Laser-assisted control of molecular orientation at high temperatures

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A method of laser-assisted field-free dynamic molecular orientation employing a short, moderately intense three-color phase-locked laser pulse is proposed. Numerical simulations show that it provides an exceedingly effective control of orientation in molecular gases even at room temperatures. The underlying mechanism is based on the specific laser-induced orientation-dependent selective excitation of molecules and subsequent self-transformation of the induced geometrical orientation into a dynamical one. It is shown that this mechanism is significantly more powerful than the widely investigated kick mechanism.

Laser-assisted molecular alignment and orientation are among the intriguing and rapidly developing areas of modern laser physics. In a simple one-dimensional case, molecular alignment means the confinement of one of the molecule-fixed axes $\vec{\zeta}$ in the direction *collinear* with the laboratory-fixed $\vec{z}$ axis. As a result, the ensemble-averaged expectation value $\langle \cos^2 \theta \rangle$, where $\theta = (\widehat{\vec{\zeta}, \vec{z}})$, is raised in values to unity, by contrast with its isotropic value of $1/3$. Recent striking progress in the development of laser alignment strategies gives us powerful methods for molecular alignment both in one and in three dimensions (see reviews [1–4]).

Molecular orientation is a more complex and much more difficult problem. It implies alignment with the *codirectional* confinement between the molecular and spatially fixed axes. Mathematically it means the breakdown of both equilibrium values $\langle \cos^2 \theta \rangle$ and $\langle \cos \theta \rangle$ (the latter serves as the conventional orientation measure). There is no straightforward way to adopt molecular alignment schemes for orientation because in most cases the effective field-molecule interaction is averaged over fast oscillations of the electric field and thus does not have necessary forward-backward asymmetry with respect to the directions of the molecular axes. One can avoid this obstacle by using one of the following strategies. First, it is possible to use a combined action of the laser field with an additional nonlaser asymmetric interaction (for instance, with an electrostatic field) [5–7]. Second, there are numerous proposals to achieve orientation with the help of a tailored laser pulse or sequences of such pulses [8–13]. Finally, the orientational effect can originate from an appropriate phase locking between the components of the multicolor laser pulses [14–17].

Although the last strategy looks most advantageous both because of its applicability to nonpolar molecules and because it avoids the need for intricate pulse shaping, it has not been confirmed experimentally to our knowledge so far. Nevertheless, both theory and a few experiments prove that at least the so-called *geometric* orientation (which by contrast with the *dynamic* orientation means the orientation-dependent accessing of the molecules, e.g., ionization, without affecting their isotropic distribution) is attainable in this way [18–20].

This work has been spurred by the fact that even a very small (about a few kelvins) initial temperature of the molecules typically crushes almost completely the efficacy of the existing methods of laser control of molecular orientation. In this paper, we propose a scenario of field-free orientation employing the multicolor laser pulse strategy, which eliminates this restriction.

The idea of our scenario is related to the recent investigations of isotope selective molecular alignment, in which it has been shown that a tiny mismatch in the moments of inertia of molecular isotopes can be efficiently utilized for separate manipulations on their rotational dynamics [21]. Our scenario rests on ideologically similar technique based on utilization of the tiny differences in molecular geometry of the ground and excited vibronic states. Specifically, we will show that macroscopic orientation in an ensemble of initially randomly oriented molecules can be produced by a sudden (with respect to the molecular rotations) excitation of a portion of molecules with well-defined orientation into a properly chosen vibronic state. Such molecular excitation is, in fact, a specific case of the geometrical orientation called the orientation-dependent selection (ODS) of molecules [22,23].

