Postpulse Molecular Alignment Measured by a Weak Field Polarization Technique

V. Renard, M. Renard, S. Guérin, Y. T. Pashayan,* B. Lavorel, O. Faucher,† and H. R. Jauslin
Laboratoire de Physique, Université de Bourgogne, UMR CNRS 5027, BP 47870, 21078 Dijon Cedex, France

(Received 20 June 2002; published 17 April 2003)

We report a direct nonintrusive observation of alignment and planar delocalization of CO_2 after an intense linearly polarized femtosecond laser pulse excitation. The effects are measured by a polarization technique involving a perturbative probe that itself does not induce appreciable alignment. We show that this technique allows one to measure a signal proportional to $\langle\cos^2\theta\rangle - 1/3$, with θ the angle between the molecular axis and the laser polarization. Simulations that support this analysis allow one to characterize the experimentally observed alignment and planar delocalization *quantitatively.*

DOI: 10.1103/PhysRevLett.90.153601 PACS numbers: 42.50.Hz, 32.80.Lg, 33.80.–b

Introduction.—Spatial manipulation of molecules by intense laser fields and, in particular, molecular alignment is of considerable importance for the control of quantum processes [1–3], e.g., in molecular optics [4].

It has been theoretically shown that the alignment by nonresonant pulses is mainly due to the anisotropic polarizability [5]. Two mechanisms have been predicted and confirmed experimentally: adiabatic and sudden alignment. The adiabatic alignment means that a (typically nanosecond) laser pulse of duration T_a such that $T_a \gg \hbar/B_0$, where B_0 is the rotational constant, allows to align the molecule by adiabatic transport during the interaction with the laser pulse [2,6,7]. The molecule goes back to its initial condition when the laser is switched off. The alignment in the sudden regime by an ultrashort (typically femtosecond to picosecond) pulse of duration T_s, such that $T_s \ll \hbar/B_0$, induces a field-free transient alignment, occurring periodically in time as long as the coherence of the process is preserved [6,8,9]. One of the principal results is the robustness of these revivals with respect to the incoherent thermal effects [6,10]. These revival structures have been recently observed by an imaging technique [11].

To our knowledge most of the measurements of alignment have been so far realized by breaking the molecule through multielectron dissociative ionization (MEDI), and consequently inducing also additional alignment (see, for instance, [11,12]). In the alignment experiment of Ref. [2], the probe was implemented by low laser intensity through a resonant dissociation followed by the ionization of the fragments. In these works the quantitative characterization of the alignment, i.e., the evaluation of $\langle\cos^2\theta\rangle$, is deduced from the angular distribution of the ionized fragments. In this article we present an alternative method based on a weak field polarization spectroscopy technique that allows one to measure a signal proportional to the difference of $\langle\cos^2\theta\rangle$ with its isotropic value 1/3 (or its square), and thus to access *directly* the measure of the alignment. If $\langle\cos^2\theta\rangle > 1/3$, the molecule is predominantly aligned in the direction of the laser polarization. If $\langle\cos^2\theta\rangle < 1/3$ the probability distribution for the axis of the molecule is concentrated around a plane orthogonal to the polarization. Since all the directions in this plane have the same probability, this case is labeled as *planar delocalization.*

We apply this polarization technique to measure the alignment of CO_2 molecules induced by a nonresonant femtosecond laser excitation which creates a rotational wave packet in the ground vibronic state. Numerical simulations, including centrifugal distorsion, are in good agreement with the experimental observations for various intensities, at room temperature and at lower temperatures in a molecular supersonic jet. We extract $\langle\cos^2\theta\rangle$ as a function of time from these simulations and observe a maximum value of $\langle\cos^2\theta\rangle \approx 0.65$ for the alignment and a minimum of $\langle\cos^2\theta\rangle \approx 0.2$ for the planar delocalization.

