

Orientation of Polar Molecules by Laser Induced Adiabatic Passage

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We show that two overlapping linearly polarized laser pulses of frequencies ω and its second harmonic 2ω can strongly orient linear polar molecules, by adiabatic passage along dressed states. The resulting robust orientation can be interpreted as a laser-induced localization in the effective double well potential created by the fields, which induces a preliminary molecular alignment. The direction of the orientation can be selected by the relative phase of the fields.

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Introduction.—Intense laser fields offer a rich variety of control processes, allowing us to manipulate the internal and external degrees of freedom of molecules (see, for example, the recent works [1–4]).

In particular a strong nonresonant linearly polarized laser field allows one to align small molecules along the electric field axis through their anisotropic polarizability [5,6]. One approach is to use an ultrashort pulse which creates a superposition of rotational states. This results in a field-free transient alignment occurring periodically in time due to revivals of rotational wave packets, as long as the coherence of the process is preserved [7–9].

On the other hand, nanosecond pulses have been shown theoretically [8] and experimentally [10] to yield alignment during the pulse (adiabatic alignment). The laser field has to be turned on slowly compared with the rotational periods in order to induce an adiabatic transport along a dressed state. This process has been interpreted as a rigid rotor dressed by an effective double-well potential whose minima are in the directions of the field polarization. The wells are deeper and thinner for a stronger field [5,8]. One considers the initial state to be $J = 0, M = 0$ and linear polarized fields. The projection M of the rotational angular momentum along the field axis is a constant of motion. The eigenvectors of the dressed Hamiltonian are called *pendular states* and are labeled with \tilde{J} . Their associated eigenenergies as a function of the field amplitude form curves that are continuously connected to the bare states $|J\rangle$. The lowest ones are well localized in the wells and correspond thus to the molecular alignment. The molecular population initially in the rotational state $|J = 0\rangle$ is *adiabatically* carried along the pendular state $|\tilde{J} = 0\rangle$ whose eigenenergy is continuously connected to the state $|J = 0\rangle$. This process can be interpreted as Stark shifts that align the molecules.

Strong electrostatic fields have been shown to yield molecular orientation for molecules through their permanent dipole moment [11,12]. Its combination with a coherent laser field has been proved theoretically to enhance significantly this orientation [4,13]. The additional electrostatic field indeed allows one to break the double-well symmetry induced by the laser field favoring one well with respect to the other one. Another technique using extremely short

electrical pulses has been shown also to give orientation [14]. Lasers resonant with the first excited vibrational state can induce a modest transient orientation [15].

The purpose of this article is to show that an off-resonant pulse of frequency ω when accompanied by its second harmonic 2ω , can transform the adiabatic alignment of molecules into orientation during the pulse. These two pulses induce a hyper-Raman type process. More precisely, the orientation is successful if the alignment can be obtained by each laser pulse taken separately and if the hyper-Raman three-photon coupling between the pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ (whose eigenenergy is continuously connected to the state $|J = 1\rangle$) allows adiabatic passage along the dressed states. The relative phase between the two pulses allows us to choose the direction of the orientation. This new mechanism we propose is robust with respect to all the pulse parameters, including the relative phase. The orientation is more efficient if the hyper-Raman coupling is assisted by a near resonant vibrational state (see Fig. 1). This mechanism can be interpreted as a natural *dynamical laser-induced localization* in the double-well alignment potential as follows.

The first step consists in identifying *oriented states*: Since the fields create a symmetric effective double well potential, the two lowest pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ are quasidegenerate and are, respectively, symmetric and antisymmetric. The two lowest states come closer to degeneracy for stronger fields. Thus the states $(|\tilde{J} = 0\rangle + |\tilde{J} = 1\rangle)/\sqrt{2}$ and $(|\tilde{J} = 0\rangle - |\tilde{J} = 1\rangle)/\sqrt{2}$ are well

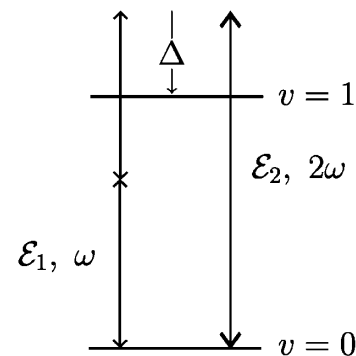


FIG. 1. Coupling scheme.

localized in one of the wells and can thus be identified as “oriented pendular states” if the field is strong enough.

