

## Time-Dependent Alignment and Orientation of Molecules in Combined Electrostatic and Pulsed Nonresonant Laser Fields

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We examine the time evolution of states created by the nonadiabatic interaction of a polar molecule with combined electrostatic and pulsed nonresonant laser fields and show that the orientation due to the electrostatic field alone can be greatly enhanced by restricting the angular amplitude of the molecule by the pulsed laser field. An analytic model indicates that in the short-pulse limit the interaction is governed by an impulsive transfer of action from the radiative field to the molecule.

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The means to align or orient the molecular axis have been boosted during the past decade by new techniques based on the hybridization of rotational states of molecules with external static electric [1] or magnetic fields [2], with radiative fields [3–5], or with their combinations [6–8]. The hybridization is due to the dipole potential, either permanent (for a polar or paramagnetic molecule in a static field) or induced (for a nonspherical polarizable molecule in a nonresonant radiative field), and gives rise to directional, pendular states in which the molecular axis is confined to librate over a limited angular range about the external field vector. Pendular states have been at the core of a host of recent developments in areas such as stereodynamics of elementary collisions [1], spectroscopy [9–11], photodissociation dynamics [12–16], molecular focusing [4,14], and slowing and trapping of molecules [17].

The orientation of a polar molecule in an electrostatic field can be dramatically enhanced by a combined action with a nonresonant laser field [6]. The latter interacts with the anisotropic molecular polarizability via a double-well potential which creates nearly degenerate tunneling doublet states of opposite parity [3]. Even a weak static field can then couple the members of a given tunneling doublet and thus create a strong first-order orientation. The requisite strength of the radiative field can be attained by focusing a pulsed nonresonant laser beam. For most small diatomic molecules, laser intensities ranging between  $10^{10}$ – $10^{13}$  W/cm<sup>2</sup> suffice to generate an alignment that corresponds to an angular amplitude of the molecular axis of about  $\pm 30^\circ$  for the lowest molecular state [3]. An electrostatic field of just 0.1–10 kV/cm is then often enough to convert this alignment into an orientation that is characterized by essentially the same narrow angular amplitude [6].

If the laser pulse duration,  $\tau$ , is such that  $\tau \gtrsim 5\hbar/B$  (where  $B$  is the rotational constant of the molecule), the interaction is adiabatic and the molecule behaves as if the field were static at any instant. The states thereby created are the stationary pendular states. For  $\tau \lesssim \hbar/B$ , the time evolution is nonadiabatic and the molecule ends up in a rotational wave packet [18]. The wave packet comprises

a finite number of free-rotor states, and thus may recur after the pulse has passed, giving rise to alignment under field-free conditions [18,19].

In this Letter we examine the states created by the nonadiabatic interaction of a polar and polarizable molecule with combined electrostatic and pulsed nonresonant laser fields. We map out the alignment and orientation as functions of the pulse duration and laser intensity and show that not just alignment but also strong orientation exceeding the one due to the electrostatic field alone can be created by the fields. We report an analytic solution to the time-dependent Schrödinger equation in the short-pulse limit. This agrees quantitatively with our computations and indicates that the rotational wave packet forms under an angular momentum “punch” delivered to the molecule by the radiative field.

We consider a  $^1\Sigma$  rotor molecule with a permanent dipole moment  $\mu$  along the molecular axis and polarizability components  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  parallel and perpendicular to the molecular axis. The molecule is subject to a collinear combination of a static electric field,  $\varepsilon_S$ , with a pulsed plane-polarized nonresonant laser field,  $\varepsilon_L$ . Because of the azimuthal symmetry about the collinear fields, the permanent and induced dipole potentials involve just the polar angle  $\theta$  between the molecular axis and the field direction and  $M$ , the projection of the molecular angular momentum  $\mathbf{J}$  on the field direction, is a “good” quantum number. We limit consideration to a pulsed plane wave radiation of frequency  $\nu$  and time profile  $g(t)$  such that  $\varepsilon_L^2(t) = \frac{8\pi}{c} I_0 g(t) \cos^2(2\pi\nu t)$  where  $I_0$  is the peak intensity. We assume the oscillation frequency  $\nu$  to be far removed from any molecular resonance and much higher than either  $\tau^{-1}$  or the rotational periods. The resulting effective Hamiltonian,  $H(t)$ , is thus averaged over the rapid oscillations. This cancels the interaction between  $\mu$  and  $\varepsilon_L$  and reduces the time dependence of  $\varepsilon_L$  to that of the time profile,  $\langle \varepsilon_L^2(t) \rangle = \frac{4\pi}{c} I_0 g(t)$ ,