The model and the alignment measurement.—The technique described in the present Letter is similar to the one used in Raman-induced polarization spectroscopy (RIPS) (see, e.g., [13]). The usual RIPS makes use of a perturbative pump field and is therefore interpreted as a coherent four-photon process. The laser fields excite the molecules perturbatively (in the sense that the four-photon perturbation theory can be used) and do not produce significant alignment. Here we use a strong pump pulse that induces efficient molecular alignment, which is probed through a two-photon Raman process that does not affect significantly the alignment process.

In what follows, we present a model that allows one to extract from the measurements the value of the $\langle\cos^2\theta\rangle$ in order to quantify the degree of alignment achieved in the experiment.

We consider a nonpolar linear molecule of Hamiltonian H_0 in its ground vibronic state, such that one can approximate it as a rotor of rotational constant B_0 with a centrifugal distorsion of constant D_0: $H_0 = B_0J^2 - D_0J^4$. The molecule is subject to a nonresonant pump laser field $\vec{\mathcal{E}}_p(t) = \vec{e}_p\mathcal{E}_{0p}\sqrt{\Lambda_p(t)}\cos\omega_p t$ (of frequency ω_p, of pulse intensity envelope $\Lambda_p(t)$ centered at $t = 0$ and of duration T_p, of peak amplitude $\mathcal{E}_{0p}$ and of fixed polarization vector $\vec{e}_p$). Since no excited electronic states and vibrational states are resonantly coupled, the effective Hamiltonian can be written as [5,14,15]

$$H_p = H_0 - \vec{\mu}_p \cdot \vec{\mathcal{E}}_p(t), \tag{1}$$

where the effective dipole moment is given by

$$\vec{\mu}_p = \frac{1}{2}\vec{\vec{\alpha}}\vec{\mathcal{E}}_p(t), \tag{2}$$

with $\vec{\vec{\alpha}}$ the dynamical polarizability tensor which includes the contribution of the excited electronic states. In the high frequency limit (with respect to the rotational frequency), this leads to

$$H_p^{\mathrm{eff}} = H_0 - \frac{1}{4}\mathcal{E}_{0p}^2\Lambda_p(t)[(\alpha_\parallel - \alpha_\perp)\cos^2\theta + \alpha_\perp]. \tag{3}$$

The polar angle between the molecular axis and the direction of the field is denoted by $\theta \in [0, \pi]$, $\alpha_\parallel$, and $\alpha_\perp$ are the components of the dynamical polarizability, respectively, parallel and perpendicular to the molecular axis.

To interpret the process at temperatures different from zero, we first consider the coherent processes with initial condition as a pure state eigenvector $|J, M\rangle$ of H_0, and then average over the incoherent thermal distribution (see, e.g., [6]). After the pump excitation, the state vector of the free molecule denoted by $\psi(t)$ is next excited by a nonresonant linearly polarized weak probe pulse $\vec{\mathcal{E}}_s(t) = \vec{e}_s\mathcal{E}_{0s}\sqrt{\Lambda_s(t-\tau)}\cos\omega_s(t-\tau)$ delayed by τ with respect to the pump pulse, and of duration T_s. This probe excitation induces a weak dipole moment $\vec{\mu}_s(t) = \frac{1}{2}\vec{\vec{\alpha}}\vec{\mathcal{E}}_s(t)$ of amplitude

$$\vec{\mu}_{0s}(t) = \frac{1}{2}\vec{\vec{\alpha}}\vec{e}_s\mathcal{E}_{0s}\sqrt{\Lambda_s(t-\tau)}. \tag{4}$$

Through a standard adiabatic perturbative analysis, requiring $T_s \gg 2\pi/\omega_s$ and $2\pi/\omega_s \ll \pi\hbar/B_0$, the intensity I_{sig} of the component of polarization $\vec{e}$ (selected by an analyzer) emitted by this dipole is proportional to

$$I_{\mathrm{sig}}(\tau) \propto \int_{\tau-T_d/2}^{\tau+T_d/2} dt|\langle\psi(t)|\vec{e}\cdot\vec{\mu}_{0s}(t)|\psi(t)\rangle|^2, \tag{5a}$$

