eqs. (4) and (5) into Eq. (2) and performing the change of variables $\tau = t' - t''$, we obtain

$$\dot{\rho}_{33}(t) = \frac{-\mu^2}{\pi\hbar^2}\int_0^{\infty} d\tau\, \mathrm{Re}\left\{\int_{-\infty}^{\infty} d\omega'\, W\left(\frac{2t-\tau}{2}, \omega'\right) \times \exp\left\{\left[i(\omega'-\Delta) - \frac{1}{T_2}\right]\tau\right\}\left[\rho_{33}(t-\tau) - \rho_{00}(t-\tau)\right]\right\} - \frac{\rho_{33}(t)}{T_1}. \tag{7}$$

Eq. (7) is exact within the assumptions of the Bloch equations. If instead we use the generalized Bloch equations [16], where $1/T_2$ is replaced by a stochastically varying frequency perturbation $\delta(t)$, we have

$$\exp\left[\frac{-\tau}{T_2}\right] \to \left\langle \exp\left[\mathrm{i}\int_0^{\tau} \mathrm{d}t'\, \delta(t') \right] \right\rangle , \tag{8}$$

which is the absorption lineshape function [17,18]. Thus this approach is valid beyond the Markovian approximation inherent in the usual Bloch equations. We now make the approximation that the decay of the lineshape function, e.g. T_2, is much shorter than any relevant pulse dynamics. This is not the same as assuming that T_2 is much shorter than the transform limited pulse duration, since a chirped pulse may last considerably longer in time. For a strongly chirped pulse, even if it has the bandwidth of a very short pulse, the frequency spectrum will evolve relatively slowly in time and the approximation can still be valid for appreciable dephasing times. By neglecting the τ variable when it is added or subtracted to a larger number, and then performing the integral over τ, we obtain

$$\dot{\rho}_{33}(t) = \frac{\mu^2}{\pi\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}\omega'\, W(t,\omega')\, A_{03}(\omega') \left[\rho_{33}(t) - \rho_{00}(t) \right] - \frac{\rho_{33}(t)}{T_1} , \tag{9}$$

where $A(\omega)$ is the Fourier transform of the lineshape function, i.e. the absorption lineshape in frequency space. We can now write Eq. (9) as the familiar-looking rate equation,

$$\dot{\rho}_{33}(t) = k_{03}(t)\left[\rho_{33}(t) - \rho_{00}(t) \right] - \frac{\rho_{33}(t)}{T_1} , \tag{10}$$

where $k(t)$ is the time-dependent transition rate, given by

$$k_{03}(t) = \frac{\mu^2}{\pi\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}\omega'\, W(t,\omega')\, A_{03}(\omega') . \tag{11}$$

As in earlier derivations of rate equations to describe monochromatic fields [13], the key here is that in the fast dephasing limit, the quantum coherences respond instantaneously to the driving field and are removed from the problem. This instantaneous response of the coherences is also the basis of the 'moving potential' approach developed by Fainberg to describe high-intensity experiments in dissipative environments [12].

It is straightforward to include effects due to a longer T_2 by expanding each time-dependent term in a Taylor series in τ and then performing the integration over τ. Such an approach has been shown to be useful in analyzing the behavior of laser amplifiers in the limit of narrow bandwidth, unchirped pulses [19]. We can also extend this analysis to multiple levels coupled to each other through absorption, emission, and relaxation, with the general result for level $|i\rangle$,

$$\dot{\rho}_{ii} = \sum_{j\neq i}^{N} k_{ij}(t)\left(\rho_{ij} - \rho_{ii} \right) + \sum_{j\neq i}^{N} \Gamma_{ji}\,\rho_{jj} - \sum_{j\neq i}^{N} \Gamma_{ij}\,\rho_{ii} , \tag{14}$$

where $k_{ij}(t)$ is proportional to the time-dependent overlap of the pulse spectrum and the absorption lineshape between levels $|i\rangle$ and $|j\rangle$, and Γ_{ij} represents the population relaxation rate from level $|i\rangle$ to level $|j\rangle$. Note that this reduces the problem of solving N coupled optical Bloch equations to that of solving N coupled rate equations.

