

Analytical Control of Molecular Excitations Including Strong Field Polarization Effects

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(Received 2 February 2006; published 22 June 2006)

An analytical scheme is presented for designing a laser pulse to excite H₂ from one specified vibrational-rotational state to another. The scheme is based on an adiabatic two-state approximation in a Floquet picture. By continuously and smoothly changing the laser frequency, we explicitly harness the dynamic Stark shifts and maintain resonance between the dressed diabatic states during laser-molecule interaction. The explicit time-dependent solution of the Schrödinger equation confirms the validity and efficacy of the analytically designed laser pulses. The scheme depends on the molecular polarizability to achieve its control objectives.

DOI: [10.1103/PhysRevLett.96.243003](https://doi.org/10.1103/PhysRevLett.96.243003)

PACS numbers: 33.90.+h, 02.30.Yy, 31.70.Hq, 82.53.Kp

Active control of molecular dynamics using specially designed laser pulses has attracted considerable attention over the past two decades, from both the theoretical [1–4] and experimental [5–10] perspectives. However, much of the past work has treated the interaction between molecules and lasers within the electric dipole approximation (see also Refs. [11,12], and references therein). For high field strengths, which exist in many experiments, polarization effects can be significant. In this regard, Sato *et al.* [13] have discussed the selective dissociation of CO₂⁺ ions by controlling the relative phase of the ω and 2ω components of a bichromatic laser; Salomon *et al.* [14] have reported the optimal control of molecular orientation and alignment in a linear rigid-rotor model including polarization effects; Shapiro *et al.* [15] have discussed vibrational and rotational excitation of homonuclear diatomics in the context of quantum computing; and, recently, a two-stage toolkit strategy for incorporating the polarization effects into optimal control calculations has been suggested by Balint-Kurti *et al.* [16,17] and applied to the vibrational and rotational excitation of H₂ molecules in a realistic manner. In spite of these successful strong field calculations and experiments, little analytical work has been done to reveal the control mechanism behind the complicated optimal pulses. In this Letter, we present an analytical pulse design scheme, including polarization effects, which is based on a two-state treatment of the dynamics in a Floquet picture. Our results show that the desired objective can be achieved through control of the time-varying instantaneous frequency of the laser pulse. The analytically derived laser pulses are verified by the accurate numerical solution of the time-dependent Schrödinger equation (TDSE). The analytic model should give reliable predictions whenever the density of quantum states is less than the width of the frequency components of the laser field. The analytically derived pulses provide a transparent explanation of the control mechanism.

Our model consists of a ground state $|g\rangle$ and an excited state $|e\rangle$. The states are coupled by a laser field

$$\epsilon(t) = \hat{\epsilon} A_0 f(t) \cos\Phi(t), \quad (1)$$

where $\hat{\epsilon}$ is the polarization vector, A_0 is the field strength, $f(t)$ is the normalized pulse envelope, and $\Phi(t)$ is the temporal phase of the field. The Hamiltonian of this two-level model may be written as

$$H = \begin{pmatrix} E_g - \alpha_{gg}\epsilon^2(t)/2 & -\alpha_{eg}\epsilon^2(t)/2 \\ -\alpha_{ge}\epsilon^2(t)/2 & E_e - \alpha_{ee}\epsilon^2(t)/2 \end{pmatrix}, \quad (2)$$

where E_i is the field-free energy of state $|i\rangle$ and $\alpha_{ij} = \langle i|\hat{\epsilon} \cdot \boldsymbol{\alpha} \cdot \hat{\epsilon}|j\rangle$ is a matrix element of the polarizability tensor $\boldsymbol{\alpha}$. If the pulse envelope $f(t)$ and laser frequency $\omega(t) \equiv d\Phi/dt$ are both slowly varied in comparison to the fast optical oscillations, we can invoke the two-photon rotating wave approximation and transform Eq. (2) into a Floquet representation [18]. The corresponding Floquet Hamiltonian may be written as:

$$\tilde{H} = \begin{pmatrix} \tilde{E}_g + 2\hbar\omega(t) & -\hbar\Omega_{ge}(t)/2 \\ -\hbar\Omega_{eg}(t)/2 & \tilde{E}_e \end{pmatrix}, \quad (3)$$