$$\propto |\langle\vec{e}\cdot\vec{\vec{\alpha}}\vec{e}_s\rangle_{\psi(\tau)}|^2, \tag{5b}$$

where $T_d \gg T_s$ is the response time of the detection device. For simplicity the convolution of the probe pulse is omitted in Eq. (5b) (when $T_s \ll \pi\hbar/B_0$), but it is included in the numerical calculations. The sensitivity of the polarization technique is maximized when the probe field is polarized at $\pi/4$ with respect to the pump and the analyzer is orthogonal to the probe field, which gives

$$\vec{e}\cdot\vec{\vec{\alpha}}\vec{e}_s = \frac{1}{2}(\alpha_\parallel - \alpha_\perp)(\cos^2\theta - \sin^2\theta\sin^2\varphi), \tag{6}$$

where φ is the azimutal angle. Since the state vector can be written as $\psi(\theta, \varphi, t) = \phi(\theta, t)\exp(iM\varphi)$, we obtain

$$I_{\mathrm{sig}}^{\mathrm{hom}}(\tau) \propto \left[\langle\cos^2\theta\rangle_{\phi(\tau)} - \frac{1}{3}\right]^2. \tag{7}$$

This establishes that this pump-probe setup gives a direct quantitative measurement of the alignment.

Equation (7) is derived for *homodyne* detection, i.e., when the signal is directly proportional to the square modulus of the electric field component (selected by an analyzer). In the presence of permanent birefringence produced by optical components, the detection becomes *heterodyne* and Eq. (7) has to be replaced by

$$I_{\mathrm{sig}}^{\mathrm{het}}(\tau) \propto \left[\langle\cos^2\theta\rangle_{\phi(\tau)} - \frac{1}{3} + C\right]^2, \tag{8}$$

where C is a constant proportional to the electric probe field [13]. In the case of pure heterodyne detection [i.e., C much larger than $\langle\cos^2\theta\rangle_{\phi(\tau)}$], the signal becomes proportional to $\langle\cos^2\theta\rangle_{\phi(\tau)}$.

The experimental data will be quantitatively interpreted in terms of alignment by Eqs. (7) or (8) as follows: (i) Taking into account the estimated experimental conditions (temperature, pump pulse shape, and peak intensity), we calculate numerically the wave function $\psi_p(\theta, t)$ during the pump interaction by solving the time dependent Schrödinger equation, for each initial condition (J, M) relevant to the thermal Boltzmann distribution; (ii) the expected value of $\langle\cos^2\theta\rangle(\tau)$ is evaluated after the pump interaction and then averaged over the Boltzmann distribution; (iii) according to Eqs. (7) and (8), the numerical result is fitted to the experimental data by applying an appropriate scale factor and by adjusting the pump intensity in the preceeding calculations around its experimental value to find the best agreement. The effective intensity used in the calculation takes into account, among others, the volume effect not included in the model.

Experimental.—We have investigated the post-pulse alignment of the CO_2 molecules at room temperature in a static cell, and at a lower temperature, in a supersonic free jet expansion. We give below the salient features of the experimental arrangement described in detail in Ref. [13]. The laser system consists of a chirped pulse amplified Ti sapphire system operating at 800 nm and at a repetition rate of 20 Hz. The 100 fs output pulse was split into two parts to provide a strong energy pump beam and a weak energy probe beam (i.e., 2% of the pump energy) both linearly polarized at 45° with respect to each other. The time delay between the pump and probe pulses was adjusted by a variable delay line. The two beams were then focused in a crossed configuration into the gas sample. The detection was arranged to measure the electric field induced by the probe pulse along the direction perpendicular to the polarization vector of the probe.

In the static cell, the pressure was adjusted to 150 Torr and the measurements were carried out with homodyne detection, where the signal is described by Eq. (7).

The supersonic jet of CO_2 was produced from a stagnation pressure of 7 bars through a 500 μm diameter nozzle. The distance between the laser foci and the jet nozzle was set at 1.5 mm. At a larger distance, the decrease of the number density did not allow to perform measurements in suitable conditions. Because of the small birefringence of the vacuum chamber windows, the signal obtained in the jet configuration was heterodyned with a part of the probe laser, which is thus described by Eq. (8).