$$H(t) = B[\mathbf{J}^2 - \Delta\omega(t)\cos^2\theta - \omega_{\perp}(t) - \omega\cos\theta]. \quad (1)$$

The dimensionless interaction parameters are given by  $\omega_{\parallel,\perp}(t) = \frac{2\pi\alpha_{\parallel,\perp}I_0}{Bc} g(t) \equiv \omega_{\parallel,\perp}g(t)$ ;  $\Delta\omega(t) = \omega_{\parallel}(t) - \omega_{\perp}(t)$ ;  $\omega \equiv \frac{\mu\varepsilon_S}{B}$ . The corresponding time-dependent

Schrödinger equation can be cast in a dimensionless form

$$i \frac{\hbar}{B} \frac{\partial \psi(t)}{\partial t} = \frac{H(t)}{B} \psi(t) \quad (2)$$

and the wave functions expanded in terms of a series in field-free rotor wave functions  $|JM\rangle \equiv Y_{JM}$  (pertaining to eigenenergies  $E_J$ )

$$\psi[\Delta\omega(t), \omega] = \sum_J d_J[\Delta\omega(t), \omega] |J, M\rangle \exp\left[-\frac{iE_J t}{\hbar}\right], \quad (3)$$

whose time-dependent coefficients,  $d_J[\Delta\omega(t), \omega] \equiv d_J(t)$ , solely determine the solutions at given values of the dimensionless parameters  $\Delta\omega(t)$  and  $\omega$  and at given initial conditions (in the interaction representation). The expansion (or *hybridization*) coefficients  $d_J(t)$  can be found from the differential equations

$$i \frac{\hbar}{B} \dot{d}_J(t) = -\sum_{J'} d_{J'}(t) \langle J, M | \Delta\omega(t) \cos^2\theta + \omega_{\perp}(t) + \omega \cos\theta | J', M \rangle \exp\left[-\frac{i(E_{J'} - E_J)t}{\hbar}\right]. \quad (4)$$

Note that the  $\cos^2\theta$  and  $\cos\theta$  operators connect states that differ in  $J$  by 0,  $\pm 2$ , and  $\pm 1$ , respectively. In what follows, we consider the molecule to be in the ground rotational state,  $|0, 0\rangle \equiv Y_{0,0}$ , before switching on any of the fields [i.e., for  $\omega_{\parallel, \perp}(t=0) = 0$  and  $\omega = 0$ ]. We take the pulse shape function to be a Gaussian,  $g(t) = \exp(-\frac{t^2}{\sigma^2})$ , characterized by a full width at half maximum,

$$d_J(t \geq t_a) \approx 2\pi \int \langle \tilde{J}, 0; 0, \omega | \bar{\psi}(t \geq t_a) \sin\theta d\theta \equiv \bar{d}_J(t \geq t_a) = 2\pi \langle \tilde{J}, 0; 0, \omega | \exp\left[\frac{iB\pi^{1/2}\sigma\Delta\omega}{2\hbar} \cos^2\theta\right] | \tilde{0}, 0; 0, \omega \rangle. \quad (7)$$