where $\tilde{E}_i = E_i - \alpha_{ii}A_0^2f^2(t)/4$ is the polarization-shifted energy of state $|i\rangle$ and $\Omega_{eg}(t) = \alpha_{eg}A_0^2f^2(t)/4\hbar$ represents the effective laser-molecular coupling (Rabi frequency) between the ground and excited states. The diabatic energies, i.e., the diagonal elements of \tilde{H} , cross at the polarization-shifted two-photon resonance $\omega_{2r} = (\tilde{E}_e - \tilde{E}_g)/2\hbar$, and the adiabatic energies, i.e., the eigenvalues of the full \tilde{H} , cannot cross. An avoided crossing arises at $\omega = \omega_{2r}$ with the energy gap proportional to $\Omega_{eg}(t)$, which induces a (localized) nonadiabatic transition between the two adiabatic states. Molecular motion in an intense laser field can thus be controlled directly by managing these nonadiabatic transitions with changes in laser parameters such as amplitude, frequency, and chirping. Following this idea, various classes of control pulses can be designed by analogy with single-photon transitions [18,19]. In order to concentrate on the essential physics, we consider only the most fundamental case, i.e., complete vibrational and rotational excitations of homonuclear diatomic molecules by a phase-shaped two-photon π pulse.

The details of other controls and extension to general molecules are discussed elsewhere [20].

If the instantaneous frequency of the field $\omega(t)$ is modulated so as to continually maintain degeneracy between the two diabatic Floquet levels, i.e.,

$$\omega(t) = \frac{E_e - E_g}{2\hbar} - \frac{\alpha_{ee} - \alpha_{gg}}{8\hbar} A_0^2 f^2(t), \quad (4)$$

the Floquet Hamiltonian [Eq. (2)] can be diagonalized by a simple rotation of $\pi/4$ in the two-level functional space of the model. The associated time-dependent Floquet Schrödinger equation in the adiabatic representation can then be integrated analytically. The evolution operator over the entire duration of the pulse \tilde{T} may be written as:

$$\tilde{T} = e^{-i\delta} \begin{pmatrix} \cos\frac{\varphi}{2} & -i \sin\frac{\varphi}{2} \\ -i \sin\frac{\varphi}{2} & \cos\frac{\varphi}{2} \end{pmatrix}, \quad (5)$$

where $\varphi = \int_0^\tau \Omega_{eg}(t) dt$, $\delta = \int_0^\tau [\tilde{E}_e + \tilde{E}_g + 2\hbar\omega(t)] dt / 2\hbar$, and Eq. (5) is in the original diabatic representation. In the above derivations, we assume that the pulse starts at $t = 0$ and ends at $t = \tau$. The excitation probability P_{eg} is then seen to be

$$P_{eg} = \sin^2 \frac{\varphi}{2}, \quad (6)$$

and complete excitation is achieved when

$$\varphi = \frac{\alpha_{eg} A_0^2 \tau s_0}{4\hbar} = \pi, \quad (7)$$

where $s_0 = \int_0^\tau f^2(t) dt / \tau$ depends on the shape of the pulse envelope. Equation (7) shows that the polarization-shifted resonant two-photon absorption depends on only one parameter $A_0^2 \tau s_0$, which we can loosely refer to as the ‘‘pulse area.’’ Complete excitation can be achieved by adjusting the field strength A_0 , pulse duration τ , and pulse envelope s_0 . We note that Eqs. (5) and (7) are not new. The concept of a π pulse is widely used in various areas [11,12], and Trallero-Herrero *et al.* [21] have already discussed their use for coherent control processes in a dipole coupled model; the application of Eqs. (5) and (7) in controlling molecular motions in intense laser field including polarization effects is new.