Results and discussion.—Under this experimental arrangement, the signal observed in the pump-probe delay domain consists of four transients recurring at a period coinciding with the classical rotational period $T_r = \hbar\pi/B_0 \approx 42.7$ ps [8]. During each transient there is alternatively a significant field-free alignment and planar delocalization [8,10,11].

The central peaks of the transients around $\tau = 3T_r/4$ and $\tau = T_r/4$ correspond, respectively, to an alignment of the molecular axis along the pump polarization, and to a planar delocalization in a plane orthogonal to the pump polarization.

Figure 1 shows the probe signal recorded in a static cell of CO_2 for three different laser intensities with a pump-probe delay tuned around $T_r/2 \approx 21.4$ ps. The properties that we discuss here for the second transient are also observed at the other transients. The intensity dependence of the observed signal is dominated by the structural change of the recurrence with increasing pump field strength. This dependence is well reproduced by the numerical simulation of Eq. (7) performed at 296 K. This is displayed on the same graphs, where the background and the ordinate scale have been adjusted. The best agreements with the experimental data have been found by using effective pump intensities 30% lower than the measured peak intensities. We point out that collisional processes have not been included in the theoretical model. In fact, the perturbation of the alignment due to collisions is negligible on the time scale explored in Fig. 1. Therefore, at room or lower temperatures and at low pressure, the collisions do not modify the structural shape of a given transient but rather change the relative amplitudes between the different transients. The scaled right axis of the graphs displayed in Fig. 1 indicates the corresponding value of $\langle\cos^2\theta\rangle$.

Permanent postpulse alignment has been discussed in Refs. [8,10,16]. In the present experiment we observe a tiny permanent alignment with $\langle\cos^2\theta\rangle$ slightly different from 1/3. It comes from the contribution to the rotational wave packet of eigenstates of the field-free molecule having a rotational angular momentum J larger than its projection M along the polarization axis, since the pump field allows one to excite higher J states starting from initial values J_i and M_i, with the latter conserved during the interaction.

For the larger intensity of 75 TW/cm^2, $\langle\cos^2\theta\rangle$ varies between the peak values 0.21 and 0.52, which correspond, respectively, to a planar delocalization and an alignment of the molecule. At this intensity, after the extinction of the pump the distribution of the rotational population is broadened and shifted towards the large J values with respect to the initial thermal distribution. We have checked numerically that the second-order hyperpolarizability plays a negligible role for CO_2 (the first-order hyperpolarizability is zero), even for the strongest intensity used in the present work. The simulation shows that a larger alignment is achieved for the transient around $\tau = 3T_r/4$ with $\langle\cos^2\theta\rangle \approx 0.56$.

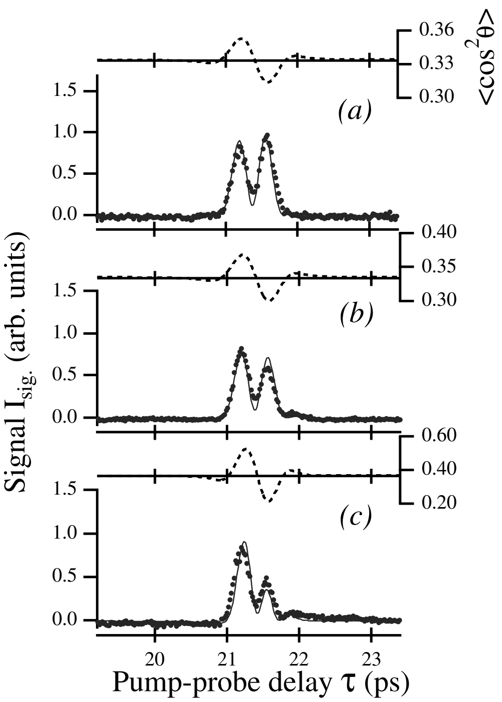

FIG. 1. Homodyne signal (dotted curve) as a function of the pump-probe delay τ in CO_2 at room temperature. Numerical simulation (full curve) of Eq. (7) at 296 K for a Gaussian pump envelope of 100 fs pulse duration and peak intensities (a) $I =$ 8 TW/cm^2, (b) $I =$ 14 TW/cm^2, and (c) $I =$ 75 TW/cm^2. The corresponding values of $\langle\cos^2\theta\rangle$ are depicted on the right line scale (dashed curve).