The expansion coefficients were computed by numerically solving Eq. (4) and used to evaluate  $\langle \cos^2\theta \rangle$  and  $\langle \cos\theta \rangle$  that characterize, respectively, the alignment and orientation of the molecular axis (alignment and orientation cosines). We chose a permanent dipole interaction characterized by  $\omega = 1$ , which is attainable for most small ground-state polar molecules with electrostatic fields of up to 50 kV/cm; e.g.,  $\epsilon_S = 730$  V/cm for ground-state KCl. The chosen range of  $\Delta\omega$  includes values of up to 1000, which is attainable for some of the above molecules with nonresonant laser intensities of less than  $5 \times 10^{12}$  W/cm<sup>2</sup>; e.g.,  $\Delta\omega = 240$  for KCl at  $10^{12}$  W/cm<sup>2</sup>. However, strong effects are in place at much lower  $\Delta\omega$  values (see below). Note that  $\sigma = 1\hbar/B$  corresponds to 5.3 ps for  $B = 1 \text{ cm}^{-1}$ .

Figure 1 shows the dependence of the alignment and orientation cosines on time (expressed in units of  $\sigma$ ) for different values of  $\sigma$  and fixed  $\Delta\omega = 100$  and  $\omega = 1$ . At  $\sigma = 0.01 \hbar/B$  (upper panel), the pulse creates a rotational wave packet whose alignment and orientation lag behind the pulse shape function and recur with a period deter-

$\tau = 2(\ln 2)^{1/2} \sigma \approx \frac{5}{3} \sigma$ . In the long-pulse (adiabatic) limit, i.e., for  $\sigma \rightarrow \infty$ ,  $g(t) \rightarrow 1$  and Eq. (2) yields the stationary solutions (*pendular states*),  $|\tilde{J}, M; \Delta\omega, \omega\rangle$ , that pertain to eigenvalues  $\lambda_{\tilde{J}, M} = E_{\tilde{J}, M}/B + \omega_{\perp}$ . Here  $\tilde{J}$  is the nominal value of angular momentum of the field-free rotor state that adiabatically correlates with the high-field hybrid function. With just the static field on, the molecule is in the ground pendular state,  $|\tilde{J}, M; \Delta\omega, \omega\rangle = |\tilde{0}, 0; 0, \omega\rangle$ .

In the short-pulse limit, the time evolution of the initial wave function  $|\tilde{0}, 0; 0, \omega\rangle$  under the Hamiltonian  $H(t)$  is approximated, up to order  $\sigma$ , by a propagator  $S(t) = \exp[-\frac{i}{\hbar} \int H(t') dt']$ , which yields an approximate wave function

$$\begin{aligned} \bar{\psi}(t) &= S(t) |\tilde{0}, 0; 0, \omega\rangle \\ &= \exp\left[-\frac{i}{\hbar} B[t\mathbf{J}^2 - t\omega \cos\theta - \Delta\omega \cos^2\theta G(t)]\right] \\ &\quad \times |\tilde{0}, 0; 0, \omega\rangle, \end{aligned} \quad (5)$$

with  $G(t) = \int_{-\infty}^t g(t') dt' = \frac{1}{2} \pi^{1/2} \sigma [1 + \text{erf}(t/\sigma)]$ ; see also Ref. [20]. For  $t \gtrsim 12\sigma \equiv t_a$ , the approximate wave function can be further reduced to

$$\begin{aligned} \bar{\psi}(t \geq t_a) &\approx \exp\left[-\frac{i}{\hbar} Bt(\mathbf{J}^2 - \omega \cos\theta)\right] \\ &\quad \times \exp\left[\frac{iB\pi^{1/2}\sigma\Delta\omega}{2\hbar} \cos^2\theta\right] |\tilde{0}, 0; 0, \omega\rangle. \end{aligned} \quad (6)$$