To show how the ODS can result in orientation, let us clarify it on the example of BF molecules. For this particular molecule, we define the unit vector directed from the boron to the fluorine atom as the controlled molecular direction $\vec{\zeta}$ (see the definition in the introductory part of the paper). Suppose also that the ODS happens at the time $t = 0$, so that the portion n of the molecules with angles $\theta|_{t=0}$ close to zero is suddenly transferred from the ground vibronic state $|0\rangle$ to the excited state $|1\rangle$. Denoting the degrees of orientation of the molecules in the ground and excited vibronic states as $\langle \cos \theta \rangle_0$ and $\langle \cos \theta \rangle_1$, respectively, we can write $\langle \cos \theta \rangle = (1-n)\langle \cos \theta \rangle_0 + n\langle \cos \theta \rangle_1$, where $\langle \cos \theta \rangle|_{t=0} = 0$ in the sudden impact limit. However, in accordance with the definition of the ODS, $\langle \cos \theta \rangle_1|_{t=0} = \xi > 0$ and $\langle \cos \theta \rangle_0|_{t=0} = -[n/(1-n)]\xi < 0$.

The general features of the field-free rotational dynamics of molecules, which follows the ODS, spring from an approximate commensurability of the rotation energies of the rotational sublevels of each vibronic level. Let us briefly recall that for a free linear rigid rotor with the rotational constant B the rotation energies are given by the expression
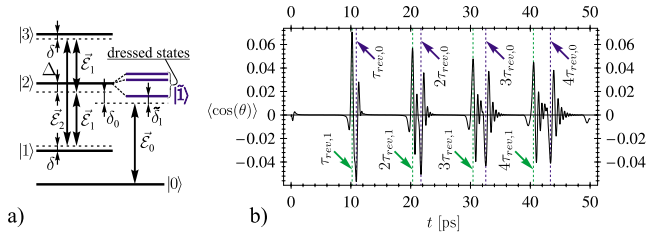
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FIG. 1. (Color online) (a) Scheme of laser-induced transitions employed in the ODS process. (b) Degree of orientation $\langle \cos \theta \rangle$ as the function of time. The corresponding frequencies and the peak intensities I_k of the laser pulse components are as follows: ω_0 $=2.577 \times 10^{15}$ Hz (116.3 nm) [24], $I_0 = 4.67 \times 10^{11}$ W/cm^2; ω_1 $=5.384 \times 10^{14}$ Hz (556.8 nm), $I_1 = 1.82 \times 10^{11}$ W/cm^2, $\omega_2 = 1.076$ $\times 10^{15}$ Hz (278.4 nm), $I_2 = 1.64 \times 10^{12}$ W/cm^2. The components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ are phase matched, so that $\varphi_2 = 2\varphi_1 + 2.9$. The molecules initially had the temperature of 300 K. We also neglect the relaxation for simplicity.

$E_{\rm rot} = BJ(J+1)$ with J being the total angular momentum quantum number, i.e., they are divisible by $2B$. As a result, an initial oriented state of such rotors at $t=0$ will be precisely reconstructed at the revival time instants $m\tau_{\rm rev}$ (m $=1,2,\ldots$), where $\tau_{\rm rev} = h/2B$. At the interval between successive revivals the components of the rotation wave packet are essentially out of phase, so that the degree of orientation is perfectly close to zero anywhere except in narrow areas around the revival time instants, resulting in the well-known rotational revival pattern.

Returning to the analysis of the post-ODS dynamics, we can conclude that the rotational wave packets for molecules in the ground and excited vibronic states should revive differently due to the small differences between the corresponding rotational constants B_0 and B_1 and, consequently, between the revival time instants $\tau_{\rm rev,0}$ and $\tau_{\rm rev,1}$. As a result, $\langle \cos \theta \rangle_1 |_{t=m\tau_{\rm rev,1}} \simeq \xi$, whereas $\langle \cos \theta \rangle_0 |_{t=m\tau_{\rm rev,1}} \simeq 0$ and, similarly, $\langle \cos \theta \rangle_0 |_{t=l\tau_{\rm rev,0}} \simeq -\xi$, whereas $\langle \cos \theta \rangle_1 |_{t=l\tau_{\rm rev,0}} \simeq 0$, except for cases where $l\tau_{\rm rev,0} \simeq m\tau_{\rm rev,1}$ (m and l are the arbitrary natural numbers). The overall effect is that the degree of orientation $\langle \cos \theta \rangle$ behaves in a revival-like manner, demonstrating positive spikes with amplitude close to $n\xi$ near t $=m\tau_{\rm rev,1}$ and negative ones with almost the same amplitude near $t=m\tau_{\rm rev,0}$.