In order to demonstrate the efficiency and robustness of our formalism, we consider the complete vibrational and rotational excitations of H_2 molecules

$$H_2(v=0, j=0, m=0) \rightarrow H_2(v=1, j=0, m=0), \quad (8a)$$

$$H_2(v=0, j=0, m=0) \rightarrow H_2(v=1, j=2, m=0), \quad (8b)$$

$$H_2(v=0, j=1, m=0) \rightarrow H_2(v=1, j=1, m=0). \quad (8c)$$

The H_2 molecule was chosen for this study as we were able in this case to compute, *ab initio*, all the necessary molecular properties to a very high degree of accuracy [16]. Within the electric-nuclear Born-Oppenheimer approximation [16,17], the evolution of molecule is governed

by the time-dependent nuclear Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = \{\hat{T}_{nu} + V[\mathbf{R}, \boldsymbol{\epsilon}(t)]\} \Psi(\mathbf{R}, t), \quad (9)$$

where \hat{T}_{nu} is the kinetic energy operator, and $V[\mathbf{R}, \boldsymbol{\epsilon}(t)]$ is the potential energy of H_2 at an internuclear separation \mathbf{R} and in the presence of an external electric field $\boldsymbol{\epsilon}(t)$. If the field strength $\boldsymbol{\epsilon}$ is not very high, $V[\mathbf{R}, \boldsymbol{\epsilon}(t)]$ may be approximated by

$$V[\mathbf{R}, \boldsymbol{\epsilon}(t)] \simeq V_0(R) - \frac{\boldsymbol{\epsilon}^2(t)}{2} [\Delta\alpha(R) \cos^2\theta + \alpha_\perp(R)], \quad (10)$$

with

$$\Delta\alpha(R) = \alpha_\parallel(R) - \alpha_\perp(R), \quad (11)$$

where $V_0(R)$ is the field-free potential energies, θ is the orientational angle of the H_2 molecular axis with respect to the field polarization vector, and α_\perp and α_\parallel refer to the perpendicular and parallel components of polarizability, respectively. As an illustration, we plot the model potentials of Eq. (10) against the *ab initio* computed potential [16,17] in Fig. 1, at the orientational angle $\theta = 0^\circ$ and an electric field of $\epsilon = 0.03$ atomic units (a.u.). In the region in which the wave function of the $v = 1$ vibrational level is significant, the error never exceeds 3 cm^{-1} . The errors become even smaller for nonzero values of θ . We may expand the total nuclear wave function $\Psi(t)$ in terms of the rovibrational eigenfunctions $|i\rangle$ of free H_2 as $\Psi(t) = \sum_i c_i(t) |i\rangle$ and rewrite Eq. (9) as $i\hbar \dot{c}_i(t) = E_i c_i(t) - \sum_j \langle i | \alpha \boldsymbol{\epsilon}^2(t) | j \rangle c_j(t)$. The two-photon frequency is chosen to be approximately resonant with the $g \rightarrow e$ transition. If the detunings from all other close-lying states s are great compared to the Rabi frequencies Ω_{sg} and Ω_{se} , we may ignore transitions to intermediate m states and represent the dynamics of H_2 by a simple two-level model.

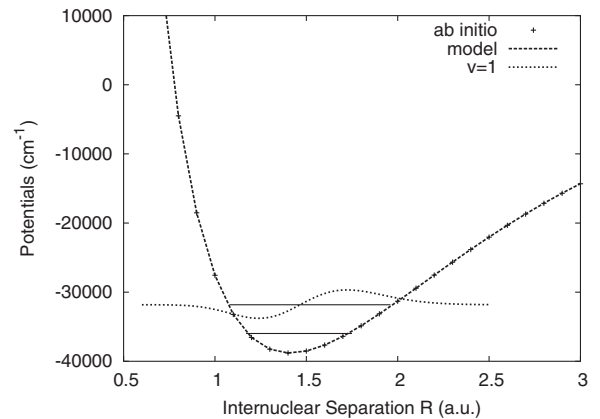


FIG. 1. Comparison of the modeled potential of H_2 molecules, i.e., Eq. (10), with the *ab initio* calculated [16,17] potential energies at orientational angle $\theta = 0^\circ$ and electric field $\epsilon = 0.03$ a.u. The wave function for the $v = 1$ vibrational level is superimposed on the plot.