The expansion coefficients in the nonadiabatic limit are obtained by the transformation

mined by  $\sigma$  and  $\Delta\omega$  (nonadiabatic behavior). On the time scale of  $\tau$ , the orientation closely follows the alignment as the permanent electric dipole moment is confined to an angular range preordained by the dominant induced dipole interaction with the laser field. At  $\sigma = 1\hbar/B$  (lower panel), the time dependence of  $\langle \cos^2\theta \rangle$  and  $\langle \cos\theta \rangle$  mimics the pulse shape function and by the time the pulse is over, the alignment and orientation of the initial wave function,  $|\tilde{0}, 0; 0, \omega\rangle$ , are nearly recovered (see the nearly stationary oscillations in  $\langle \cos^2\theta \rangle$  and  $\langle \cos\theta \rangle$ , characteristic of the eigenstates). A full such recovery would correspond to the adiabatic limit when the molecule ends up in its initial eigenstate. The middle panel of Fig. 1 shows a case when the pulse establishes a phase relationship among the components of the wave packet that happens to suppress the recurrences of both the alignment and orientation. Such a behavior is anomalous and reflects the accidental phase matching among the eigenstates at the end of the pulse.

An intriguing feature of the rotational wave packet created by a strongly nonadiabatic pulse in the combined

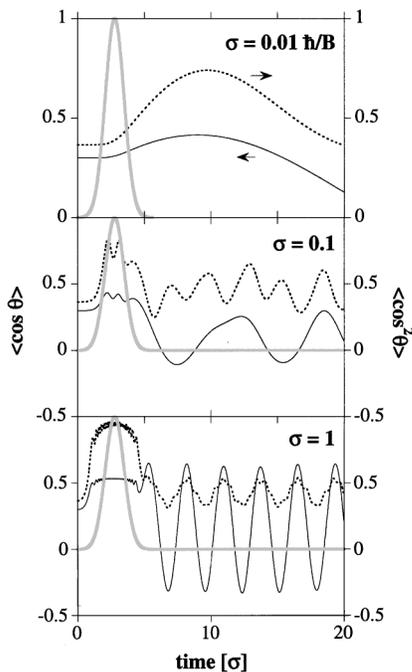


FIG. 1. Dependence of the alignment (dotted lines) and orientation (full lines) cosines on time (expressed in terms of  $\sigma$ ) for different pulse durations  $\tau$  and fixed  $\Delta\omega = 100$  and  $\omega = 1$ . The grey curves show the pulse shape function.

fields is revealed when another, second pulse is sent in. If the first pulse creates a wide wave packet (comprised of many  $|\tilde{J}, 0; 0, \omega\rangle$  states), the second pulse, while on, can either restore, suppress or reverse the orientation the wave packet had during the first pulse. The outcome depends on the delay between the two pulses. We found that, in effect, the second pulse can juggle the wave packet between the two equivalent wells of the  $\cos^2\theta$  potential. The well centered at  $0^\circ$  overlaps with the attractive part of the  $\cos\theta$  potential while the well centered at  $180^\circ$  overlaps with its repulsive branch. Therefore, when the wave packet falls into either of the  $\cos^2\theta$  minima, it becomes localized, resulting in a net orientation. A near hit of the repulsive barrier between the minima spreads the wave packet about equally between them, which cancels the average orientation. The alignment is left essentially intact by the second pulse. For a delay of the second pulse that corresponds to a full rephasing of the wave packet, the orientation is the same as that created during a single pulse with the same  $\sigma$  and  $\Delta\omega$ .

Figure 2 shows the expansion coefficients  $d_{\tilde{J}}(t_a)$  for  $\tilde{J} \leq 3$  as a function of the induced dipole interaction parameter  $\Delta\omega$  for a fixed permanent dipole interaction parameter  $\omega$  and for different  $\sigma$ . The expansion coefficients pertain to a time  $t_a$  after the nonresonant laser pulse (which is centered at  $t = 6\sigma$ ). We found that for  $t \geq t_a$  the  $d_{\tilde{J}}(t)$ 's evolve, within  $\approx 1\%$ , to values which they maintain "ever after." Therefore, the  $d_{\tilde{J}}(t_a)$  coefficients make it possible to fully reconstruct the wave function  $\psi(t)$  at any time  $t \geq t_a$ .