The second step consists in finding the pulse parameters which will carry in a robust way the dynamics into one of these oriented states from the initial state $|J = 0\rangle$. For increasing fields, the induced pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ come closer to the degeneracy and the hyper-Raman process $(2\omega, \omega)$, initially off resonant, comes closer to the three-photon resonance. This gives rise to a dynamical resonance which is characterized, as a function of the field amplitudes, by an avoided crossing. Far after this avoided crossing, we will show that the two dressed branches will be identified with a very good approximation as the previously defined oriented states if the relative phase ϕ between the two fields is *not close* to $\pi/2(\text{mod } \pi)$. Thus under this condition, the adiabatic passage along this avoided crossing will yield molecular orientation. Choosing ϕ around either 0 or π will allow control of the direction of the orientation in a robust way.

We will develop more precisely the strategy for orientation described above and will show numerically the efficiency of this strategy on the example of HCN molecules.

The strategy for orienting.—We consider a linear polar molecule, modeled as a rigid rotor, in its ground electronic and vibrational state, subject to a laser field. The molecule interacts with the field through its permanent dipole moment $\mu_0(R)$, coupling the vibrations (of coordinate R) with one-photon processes, and, if one considers its frequency sufficiently far from any resonances with the excited electronic states, through its polarizability, coupling the vibrations by Raman processes. The dynamical polarizability includes the components $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$, respectively, parallel and perpendicular to the molecular axis. The Hamiltonian between vibrational blocks $H_{v',v} = \langle v'|H|v\rangle$, of energy E_v and of rotational constant B_v , reads in this case [6]

$$H_{v',v} = (E_v + B_v J^2) \delta_{v',v} - \mu_{0,v'v} \mathcal{E}(t) \cos \theta - \frac{1}{2} \mathcal{E}^2(t) [(\alpha_{\perp,v'v} - \alpha_{\parallel,v'v}) \sin^2 \theta + \alpha_{\parallel,v'v}], \quad (1)$$

with $\mu_{0,v'v} = \langle v'|\mu_0|v\rangle$, $\alpha_{\perp,v'v} = \langle v'|\alpha_{\perp}|v\rangle$, $\alpha_{\parallel,v'v} = \langle v'|\alpha_{\parallel}|v\rangle$, J the angular momentum. θ is the polar angle between the molecular axis and the direction of the field $\mathcal{E}(t) = \mathcal{E}_0 \sqrt{\Lambda(t)} \cos \omega t$, with ω the carrier frequency, \mathcal{E}_0 the peak amplitude, and $\Lambda(t)$ the envelope of the field intensity. It is a good approximation to choose α_{\parallel} and α_{\perp} as the static polarizabilities when the laser frequencies are far red detuned from the excited electronic states (i.e., low frequencies with respect to the electronic surfaces). If additionally the field is off resonant between the ground and the excited vibrational states, the dressed Hamiltonian in the ground vibrational state can be approximated in the high frequency limit (with respect to the rotational constant B_0) [16] as

$$H_{00}^{\text{eff}} = E_0 + B_0 J^2 + \mathcal{E}_0^2 \Lambda(t) a_{00}(\omega), \quad (2)$$

with

$$a_{vv}(\omega) = \alpha_{vv}^{\text{eff}}(\omega) \sin^2 \theta - \alpha_{\parallel,vv}/4 \quad (3)$$

and

$$\alpha_{vv}^{\text{eff}}(\omega) = \frac{B_0 |\mu_{0,vv}|^2}{2(\hbar\omega)^2} + \frac{\alpha_{\parallel,vv} - \alpha_{\perp,vv}}{4}. \quad (4)$$

For linear molecules ($\alpha_{\parallel} > \alpha_{\perp}$), the rigid rotor $B_0 J^2$ is thus effectively subject to a double-well potential, with minima at $\theta = 0$ and $\theta = \pi$ for $M = 0$ [5]. This potential is deeper and thinner for stronger fields. The condition for adiabatic transport has been identified as

$$\tau \gg \hbar/B_0 \quad (5)$$

by Ortigoso *et al.* [8], with τ characterizing the pulse duration. In practice, if we consider smooth pulses, such as Gaussian pulses of shape $\Lambda(t) = \exp[-(t/\tau)^2]$, the adiabatic regime is already well attained for $B_0 \tau = 5\hbar$. For a given pulse amplitude \mathcal{E}_0 , the dimensionless quantity which characterizes the alignment regime is [8]

$$\gamma = \mathcal{E}_0^2 \alpha_{00}^{\text{eff}}(\omega)/B_0. \quad (6)$$

Already for $\gamma = 30$, one obtains in the adiabatic regime $\langle \cos^2 \theta \rangle \approx 0.8$.

