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Using molecular alignment to track ultrafast collisional relaxation

G. Karras,[1] E. Hertz,[1] F. Billard,[1] B. Lavorel,[1] J.-M. Hartmann,[2] and O. Faucher[1]
[1]*Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS–Université de Bourgogne, 9 Avenue A. Savary, Boîte Postale 47 870, F-21078 Dijon Cedex, France*
[2]*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS–Université Paris Est Créteil, Université Paris Diderot, Institut Pierre-Simon Laplace, 94010 Créteil Cedex, France*

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Field-free molecular alignment has been used in order to track the collisional relaxation occurring in a molecular gas. CO_2 molecules were initially irradiated by a short linearly polarized laser pulse resulting in the increase of their rotational energy. The evolution of the subsequent ultrafast relaxation process was optically probed after irradiating the sample with a second, weaker, short pulse leading to the alignment of the preheated molecules. Using classical molecular dynamic simulations, we were able to quantitatively reproduce the experimental shapes and amplitudes of the recorded revival transients for a time interval extending from 25 to 500 ps until thermalization of the gas sample is reached.

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I. INTRODUCTION

One of the most effective ways to induce alignment in a molecular ensemble is to irradiate it with a laser pulse. Even though the number of molecules that will be aligned is relatively small, compared to other techniques employing external fields supplied by electrodes, the efficiency of this method has established it as the most widely used in the scientific community [1–3]. Laser-induced molecular alignment was successfully used in the tomography of molecular orbitals [4] and in the tracking of ultrafast molecular reactions [5]. Electron diffraction of aligned molecules has been used to determine their molecular structure [6] and field-free alignment transients have been shown to act as efficient laser-pulse shapers [7]. Higher-order-harmonic generation through aligned molecules has also been studied extensively [8,9] and very recently a method has been proposed for the control of the polarization of harmonic radiation [10].

In the simplest scenario a linearly polarized laser pulse with moderate intensity, far from any resonances with the molecular energy levels, is used to align a molecule along its polarization axis. Since for most molecules the electronic polarizability is anisotropic, its coupling with the laser electric field leads to their alignment through two-photon Raman transitions. Alignment is then often described by the expectation value $\langle\cdots\rangle$ of $\cos^2\theta$, where θ is the angle between the molecular and the laser polarization axes. For a randomly oriented molecule $\langle\cos^2\theta\rangle$ is 1/3, while its value increases for alignment along the laser polarization axis and decreases when the molecule is delocalized in a plane lying perpendicular to the latter. If the duration of the laser pulse is much shorter than the rotational period of the molecule, then alignment periodically revives (transient component) after the pulse is switched off in time intervals spaced by $\tau = pT_r/4$, where p is a positive integer and T_r is the rotational period. In addition to this transient alignment, relatively high laser intensities lead also to a steady-state component known as permanent alignment [11]. Although most studies on this topic deal with linearly polarized laser fields and isolated molecules, the motivation towards more sophisticated aspects of the alignment was always high. Some of these aspects concern, for example, the use of elliptically polarized laser pulses so as to produce alignment in three dimensions [12–14], and very recently alignment induced in a molecule embedded in another environment has been studied [11,15].

On the same grounds as the above, the scope of the present work is to use molecular alignment as a tool for probing the relaxation dynamics taking place in dissipative environments. The theoretical models were proposed by Ramakrishna and Seideman [16,17] and Hartmann and Boulet [18], while the primary experimental demonstration was reported in [11,19,20]. Our goal in the current paper is to extend these previous studies further by showing how field-free alignment can be used to probe the relaxation dynamics in a molecular ensemble that has been previously irradiated with a strong laser pulse. As already reported under ambient and high-pressure conditions [11,20], intermolecular collisions affect differently the permanent and the transient components of the alignment through both elastic and inelastic collisions. The latter result in population transfers from J to J' either by retaining the projection M of J along the quantization axis or not (reorienting collisions), while the former can be either of a reorienting nature or have a purely dephasing character. Even though reorienting elastic and inelastic collisions were found to have a significant effect on both transient and permanent components, the dephasing elastic collisions affect only the transient alignment by a negligible amount [18].

In the following we present a series of experimental data concerning the dissipation dynamics of the energy that has been initially deposited into the rotational degrees of freedom of a gas sample at ambient conditions by irradiating it with a strong femtosecond laser pulse. Our results are analyzed quantitatively using requantized classical molecular dynamic simulations (RCMDSs) as described in [18]. A good agreement between experimental and theoretical results is obtained bringing, after Ref. [20], further confirmation of the interest of RCMDSs.

II. EXPERIMENTAL SETUP

Since the experimental setup used here is very similar to the one described previously [19] only a few major

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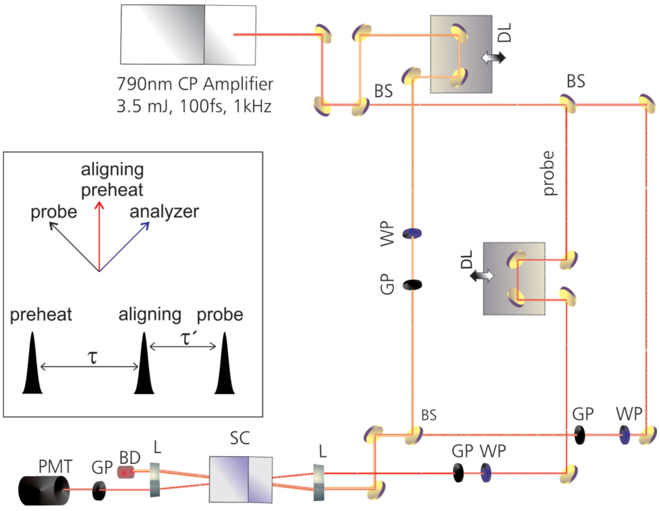