While $k_{ij}(t)$ is in general a complicated function that must be evaluated numerically, for the sake of clarity we will assume that both the laser field spectrum $E(\omega)$ and the molecular absorption and emission spectra ($A(\omega)$ and $F(\omega)$, respectively) are Gaussian:

$$E(\omega) = \varepsilon \exp\left[-\sigma_L^2\omega^2 + \mathrm{i}b\omega^2 \right] , \tag{15a}$$

$$A(\omega) = \exp\left[-\sigma_A^2(\omega - \Delta_A)^2 \right] , \tag{15b}$$

$$F(\omega) = \exp\left[-\sigma_F^2(\omega - \Delta_F)^2 \right] . \tag{15c}$$

The phase term $\mathrm{i}b\omega^2$ results in a linearly chirped pulse in the time domain,

$$E(t) = \left(\frac{\pi}{\sigma^2 - \mathrm{i}b} \right)^{1/2} \exp\left[\frac{-\sigma^2 t^2 + \mathrm{i}bt^2}{4(\sigma^4 + b^2)} \right] , \tag{16}$$

with the Wigner transform,

$$W(t,\omega) = \frac{(2\pi)^{3/2}}{\sigma} \exp\left\{ -\frac{t^2}{2\sigma_c^2} - 2\sigma_c^2[\omega - \omega(t)]^2 \right\}, \tag{17a}$$

$$\sigma_c^2 = \frac{\sigma^4 + b^2}{\sigma^2}, \tag{17b}$$

$$\omega(t) = \frac{bt}{2(\sigma^4 + b^2)}, \tag{17c}$$

resulting in the analytical expression for the time-dependent rate,

$$k_{03}(t) = \frac{\mu^2}{\hbar^2}|\varepsilon|^2 \frac{2\sqrt{2}\pi^2}{\sigma\sqrt{2\sigma_c^2 + A^2}} \exp\left[-\frac{t^2}{2\sigma_c^2} - \frac{2\sigma_c^2 A^2}{2\sigma_c^2 + A^2}\left(\frac{bt}{2(\sigma^4 + b^2)} - \Delta^2 \right) \right].$$

In the rest of this Letter we show that these rate equations are sufficient to describe some qualitative features of recent chirped pulse experiments [9–11].

Fig. 2 shows the population left in the excited state $|2\rangle$ after interaction with Gaussian pulses of varying linear chirp. The frequency units are arbitrary, but may be taken to be ps^{-1} to facilitate comparison with experiment. In this case, the full-width-half-maximum (FWHM) of the pulse spectrum is 20 ps^{-1}, corresponding to a transform limited pulsewidth of 22 fs. The largest chirp, $b = 0.01$, then results in a chirped pulsewidth of 2.5 ps. The absorption $A(\omega)$($0 \rightarrow 3$ transition) and emission $F(\omega)$($2 \rightarrow 1$ transition) spectra have FWHM of 60 and detunings $\Delta_{A,F} = \pm 30$, respectively, from the central laser frequency. The vibrational relaxation rate Γ is set to 100 ps^{-1} and represents a very rapid Stokes shift. The transition rate amplitude represents the product $(\mu^2/\pi\hbar^2)|\varepsilon|^2$ and can be scaled by varying either the transition dipole μ or the field strength ε. We will assume that the amplitude is modified by changing the field strength, which is most likely to be the case experimentally. From Fig. 2a we see that at the lowest-amplitude (-intensity) linear chirp has no effect on the final amount of population deposited in the excited state, in accordance with theoretical prediction [20] and experimental measurements [9–11]. As the pulse energy is increased by a factor of 10, a clear asymmetry with respect to chirp is observed, with a positively chirped pulse leaving almost twice as many molecules in the excited state. Another factor of 5 increase in the pulse energy drives the system deeply into saturation, with the positively chirped pulse resulting in almost 100% inversion, while a negatively chirped pulse pumps and then dumps almost 100% of the population. In Fig. 2b we show curves for different vibrational relaxation rates Γ for the intermediate transition amplitude of 0.01. As Γ decreases, the curves lose

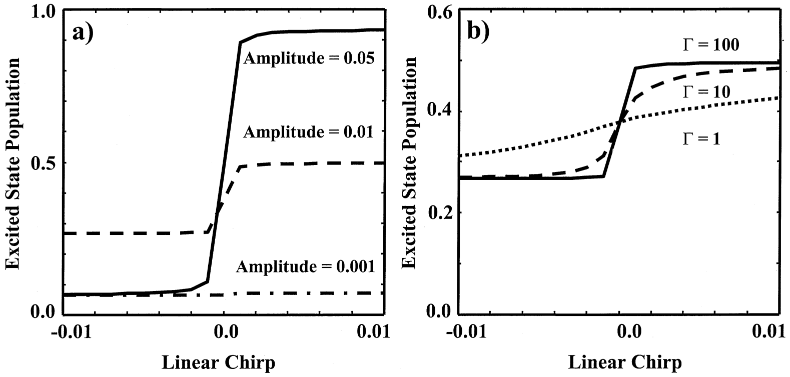

Fig. 2. (a) The chirp-dependent excited state population in level $|2\rangle$ left after excitation by chirped pulses with $\Gamma = 100$ and transition amplitudes of 0.1 (solid), 0.01 (dashed), and 0.001 (short-and-long dashed). (b) For the intermediate transition amplitude of 0.01, the effect of different relaxation rates on the chirp dependence of the final excited state population is shown: $\Gamma = 100$ (solid), $\Gamma = 10$ (dashed), and $\Gamma = 1$ (short dashed).