In the dressed state representation as a function of the field intensity, stronger fields induce pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$, of respective dressed energies λ_0 and λ_1 becoming closer to degenerate as shown as dashed lines in Fig. 2, meaning a more efficient alignment. We have found numerically that, under the condition $\gamma \leq 30$, this degeneracy can be quite well represented by

$$\lambda_1 - \lambda_0 = 2B_0 \exp(-0.17\gamma). \quad (7)$$

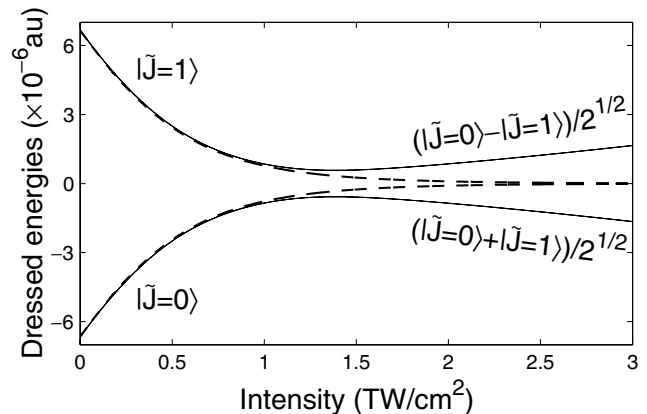


FIG. 2. The dressed energies as a function of the field intensity I_1 for the example of HCN (see text for details) characterizing (i) the process of alignment with one field (dashed lines) and (ii) the process of orientation with the two fields (full lines). The two energies have been represented relative to their average [i.e., $\lambda_j - (\lambda_1 + \lambda_2)/2$]. They can be approximately labeled before the avoided crossing by the pendular states, and after by the oriented states.

The exponential law can be obtained from a semiclassical treatment of the tunnel splitting. Note that for $\gamma > 30$, the degeneracy follows the law $\lambda_1 - \lambda_0 \sim \exp(-a\sqrt{\gamma})$ [17].

As already noticed in the introduction, the oriented states are well identified: they are characterized by the linear combinations $(|\tilde{J} = 0\rangle \pm |\tilde{J} = 1\rangle)/\sqrt{2}$. The goal is now to reach this state by adiabatic passage. We use the hyper-Raman coupling with the combination of the two lasers $(\omega, 2\omega)$ giving the total electric field $\mathcal{E}(t) = \mathcal{E}_1(t) \times \cos\omega t + \mathcal{E}_2(t) \cos(2\omega t + \phi)$, with $\mathcal{E}_1(t) = \mathcal{E}_{01}\Lambda(t)$, $\mathcal{E}_2(t) = \mathcal{E}_{02}\Lambda(t)$, and ϕ the relative phase. The frequencies are detuned by $\Delta = E_1 - E_0 - 2\hbar\omega$ from the first excited vibrational state (see Fig. 1). The detuning Δ is chosen as small as possible and negative to prevent any detrimental multiphoton vibrational resonance (with other low vibrational states). Since we have in general $\mu_{0,00} \approx \mu_{0,11}$ and $(\alpha_{\perp,\perp})_{00} \approx (\alpha_{\parallel,\perp})_{11}$, the Hamiltonian (1) becomes in the high frequency limit and in the quasi-resonant approximation (rotating wave approximation) [18] (where the constant energy E_0 has been omitted)

$$H_{00}^{\text{eff}} = B_0 J^2 + \mathcal{E}_1^2 a_{00}(\omega) + \mathcal{E}_2^2 a_{00}(2\omega), \quad (8a)$$

$$H_{11}^{\text{eff}} = B_1 J^2 + \mathcal{E}_1^2 a_{11}(\omega) + \mathcal{E}_2^2 a_{11}(2\omega) + \Delta, \quad (8b)$$

$$H_{01}^{\text{eff}} = (H_{10}^{\text{eff}})^* = -\frac{\mu_{0,01}}{2} \mathcal{E}_2 e^{i\phi} \cos\theta - \mathcal{E}_1^2 \left(\frac{\alpha_{\perp,01} - \alpha_{\parallel,01}}{8} \sin^2\theta + \frac{\alpha_{\parallel,01}}{8} \right). \quad (8c)$$

The pendular states are defined as the eigenvectors of the Hamiltonian (8a) when the coupling (8c) is zero. This coupling between the two pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ gives initially and for sufficiently low field a three-photon off-resonant process. For stronger fields, the Stark shifts in H_{00}^{eff} make $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ become closer to degeneracy (alignment process) until the three-photon hyper-Raman coupling has a non-negligible effect. This leads to a dynamical resonance characterized by an avoided crossing of the eigenvalues $\tilde{\lambda}_{\pm}$ of the Hamiltonian (8) (full lines in Fig. 2).