Our pulse design strategy may be stated as: (i) estimate the pulse area according to the π condition given by Eq. (7); (ii) shape the phase of pulse to be

$$\Phi(t) = \Phi_0 + \int_0^t \omega(t') dt', \quad (12)$$

where Φ_0 is an initial phase; (iii) check the accuracy of the analytical predicted pulses by performing the numerical solution of Eq. (9) with the *ab initio* computed potential [16,17] in full three dimensions and without the “two-level” approximation. Equation (7) shows also that the resonant two-photon absorption does not depend on the details of the pulse shape. A Gaussian pulse envelope $f(t) = \exp[-(t - \tau/2)^2/(\tau/4)^2]$ is employed throughout this Letter, as this form is the most convenient for experimental applications. All quoted yields are from numerical integration of the TDSE.

A laser pulse designed according to the above procedure, with peak strength $A_0 = 0.03$ a.u., transforms 98.4% of $\text{H}_2(v = 0, j = 0, m = 0)$ into $\text{H}_2(v = 1, j = 0, m = 0)$ for a pulse duration of 1.441 ps (see Table I). The variations of the pulse envelope, instantaneous frequency, and populations of H_2 in states $v = 0, j = 0, m = 0$ and $v = 1, j = 0, m = 0$ are plotted in Fig. 2. The laser frequency $\nu(t)$ is chirped down and then up to synchronize with the polarization-shifted two-photon resonance. At the pulse center, $\nu(t)$ is ~ 0.33 THz below the field-free two-photon resonance. This negative frequency shift arises because the diagonal matrix element of the polarizability tensor α of state $v = 1, j = 0, m = 0$ is larger than that of state $v = 0, j = 0, m = 0$. The dynamic Stark shift induced by polarization effects is of the same order as the Rabi frequency and pushes the states out of resonance. Without this frequency chirping (or phase tailoring), freezing $\nu(t) \approx 63.2$ THz (the field-free two-photon resonance frequency), say, the transition probability is found to be negligibly small and H_2 remains in its initial state after the termination of the pulse. This example shows that the dynamic Stark shift can, and must, be canceled by shaping the phase of the pulse to achieve an efficient population transfer. In order to avoid the competing processes due to hyperpolarization effects or multiphoton ionization, we have limited the electric field strength to be less than 0.03 a.u. (see Ref. [16]).

An important point to address is to determine how robust the designed pulses are to variation of the optimal pulse parameters. This is relatively easily assessed through the

TABLE I. Phase-shaped two-photon π pulse for complete vibrational and rotational excitation of H_2 molecules.

Transitions	ω_{eg} (cm $^{-1}$)	A_0 (a.u.)	τ (ps)	P_{eg}
Equation (8a)	4157.92	0.03	1.441	98.4%
Equation (8b)	4494.11	0.03	6.260	99.1%
Equation (8c)	4152.02	0.03	1.178	99.7%

use of the analytic forms given in Eqs. (6) and (7). We find that a 5% error in the pulse amplitude A_0 leads to a decrease of 5% in the excitation probability, while an error of 5% in the pulse length reduces the excitation probability by 1.2%. Through a more complicated analysis, which we will describe in a future publication, we estimate that an error of 5 cm $^{-1}$ in the frequency will lead to a 4.4% decrease in the excitation probability. The laser pulse we have designed to accomplish the transformation of Eq. (8a) requires a radiation intensity of 3.16×10^{17} W m $^{-2}$. Such intensities are certainly realizable using a free electron laser [22], if the beam is focused down to a small, but realizable, width.

We now consider the vibrational and rotational excitation of H_2 represented by Eqs. (8b) and (8c) with the laser parameters given in Table I. Note that we use linearly polarized light with the polarization vector of the light defining the z axis. In this case, the z component of the rotational angular momentum m is conserved, but the