For realization of the sudden ODS we will employ a degenerate variant of the scheme introduced in Ref. [23] [see Fig. 1(a)]. In this scheme, the ODS is induced by the electrodipole interaction with a three-color femtosecond linearly polarized laser pulse $\vec{\mathcal{E}}(t) = \Sigma_{k=0}^{2} \vec{\mathcal{E}}_k = 2\vec{e}_z \Sigma_{k=0}^{2} A_k \cos(\omega_k t + \varphi_k)$, where A_k, ω_k, and φ_k are the envelopes, carrier frequencies, and phases of the corresponding components. The pulse should be short enough to view the molecules as rotationally frozen during the laser impact. The purpose of the phase-locked components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ with the frequencies $\omega_2 = 2\omega_1$ is to perform resonant adiabatic passage (RAP) in a subspace of three initially unpopulated near-equidistant excited vibronic states $|1\rangle$, $|2\rangle$, and $|3\rangle$. During the pulse propagation each of these three states is *adiabatically* transformed into a dressed one. It has been shown recently [17] that the RAP is

an extremely effective tool for controlling molecular orientation, because of the strong orientational dependence of the effective energies of this sort of dressed state. In our scheme, we utilize the dependence of both the structure and energy of one of the dressed states on the orientation to produce orientation-dependent frequency detunings and absolute values of the transition dipole moment for *nonadiabatic* excitation induced by the component $\vec{\mathcal{E}}_0$, which is tuned in the vicinity of the resonance with the transition $|0\rangle \leftrightarrow |2\rangle$. With this, the appropriate choice of phase relationships between the components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ determines the preferable molecular orientation with respect to the $\vec{z}$ axis of the laboratory frame for the selection process. Hereafter, we will assume that the states under consideration are linked by parallel transitions only. Then, for each particular molecular orientation, the corresponding effective interaction Hamiltonian of the ODS in the rotating wave approximation can be written in the basis of (time-independent) eigenstates $\{|0\rangle, |1\rangle, |2\rangle, |3\rangle\}$ as

$$\hat{H}(t,\theta) = \hbar \begin{pmatrix} \delta_0 & 0 & \Omega_{0,2}^{(0)} & 0 \\ 0 & \delta & \Omega_{1,2}^{(1)} & \Omega_{1,3}^{(2)} \\ \Omega_{0,2}^{(0)*} & \Omega_{1,2}^{(1)*} & \Delta & \Omega_{2,3}^{(1)} \\ 0 & \Omega_{2,3}^{(2)*} & \Omega_{2,3}^{(1)*} & -\delta \end{pmatrix}, \quad (1)$$

where $\Omega_{i,j}^{(k)}(t,\theta) = (\vec{\zeta} \langle i | \hat{\vec{d}} | j \rangle) A_k(t) \cos(\theta) e^{i\varphi_k}$ and $\hat{\vec{d}}$ is the dipole moment operator. We define the RAP dressed states as eigenvectors of the form $|\widetilde{m}\rangle = \Sigma_{l=1}^{3} C_{m,l}(t,\theta) |l\rangle$ of (1), in which $\Omega_{0,2}^{(0)}$ is artificially set to zero and $C_{m,l} \rightarrow 0$ for $l \neq m$ in the zero-field limit. The population transfer efficacy from the ground state $|0\rangle$ into each of these dressed states induced by $\vec{\mathcal{E}}_0$ can be controlled by (i) the value of the detuning $\widetilde{\delta}_m$ $= \widetilde{E}_m(t,\theta)/\hbar - \delta_0$, where $\widetilde{E}_m$ is the effective dressed energy, and (ii) the value of the transition dipole moment $\langle 0 | \hat{\vec{d}} | \widetilde{m} \rangle$, which is proportional to the expansion coefficient $C_{m,2}$.