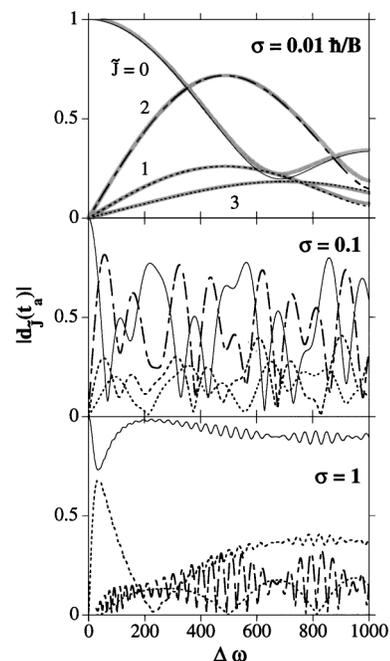


FIG. 2. Expansion coefficients  $d_{\tilde{J}}(t_a)$  of the time-dependent wave function for  $\tilde{J}$  up to 3 as a function of the induced dipole interaction parameter  $\Delta\omega$  for a fixed permanent dipole interaction parameter  $\omega = 1$  and for different pulse durations  $\tau$ . The grey lines in the upper panel show the approximate  $\tilde{d}_{\tilde{J}}(t_a)$  coefficients obtained in the nonadiabatic limit, Eq. (7).

The upper panel of Fig. 2 shows the  $d_{\tilde{J}}(t_a)$  coefficients for  $\sigma = 0.01\hbar/B$ . This corresponds to a strongly nonadiabatic regime, when many of the  $d_{\tilde{J}}(t_a)$  coefficients contribute to the wave function after the pulse passes over (up to  $\tilde{J} = 8$  at  $\Delta\omega = 900$ ).

We also plot the approximate  $\tilde{d}_{\tilde{J}}(t_a)$  coefficients obtained in the nonadiabatic limit, Eq. (7). The agreement with the exact results is excellent, just within a few percent. This implies that the interaction at  $\sigma = 0.01\hbar/B$  is governed, over a wide range of field strengths, by an impulsive transfer of action,  $A$ , from the radiative field to the molecule: since the angular momentum is  $L = B \times \int \frac{d}{d\theta} [\Delta\omega(t) \cos^2\theta + \omega_{\perp}(t)] dt = -B\Delta\omega G(t) \sin 2\theta$ , the action  $A = \int L d\theta = B\Delta\omega G(t) \cos^2\theta$ . Therefore, the operator that creates the rotational wave packet in the nonadiabatic limit, Eq. (6), is indeed  $\exp[iA/\hbar]$ . Note that the  $d_{\tilde{J}}(t)$  coefficients in the nonadiabatic limit scale, at any given time, according to the value of the product  $\sigma\Delta\omega$ .

The lower panel of Fig. 2 shows all the contributing  $d_{\tilde{J}}(t_a)$  coefficients for a pulse with  $\sigma = 1\hbar/B$ . One can see that at small  $\Delta\omega$ , the wave function consists mainly of a single contribution, namely, the  $|\tilde{0}, 0; 0, \omega\rangle$  initial state. This is a signature of an adiabatic behavior when the wave function follows the radiative field as if it were static at any field strength along the pulse profile. As  $\Delta\omega$  increases, deviations from the adiabatic behavior become evident in the augmented contributions from higher  $|\tilde{J}, 0; 0, \omega\rangle$  states. The middle panel of Fig. 2 pertains to the intermediate case characterized by  $\sigma = 0.1\hbar/B$  when the behavior falls