After a standard adiabatic elimination, the effective two-level avoided crossing between $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ can take the following approximate form, in the basis of the pendular states $\{|\tilde{J} = 0\rangle, |\tilde{J} = 1\rangle\}$:

$$\tilde{H}^{01} = \begin{bmatrix} \lambda_0 + s_0 & \kappa \mathcal{E}_1^2 \mathcal{E}_2 \cos\phi \\ \kappa \mathcal{E}_1^2 \mathcal{E}_2 \cos\phi & \lambda_1 + s_1 \end{bmatrix}, \quad (9)$$

with $\lambda_1 - \lambda_0$ as in Eq. (7) with $\gamma = [\mathcal{E}_1^2 \alpha_{00}^{\text{eff}}(\omega) + \mathcal{E}_2^2 \alpha_{00}^{\text{eff}}(2\omega)]/B_0$, κ the three-photon coupling strength, and $s_j, j = 0, 1$ the additional dynamical Stark shifts of the pendular state $|j\rangle$ induced by the three-photon process, and which depend on the field amplitudes and on the frequency ω . The Hamiltonian (9) shows that, when the relative laser phase is $\phi = \pi/2 \pmod{\pi}$, the coupling vanishes and the two levels become decoupled. In this case, we recover the process of alignment (represented in the dressed energy diagram of Fig. 2 by the dashed lines) without any

orientation. This can be interpreted as destructive interferences of the two fields with respect to the orientation. The strongest coupling is obtained when ϕ is 0 or π .

If we consider a strong field, we have $\lambda_1 \rightarrow \lambda_0$ (aligned molecule). Furthermore, we consider additionally $|\Delta| \gg B_0, B_1$, so that one has $s_0 \approx s_1$. This means that the three-photon coupled $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ states experience the same Stark shifts because the fields act very similarly on these states. Under these considerations, beyond the avoided crossing, the dressed states read

$$|\tilde{J}_{\pm}\rangle = \frac{1}{\sqrt{2}} [|\tilde{J} = 0\rangle \pm \text{sgn}(\cos\phi)|\tilde{J} = 1\rangle], \quad (10)$$

where $\text{sgn}(\cos\phi)$ is 1 (respectively -1) for positive (respectively negative) $\cos\phi$ and where $|\tilde{J}_{+}\rangle$ (respectively $|\tilde{J}_{-}\rangle$) connects the field-free state $|J = 1\rangle$ (respectively $|J = 0\rangle$). The two dressed states, beyond the avoided crossing, are thus the oriented states previously identified. Thus passing *adiabatically* along the avoided crossing will lead to an oriented molecule. Any nonidentical Stark shifts between the pendular states in the Hamiltonian (9) would give different linear combinations and would be detrimental for the orientation by adiabatic passage. On the opposite situation, passing very fast (*diabatic* passage), meaning that the coupling is ignored, would lead to $|\tilde{J} = 0\rangle$, the aligned state without orientation, meaning that the oriented states $|\tilde{J}_{+}\rangle$ and $|\tilde{J}_{-}\rangle$ would be equally populated beyond the avoided crossing. We thus remark that this avoided crossing has different properties from the Landau-Zener avoided crossing, especially concerning the diabatic passage.

In summary the guideline to achieve the orientation in the ground vibrational state is as follows: One has to apply sufficiently strong fields such that $\gamma \gg 1$ to ensure alignment. These fields have to be adiabatically switched on such that the avoided crossing is passed adiabatically. The laser frequencies have to be chosen with a negative detuning Δ with an absolute value as small as possible such that the excited vibrational state assists the three-photon transition. On the other hand, the detuning Δ has to be large enough, such that $|\Delta| \gg B_0, B_1$, to ensure parallel Stark shifts.