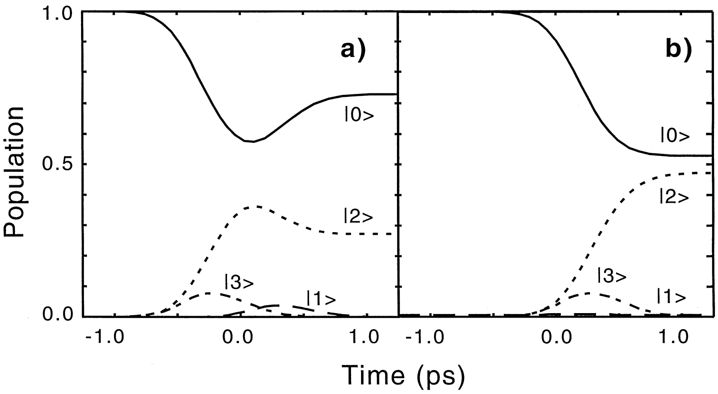

Fig. 3. (a) Time-dependent level populations during excitation with a negatively ($b = -0.005$) chirped pulse. The transition amplitude is 0.01 and Γ is 10. The ground state levels are $|0\rangle$ and $|1\rangle$, while the excited state levels are $|2\rangle$ and $|3\rangle$. (b) Same as part (a) but for a positively ($b = 0.005$) chirped pulse.

their step function appearance and the asymmetry with chirp decreases. This is because as Γ decreases, population resides in state $|3\rangle$ for a longer time and does not experience the change in energy that allows it to avoid getting dumped back to the ground state. With $\Gamma = 1$, the 4-level system looks almost like a 2-level system on the timescale of the pulses considered here. If the population stays in state $|3\rangle$ after excitation, then only rate $k_{03}(t)$ comes into play, and the rates of absorption and emission are the same, as in traditional 2-level rate theory [13].

To investigate the temporal evolution of the populations, we set the linear chirp $b = \pm 0.005$. Negative and positive chirps are shown in Fig. 3a and b, respectively. The populations in Fig. 3a clearly show the pump–dump process occurring during the negatively chirped pulse. The decrease and subsequent recovery of the ground state $|0\rangle$ population coincides exactly with the rise and fall of the excited state population in state $|2\rangle$. Fig. 3b shows that a positively chirped pulse only pumps population from the ground state, without any dumping. There is not 100% population transfer because the bandwidth of the pulse is narrower than the absorption spectrum [21,22]. The transient populations in states $|1\rangle$ and $|3\rangle$ are also shown. Note that both positively and negatively chirped pulses excite the same amount of population into state $|3\rangle$, but that only the negatively chirped pulse creates appreciable population in $|1\rangle$ via stimulated emission.

The increased inversion with positive chirp recalls the molecular π pulse [21,22], where a high-energy, broadband, positively chirped pulse was shown to be able to invert the molecular population. That work took the full quantum dynamics into account, including the electronic and vibrational coherences, and relied on a combination of wavepacket motion and adiabatic passage to achieve inversion. The present calculations ignore all coherences and hence those two effects cannot play a role. Instead, it is the rapid, irreversible relaxation to level $|2\rangle$ that results in the chirp dependence and inversion with positive chirp. Although different in the details, the fundamental idea in both the present work and the theory of the molecular π pulse is the same: initially excited population moves to lower energies and out of resonance with the trailing high-frequency components of the positively chirped pulse so that it cannot undergo stimulated emission back to the ground state. This motion may result from either incoherent relaxation or coherent wavepacket motion.

3. Conclusions

In conclusion, we have derived a theory of strong-field-pulsed optical excitation of molecules in condensed media based on rate equations with time-dependent coefficients. It allows for at least a qualitative understanding of recent quantum control experiments involving electronic state population transfer in large molecules in the condensed phase [9–11], and provides a framework for the quantitative comparison of theory and experiment. The coupled differential equations resulting from the theory can be easily solved, with the only inputs being the absorption and emission spectra and the Wigner transform of the electric field, all of which can be measured experimentally. The theory can be extended to take finite dephasing rates and multiple levels into account. This theoretical approach may be useful for the design and optimization of molecular sensors whose optical properties change in response to their local environment, such as pH [23], or for the design of laser fields that can optimally drive multiphoton photochemistry [24] or molecular optical switches [25].

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