For the ODS, one needs to enhance the population transfer to the excited state $|1\rangle$, if the angle θ is close to zero, and suppress it otherwise. For this, first of all, only the dressed state $|\widetilde{1}\rangle$ should be accessed for population, so that it should be energetically well separated from any other state. Second, the coefficient $C_{1,2}$ should achieve its maximum near the value $\theta = 0$ and fall to zero both at $\theta = 0$ and in the absence of dressing (i.e., when both $\vec{\mathcal{E}}_1 = 0$ and $\vec{\mathcal{E}}_2 = 0$). Third, the detuning $\widetilde{\delta}_m$ should approach zero near $\theta = 0$ and be as large as possible otherwise.

The conditions listed above allow us to determine the optimal parameters of laser impact. For the BF molecule we suppose that all the components of the laser pulse have similar shapes: $A_k(t) = \mathcal{A}_k \exp[-t^2/(2\tau^2)]$, with $\tau = 70$ fs. Using the above conditions we found the optimal frequencies, intensities, and relative phases φ_k of the components at the peak of the laser pulse. These results were then used as a starting point for further numerical optimization. In the simulations, we restrict the peak intensity to the value of $\sim 10^{12}$ W/cm^2 to be confident of the absence of tunneling

ionization. We choose as the states $|1\rangle$, $|2\rangle$, and $|3\rangle$ the lowest vibrational levels of the second, third, and fourth excited electronic levels of $^1\Sigma$ symmetry (their *ab initio* calculated energies with respect to the ground vibronic state are equal to 68 300.3, 87 111.9, and 104 415.0 cm^{-1}, respectively).

Numerical simulation of the laser-induced dynamics was carried out using the short-pulse approximation (SPA) [25]. To quantify the contribution of the off-resonant interaction, we explicitly included in the calculations 11 electronic terms with the different symmetries. Also, the effect of centrifugal distortion via the first-order corrections was taken into account.

Figure 1(b) shows the calculated degree of orientation, induced by one of the optimal laser pulses in the molecules at the room temperature. The parameters of interaction are such that just after the laser impact at $t=0$ nearly 97% of the population resides on the vibronic levels $|1\rangle$ ($\sim88.7\%$) and $|0\rangle$ ($\sim8.3\%$), and only 3% is transferred to the levels $|2\rangle$ and $|3\rangle$, while population of other levels is negligibly small. This confirms the fact that the adiabatic regime of dressing during the ODS holds rather well. Therefore, the observed revival pattern is mainly composed of a sum of two series of rotational revivals of the molecules in the vibronic states $|1\rangle$ (with the revival time $\tau_{\mathrm{rev},1}=10.1$ ps) and $|0\rangle$ ($\tau_{\mathrm{rev},0}=10.8$ ps). However, the molecular nonrigidity becomes an essential factor, especially at high temperatures, so that, in contrast to the rigid rotor model any subsequent revival in each series is not the exact clone of the former one and is essentially less pronounced and more smeared.

The most striking feature in Fig. 1(b) is that the degree of orientation reaches extremely high values of up to 0.0706. To our knowledge, there is no other alternative method of molecular orientation that gives similar efficiency for field-free orientation at room temperatures. However, the complementary effect of geometrical orientation is even more impressive. For example, at the time of the first rotational revival, the degree of orientation $\langle\cos(\theta)\rangle_1$ of the excited molecules achieves its peak value equal to 0.704. Note that it is a record even for experiments with rotationally cold molecules. Moreover, the vibronic state sensitivity of the revival pattern in combination with the high efficiency of the geometrical orientation open an intriguing prospect for employing methods, similar to those recently suggested for the isotope and nuclear spin-selective control of molecular alignment [21], to the coherent vibronic state-selective control of molecular orientation.

Analysis of Fig. 1(b) leads to the conclusion that the suggested ODS-based mechanism of molecular orientation is significantly more effective than the widely discussed kick mechanism. The latter is based on a laser-induced torque, which changes the molecular angular momenta in a way that forces molecular reorientation. In this case, therefore, strong orientation is inevitably accompanied by a significant increase of the rotational temperature. The largest degree of orientation typically occurs slightly after the laser pulse.