Illustration on HCN.—We illustrate the strategy for the orientation of the bond C—H ($B_0 \approx 1.46 \text{ cm}^{-1}$) of the molecule H—C \equiv N. As in [15], we neglect the stretching motion CN and the bending motion. Accurate couplings calculated by *ab initio* methods can be found in [18]. We make the calculation with the laser fundamental frequency $\omega = 1706 \text{ cm}^{-1}$ leading to $\Delta = -200 \text{ cm}^{-1}$. We have checked that it is a good approximation to consider as the effective Hamiltonian the first two vibrational states. The overlapping pulses are Gaussian of duration $\tau = 800 \text{ ps}$. They have peak intensities $I_1 = 3 \times 10^{12} \text{ W/cm}^2$ for the field of frequency ω and $I_2 = 10^{12} \text{ W/cm}^2$ for the second harmonic field. The relative phase $\phi = \pi$ is chosen. Here $\tau B_0/\hbar \approx 220$ has been required at this intensity to satisfy adiabatic passage. Note that this is a more restrictive

condition than for the simple alignment where $\tau B_0/\hbar \gtrsim 5$ is enough.

The results are collected in Fig. 3, where $\langle \cos^2\theta \rangle(t)$ and $\langle \cos\theta \rangle(t)$, the usual measures of alignment and orientation, respectively, have been plotted as a function of time. One can observe a preliminary alignment which becomes for higher field an orientation ($\langle \cos\theta \rangle(t) \approx 0.9$) during approximately 1 ns. This orientation occurs efficiently beyond the field threshold $I_1^{\text{th}} \approx 1.4 \times 10^{12}$ W/cm² given by the position of the avoided crossing of Fig. 2, i.e., after the dynamics has passed the avoided crossing. This can be seen in the bottom of Fig. 3 where the projections $|\langle \tilde{J} | \Psi(t) \rangle|^2$ on the pendular states $|\tilde{J} = 0\rangle$ and $|\tilde{J} = 1\rangle$ of the state solution $|\Psi(t)\rangle$ have been plotted. The alignment becomes orientation when these projections are approximately 1/2.

The orientation that is obtained is robust with respect to the pulse parameters (phases, amplitudes, delay, and frequencies). Changing the relative phase ϕ from π to 0 flips the orientation of the molecule, whose efficiency at the peak intensities is well approximated by

$$\langle \cos\theta \rangle \approx 0.9[-1 + 2\Theta(\phi - \pi/2)], \quad (11)$$

where $\Theta(\phi)$ is the Heaviside step function (1 if $\phi > 0$, 1/2 for $\phi = 0$, and 0 otherwise). The orientation is lost only when ϕ comes very close to $\pi/2$.

Conclusion.—In summary, we have shown that two overlapping laser pulses of frequency ω and 2ω allow us to orient very efficiently a polar molecule by adiabatic pas-

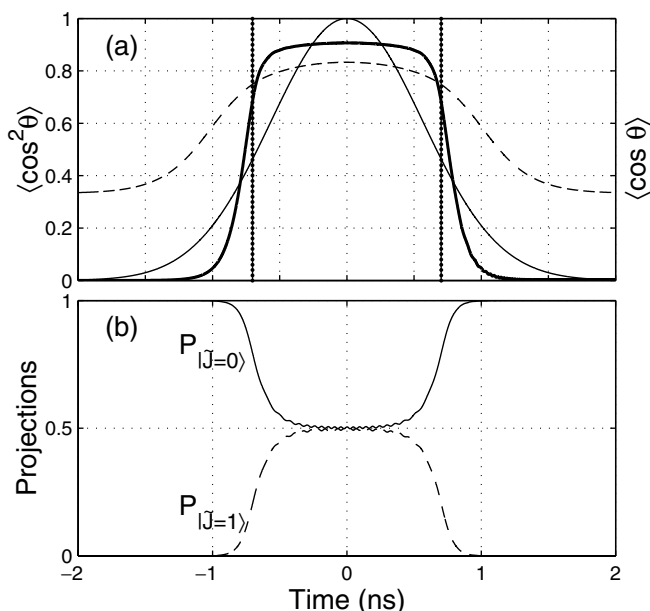


FIG. 3. (a) $\langle \cos^2\theta \rangle(t)$ (dashed line), $\langle \cos\theta \rangle(t)$ (thick full line) and the Gaussian amplitude $\Lambda(t)$ (thin full line) as a function of time. The position of the avoided crossing of Fig. 2 is represented by the vertical dotted lines. (b) The projection of the dynamics in the pendular states $|\tilde{J} = 0\rangle$ (full line) and $|\tilde{J} = 1\rangle$ (dashed line).

sage. This result is general in the sense that it can be applied for many different linear polar molecules. The main differences of the technique we propose with respect to other schemes is that it avoids the use of a static field and that it is induced by nanosecond pulses, in the vibrational infrared domain. One achieves orientation while the laser is in interaction. We have considered the example of the molecule HCN to illustrate the mechanism. Other molecules such as CO could be candidates to validate experimentally the mechanism we propose.

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