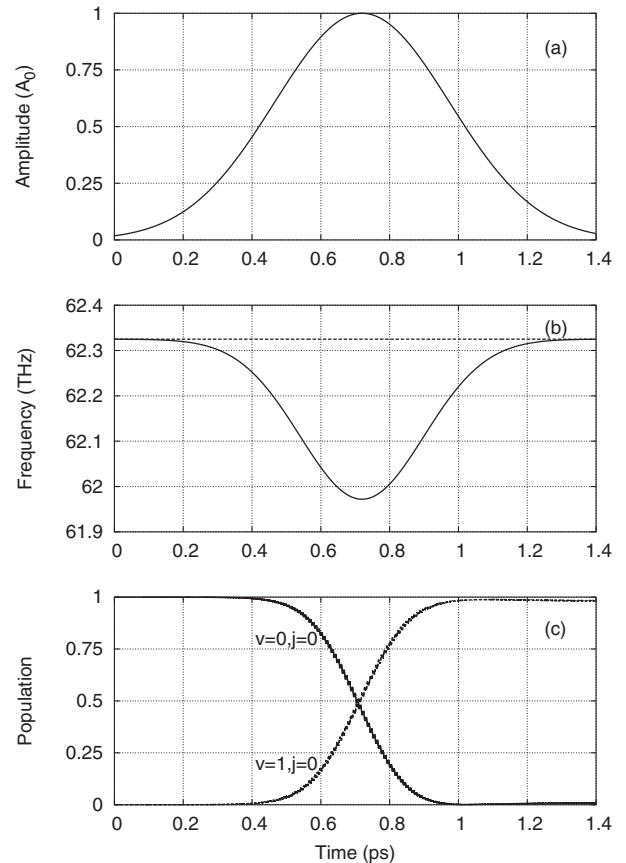


FIG. 2. Complete population inversion of H_2 molecules between the vibrational levels $v = 0, j = 0, m = 0$ and $v = 1, j = 0, m = 0$ with the use of a phase-shaped two-photon π pulse. The pulse envelope $f(t)$, instantaneous frequency $\nu(t)$, and populations of $v = 0, j = 0, m = 0$ and $v = 1, j = 0, m = 0$ are shown in panels (a), (b), and (c), respectively. The field-free two-photon resonance frequency is also presented by dashed lines in (b).

interaction matrix elements α_{gg} and α_{eg} and, therefore, the details of the laser pulse depend on the m quantum number. Numerical calculations show that we can transform 99.1% of $\text{H}_2(v=0, j=0, m=0)$ into $\text{H}_2(v=1, j=2, m=0)$ in 6.260 ps and transform 99.7% of $\text{H}_2(v=0, j=1, m=0)$ into $\text{H}_2(v=1, j=1, m=0)$ in 1.178 ps by using pulses with a peak strength of $A_0 = 0.03$ a.u. The three examples listed in Table I demonstrate that the dynamic Stark shifts induced by strong field polarization effects can be utilized to design shaped laser pulses that can achieve complete vibrational and rotational excitation even in homonuclear molecules.

Normal H_2 at room temperature has an ortho:para ratio (i.e., odd:even rotational levels) of 3:1, and, except under special circumstances, this remains constant with varying temperature. It is therefore interesting to ask if a single laser pulse is able to excite a thermal sample of H_2 from $v=0$ to $v=1$. The energy separation between $v=0$ and $v=1$ states is nearly the same for different fixed rotational quantum numbers. If the detuning of the transition frequency is less than the Rabi frequency, then the laser pulse will be likely to effectively couple the levels involved. This happens when A_0 is not too small. Thus, we are able to confirm, through the numerical solution of the TDSE, that the pulse designed to achieve the excitation of Eq. (8c) is also able to perform the excitation of Eq. (8a) with a probability of 87.6%. The same pulse also excites $v=0, j=2, m=0 \rightarrow v=1, j=2, m=0$ with a probability of 91.3%. Using our analytic model, we estimate that in a thermal sample of H_2 molecules a thermally averaged transition probability of 86.2% would be obtained at a temperature $T_{\text{rot}} = 300$ K using the laser pulse designed to accomplish the excitation of Eq. (8c) but now taking full account of all the different rotational v, j, m states present in the thermal ensemble.

In conclusion, we have developed an analytical scheme, which includes polarization effects, for designing laser pulses, involving moderately intense laser fields, to control vibrational and rotational excitation processes. Our formalism illustrates the nature of phase shaping of an optimal pulse, i.e., cancelling the dynamic Stark shifts and maintaining the resonance during laser-molecule interaction. Unlike the case of dipole coupling [23], the polarizability introduces both diagonal and off-diagonal terms into the Hamiltonian [see Eq. (2)]. Because of this, it is not possible to use the same strategies to cancel these Stark shifts, i.e., through the use of a three-level system [23].

We thank G. Duxbury and A. J. Orr-Ewing for helpful discussions.

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