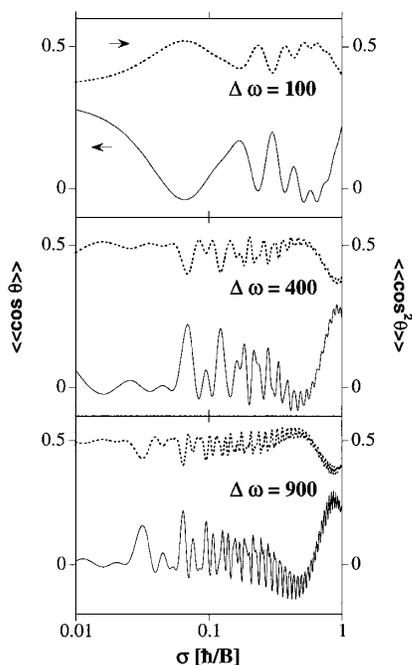


FIG. 3. Time averages of the alignment (dotted lines) and orientation (full lines) cosines as functions of the laser pulse duration  $\tau$  at fixed values of the induced dipole interaction parameter  $\Delta\omega = 100, 400,$  and  $900$  and for a fixed value of  $\omega = 1$ .

within neither limit and the numerical calculation is the only guide.

Figure 3 shows time averages,  $\langle\langle \cos^2 \theta \rangle\rangle = \sum_{\tilde{J}} |d_{\tilde{J}}(t_a)|^2 \langle \tilde{J} | \cos^2 \theta | \tilde{J} \rangle$  and  $\langle\langle \cos \theta \rangle\rangle = \sum_{\tilde{J}} |d_{\tilde{J}}(t_a)|^2 \times \langle \tilde{J} | \cos \theta | \tilde{J} \rangle$ , of the alignment and orientation cosines as functions of the laser pulse duration  $\sigma$  at fixed values of the induced dipole interaction parameter  $\Delta\omega = 100, 400,$  and  $900$  and for a fixed value of  $\omega = 1$ . One can see that both the alignment and orientation persist in the absence of the pulsed laser field. However, the recurrences of alignment and orientation qualitatively differ. While the alignment remains essentially constant, the orientation cosine exhibits large oscillations (between  $-0.1$  and  $+0.3$ ) and a tendency to increase towards the adiabatic limit (where it would reach a value of  $\approx 0.3$  corresponding to the purely electrostatic interaction). Apart from the case of small  $\sigma\Delta\omega$  (for  $\sigma \leq 0.05\hbar/B$  in the upper panel pertaining to  $\Delta\omega = 100$ ), the average orientation is actually suppressed at low  $\sigma$ . This is a consequence of the alignment and orientation of the contributing states  $|\tilde{J}, 0; 0, \omega\rangle$ . Since the states are all aligned more or less along the radiative field, their mixing does not affect the average alignment  $\langle\langle \cos^2 \theta \rangle\rangle$ . On the other hand, the orientation of the  $|\tilde{J}, 0; 0, \omega\rangle$  states with  $\tilde{J} \geq 1$  is opposite to the one of the  $|\tilde{0}, 0; 0, \omega\rangle$  state (which is along the static field). Therefore, as more of the states with  $\tilde{J} \geq 1$  contribute to the wave function, the average orientation  $\langle\langle \cos \theta \rangle\rangle$  decreases. This happens, as one can see in the upper panel of Fig. 2, in the nonadiabatic limit for  $\sigma = 0.01\hbar/B$  and

$\Delta\omega \geq 300$ . On the other hand, the range of  $\Delta\omega \leq 100$  for  $\sigma = 0.01\hbar/B$  is particularly advantageous for maintaining a large average orientation after the passage of the pulse, since the wave function is dominated by the  $|\tilde{0}, 0; 0, \omega\rangle$  state oriented along the static field.

The strong induced dipole interaction, easily attainable with pulsed nonresonant laser fields, can be used to enhance a weak permanent dipole orientation during the laser pulse. Under suitable conditions, a sizable orientation can persist even after the passage of the pulse. This should find application whenever molecular orientation is desirable, and should be taken into account in all schemes that make use of combined electrostatic and pulsed radiative fields.

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