In our case, the kick contribution to the overall orientation effect dominates only at the early time of the postpulse field-free evolution, emerging in small spikes just after the laser pulse. One can see, however, that the amplitudes of these spikes are negligibly small compared to the amplitudes of the spikes arising near $t=10$ ps. Thus, the kick-based orientational effect, even resonantly enhanced, is more than an order of magnitude smaller than the ODS-based one. Furthermore, the ODS-produced orientation of molecules in the ground state $|0\rangle$ corresponds to less than 0.6 K change in its rotational temperature. The average rotational energy of the vibronically excited molecules is ~348 K, so that it is not significantly higher than the initial temperature too.

Substantial differences between the ODS- and the kick-based mechanisms of orientation are also revealed in the distinct degree $\langle\cos^2(\theta)\rangle$ of induced molecular alignment. When the kick mechanism is employed, the laser pulse produces significant anisotropy in the spatial angular momentum distribution, so that besides the transient alignment of the molecules there is a permanent alignment prior to and after any transient revival [26]. However, no permanent alignment occurs when the orientation is induced via the ODS. In our simulations, we found that the value of $\langle\cos^2(\theta)\rangle$ between revivals at early times between 10^{-12} s and 4×10^{-12} s is almost equal (with an accuracy of about 3×10^{-4}) to its value $\frac{1}{3}$ in the isotropic case. At later times, the deviations become more pronounced thanks to the spreading of revivals caused by the Coriolis distortions.

We verified numerically that the efficiency of the orientation is fairly robust with respect to variations of the peak intensities of the components of the multicomponent laser pulse. We found, for example, that a two times lowering of the amplitudes of the revivals occurs only when the peak intensities of the pulse components are approximately two times different from the optimum values. However, the thorough tuning of the phase-locking parameter $\phi=\varphi_2-2\varphi_1$ describing the phase matching between the components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ is also crucial to make our scenario feasible. In addition, there exists an exact relation
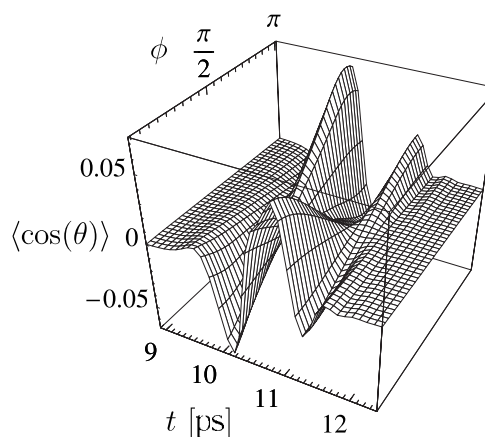

FIG. 2. Time dependence of the degree of orientation in the vicinity of the first rotational revival as a function of the phase-locking parameter ϕ. Only the interval $0<\phi<\pi$ is plotted taking into account relation (2). The frequencies and amplitudes of the pulse components are the same as in Fig. 1(b).

$$\cos \theta_{\phi=\phi_0} = -\cos \theta_{\phi=\phi_0+\pi} \qquad (2)$$

valid for any ϕ_0, from which it directly follows that the averaging over ϕ leads to the complete loss of orientational effect.

Figure 2 shows the calculated dependence of the orientational dynamics on ϕ in the neighborhood of the first revival. It is interesting to note that the orientational effect appears for *any* value of ϕ. However, the amplitude of $|\cos(\theta)|$ undergoes more than an order of magnitude change with varying ϕ, reaching minima near $\phi = \pm \pi/2$ and maxima near $\phi = 0, \pi$.

In conclusion, we have shown that the RAP and ODS techniques can be efficiently employed for the laser-assisted orientation of molecules at high temperatures, up to room temperature, and we believe that this scenario can be experimentally feasible. Numerical simulations confirm that the method also allows production of ensembles of excited molecules with well-defined vibronic states with very high (up to

0.7) degree of orientation. This may be an interesting alternative to the conventional molecular orientation in many applications, such as tomographic imaging of molecular orbitals, applications in quantum physics, control of chemical reactions, ionization, dissociation processes, and other stereochemical problems where the dynamics is essentially state dependent. In particular, in our forthcoming presentation we discuss the possibility of employing such a strategy for realization of laser-assisted laser asymmetric synthesis [23].