The benefit of using a cold molecular sample for the alignment process has been largely discussed in literature: The lower the number of initially populated rotational states, the higher alignment can be achieved. In order to confirm experimentally this assertion, we have conducted the experiment at a lower temperature in a jet. The heterodyne signals measured in the free jet expansion for two different laser intensities are shown in Fig. 2 together with the results of the theoretical model according to Eq. (8) with the constant C adjusted around a value deduced from the background signal. This parameter C only affects the relative magnitude between the peaks and the valleys while leaving the width of the transients unchanged. In the simulation, we have adjusted to 60 K the rotational temperature, which is consistent with the experimental temperature,

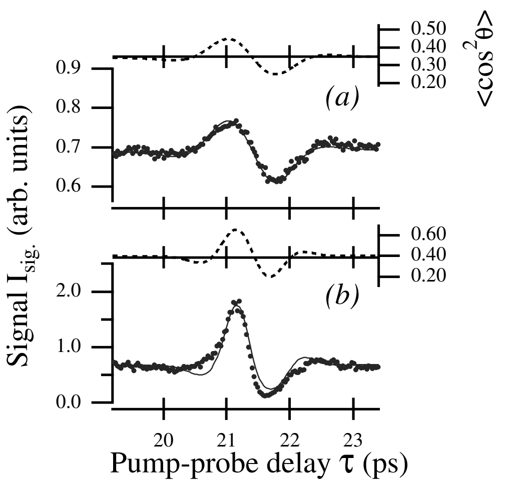

FIG. 2. Same as Fig. 1 with a heterodyne signal obtained in a supersonic free jet of pure CO_2 for the simulation of Eq. (8) performed at 60 K and (a) $I = 18\ \mathrm{TW/cm^2}$ and (b) $I = 57\ \mathrm{TW/cm^2}$.

assuming an isentropic expansion of the supersonic jet. Comparison between Figs. 1(c) and 2(b) shows that at low temperature better alignment ($\langle\cos^2\theta\rangle \approx 0.65$) and planar delocalization ($\langle\cos^2\theta\rangle \approx 0.2$) are achieved, even if the pump intensity in the jet experiment was lower than the one used at room temperature.

In Fig. 3 we have plotted the angular probability distribution $P(\theta, \tau)$ of the transient around $\tau = T_r/2$, corresponding to the experimental conditions of Fig. 2(b). For large values of $\langle\cos^2\theta\rangle$ the angular distribution is peaked around $\theta = 0$ and $\theta = \pi$ (alignment), whereas for low values of $\langle\cos^2\theta\rangle$ it is peaked around $\theta = \pi/2$ (planar delocalization). This result of Fig. 3 could be observed experimentally for instance by using an imaging technique that detects the alignment by fragmentation [2].

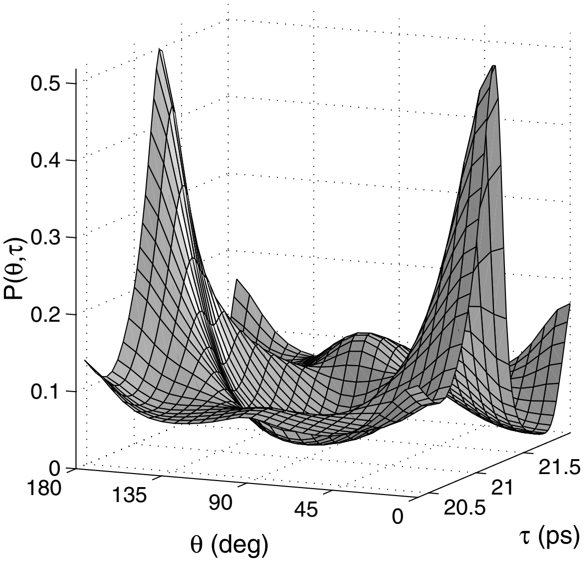

FIG. 3. Angular probability distribution $P(\theta, \tau)$ calculated for the conditions of Fig. 2(b) and around a pump-probe delay $\tau = 21$ *ps*.