The described molecular orientation technique can be applied to other linear or symmetric-top molecules. For small molecules, one can also expect that the typical laser intensities and the pulse durations will be of the same order of magnitude as those considered in the paper. The wavelengths could be taken from a more widely available range of experimental wavelengths. However, this would require, in general, the replacement of a single $\vec{\mathcal{E}}_1$ component with two components with different wavelengths and phase matching between three (instead of two) field components.

[1] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003).

[2] H. Stapelfeldt, Phys. Scr., T **110**, 132 (2004).

[3] T. Seideman and E. Hamilton, Adv. At., Mol., Opt. Phys. **52**, 289 (2006).

[4] V. Kumarappan1 *et al.*, Phys. Scr. **76**, C63 (2007).

[5] L. Cai, J. Marango, and B. Friedrich, Phys. Rev. Lett. **86**, 775 (2001).

[6] H. Sakai, S. Minemoto, H. Nanjo, H. Tanji, and T. Suzuki, Phys. Rev. Lett. **90**, 083001 (2003).

[7] H. Tanji, S. Minemoto, and H. Sakai, Phys. Rev. A **72**, 063401 (2005).

[8] I. Sh. Averbukh and R. Arvieu, Phys. Rev. Lett. **87**, 163601 (2001); M. Leibscher, I. Sh. Averbukh, P. Rozmej, and R. Arvieu, Phys. Rev. A **69**, 032102 (2004).

[9] M. Machholm and N. E. Henriksen, Phys. Rev. Lett. **87**, 193001 (2001).

[10] O. Atabek, C. M. Dion, and A. Yedder, J. Phys. B **36**, 4667 (2003).

[11] D. Daems, S. Guerin, D. Sugny, and H. R. Jauslin, Phys. Rev. Lett. **94**, 153003 (2005).

[12] D. Sugny *et al.* Phys. Rev. A **72**, 032704 (2005).

[13] E. Gershnabel, I. Sh. Averbukh, and R. J. Gordon, Phys. Rev. A **73**, 061401(R) (2006); **74**, 053414 (2006).

[14] M. Vrakking and S. Stolte, Chem. Phys. Lett. **271**, 209 (1997).

[15] K. Hoki and Y. Fujimura, Chem. Phys. **267**, 187 (2001).

[16] S. Guerin, L. P. Yatsenko, H. R. Jauslin, O. Faucher, and B. Lavorel, Phys. Rev. Lett. **88**, 233601 (2002).

[17] L. P. Yatsenko *et al.*, J. Chem. Phys. **126**, 034305 (2007).

[18] E. Charron, A. Giusti-Suzor, and F. H. Mies, Phys. Rev. A **49**, R641 (1994).

[19] H. Ohmura and T. Nakanaga, J. Chem. Phys. **120**, 5176 (2004).

[20] H. Ohmura, F. Ito, and M. Tachiya, Phys. Rev. A **74**, 043410 (2006).

[21] S. Fleischer, I. Sh. Averbukh, and Y. Prior, Phys. Rev. A **74**, 041403(R) (2006); e-print: arXiv:quant-ph/0702163.

[22] D. V. Zhdanov, B. A. Grishanin, and V. N. Zadkov, JETP **130**, 387 (2006).

[23] D. V. Zhdanov and V. N. Zadkov, J. Chem. Phys. **127**, 244312 (2007).

[24] The respective wavelength can be generated by lasing in the Lyman band of molecular hydrogen pumped by a titanium-sapphire laser [see, for example, S. Insam, R. Tommasini, and E. E. Fill, IEEE J. Sci. Food. Agric. **5**, 1510 (1999)].

[25] P. V. Leuven and B. M. Persico, J. Chem. Phys. **124**, 054319 (2006).

[26] S. Ramakrishna and T. Seideman, J. Chem. Phys. **124**, 034101 (2006).