By increasing the cooling, a much higher degree of alignment can be achieved, although it was not possible with the present polarization technique to detect its effect due to the low gas number density. A simulation performed at 2 K shows that a peak value of $\langle\cos^2\theta\rangle \approx 0.87$ can be in principle achieved.

In conclusion, we have demonstrated alignment of molecules with short laser pulses probed by a polarization technique that allows for an unambiguous evaluation of $\langle\cos^2\theta\rangle$. The perturbative probe employed in this technique offers the benefit of being nonintrusive, i.e., leaving the molecule intact while measuring its degree of alignment. This work could be in principle applied to produce and monitor the alignment of bulk molecules during a chemical process.

We thank A. Keller for stimulating discussions. We acknowledge support by the *ACI Photonique* and from the Conseil Régional de Bourgogne.

---

*Permanent address: Institute for Physical Research, Armenian National Academy of Sciences, 378410 Ashtarak, Armenia.

†Electronic address: Olivier.Faucher@u-bourgogne.fr

[1] J. Karczmarek, J. Wright, P. Corkum, and M. Ivanov, Phys. Rev. Lett. **82**, 3420 (1999).
[2] J. J. Larsen, H. Sakai, C. P. Safvan, I. Wendt-Larsen, and H. Stapelfeldt, J. Chem. Phys. **111**, 7774 (1999).
[3] J. J. Larsen, K. Hald, N. Bjerre, H. Stapelfeldt, and T. Seideman, Phys. Rev. Lett. **85**, 2470 (2000).
[4] T. Seideman, J. Chem. Phys. **111**, 4397 (1999).
[5] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
[6] J. Ortigoso, M. Rodriguez, M. Gupta, and B. Friedrich, J. Chem. Phys. **110**, 3870 (1999).
[7] A. I. Andryushin and M.V. Fedorov, JETP **89**, 837 (1999) [Zh. Eksp. Teor. Fiz. **116**, 1551 (1999)].
[8] T. Seideman, Phys. Rev. Lett. **83**, 4971 (1999).
[9] T. Seideman, J. Chem. Phys. **115**, 5965 (2001).
[10] M. Machholm, J. Chem. Phys. **115**, 10724 (2001).
[11] F. Rosca-Pruna and M. J. J. Vrakking, Phys. Rev. Lett. **87**, 153902 (2001); J. Chem. Phys. **116**, 6567 (2002).
[12] D. Normand, L. A. Lompré, and C. Cornaggia, J. Phys. B **25**, L497 (1992); J. H. Sanderson *et al.*, J. Phys. B **31**, L599 (1998); G. R. Kumar, P. Gross, C. P. Safvan, F. A. Rajgara, and D. Mathur, J. Phys. B **29**, L95 (1996); L. J. Frasinski *et al.*, Phys. Rev. Lett. **86**, 2541 (2001); J. H. Posthumus *et al.*, J. Phys. B **31**, L553 (1998); Ch. Ellert and P. B. Corkum, Phys. Rev. A **59**, R3170 (1999).
[13] B. Lavorel, O. Faucher, M. Morgen, and R. Chaux, J. Raman Spectrosc. **31**, 77 (2000).
[14] C. M. Dion, A. Keller, O. Atabek, and A. D. Bandrauk, Phys. Rev. A **59**, 1382 (1999).
[15] A. Keller, C. M. Dion, and O. Atabek, Phys. Rev. A **61**, 23409 (2000).
[16] F. Rosca-Pruna and M. J. J. Vrakking, J. Chem. Phys. **116**, 6579 (2002).