FIG. 1. (Color online) Pump-probe setup for laser-induced birefringence measurements. CP, chirped pulse; BS, beam splitter; GP, Glan polarizer; WP, wave plate; PMT, photomultiplier tube; L, lens; DL, delay line; SC, static cell; BD, beam dump. The relative polarizations of the aligning, preheat, probe, and analyzer beams along with a relative timing chart are shown in the inset. τ and τ' correspond to the delay between the preheat and the aligning and the aligning and the probe pulses, respectively.

points will be recalled below. As we can see from Fig. 1 it is a typical pump-probe setup employing time-resolved birefringence detection [21] so as to record the nonadiabatic alignment of pure CO_2 molecules. The technique exploits the depolarization experienced by a weak beam (probe) after interacting with an already aligned molecular ensemble, and the resulting homodyne signal S is given by

$$S \propto \int_{-\infty}^{\infty} I_{\text{probe}}(t-\tau)[\Delta n(t,I_{\text{pump}})]^2 dt, \qquad (1)$$

where Δn is the difference between the refractive index components along and perpendicular to the pump polarization axis and I_{probe} (I_{pump}) is the intensity of the probe (pump) beam. The laser source used for the measurements is a Ti:Al_2O_3-based chirped-pulse amplified system delivering linearly polarized pulses centered at 800 nm with a duration of 100 fs and a maximum energy of 3.5 mJ per pulse. Energy and polarization control of the beams were obtained using zero-order wave plates and polarizers. A Mach-Zehnder interferometer was inserted in the pump beam path, dividing it into two, the aligning and preheat beams, whose polarization was kept the same. The time delays between the three beams were easily adjusted using computer-controlled motorized stages. The experiment was performed inside a static cell where the pressure was kept at 1 bar and the temperature prior to the launch of the preheat pulse was 295 K. The beam diameters at the focus were measured as 54 μm and the intensities of the aligning and the preheat pulses were estimated as 23 and 42 TW/cm^2, respectively, using the corresponding alignment traces. The intensity of the probe beam was two orders of magnitude lower, making its contribution to the alignment fully negligible. The launch of the preheat pulse prior to the arrival of the aligning results in the alignment of the molecules and consequently in the increase of their rotational energy. As has been already experimentally and theoretically shown in [19] this leads to a significant modification of the revival transients produced by the aligning pulse, once thermalization is reached, i.e., for preheat-aligning delay times τ of about 500 ps. Furthermore, theoretical calculations [19] indicate that these transients depend strongly on the latter time delays, thus enabling one to "follow" and probe the relaxation process. The aim of the present study is to check these predictions. Hence, we monitored the evolution of the excited system until it reached equilibrium by recording the profile of the revivals created by the aligning pulse for different time delays between the aligning and the preheat pulses. Note that the launch of the aligning pulse takes place in between the revivals corresponding to the preheat pulse. In order to ensure that our measurements were not affected by thermal effects in the optical components, we launched the preheat pulse well after the probe pulse and checked that the signal was the same as compared with the one obtained with the preheat pulse turned off.

III. RESULTS AND DISCUSSION

Before presenting the results, note that the theoretical predictions were made, free of any adjusted parameters, using the RCMDS approach described in [18] and successfully tested in [20]. The preheat and aligning pulses were introduced in the calculations with proper intensities, shapes, and delays and intermolecular collisions were modeled using the potential of [22]. This provides, as mentioned before, the time evolution of the average rotational and translational energies as well as that of $\cos^2\theta$.

In Fig. 2 we present examples of recordings obtained with the aligning pulse alone, Fig. 2(a), the preheat pulse alone, Fig. 2(b), and their combination, Fig. 2(c). In Fig. 2(a) the homodyne signal is presented for a time interval of 30 ps revealing the position of the first quarter and half revival transients. As we can see, the contribution of the permanent component of the alignment is very small, as expected from the relatively weak intensity of the aligning pulse. On the contrary, the experimental trace obtained with the significantly stronger preheat pulse [Fig. 2(b)] shows a non-negligible permanent component. In addition Fig. 2(b) also shows a noticeable dissipation (due to collisions) of the transient alignment, even at a pressure of 1 bar. Indeed, as shown in [11,20], the time decay of the alignment revivals in CO_2 is about two times faster than that of the permanent component due to the propensity of collisions to conserve the orientation of the angular momentum J [18]. In Figs. 2(a) and 2(b) we illustrate the response of a molecular ensemble to an applied laser pulse, at essentially two distinct intensity regimes, without prior excitation. Figure 2(c) shows the birefringence signal recorded with both preheat and aligning pulses together with the numerical simulation. In this case, the aligning pulse probes the evolution of the prior rotational excitation induced by the preheat pulse, allowing us to extract information about the relaxation dynamics. Before analyzing the results, let us recall that for weak laser pulses the recorded trace would be just a sum of the traces produced by the isolated pulses [23], i.e., such as adding the ones in Figs. 2(a) and 2(b). In the strong-field regime this perturbative approach

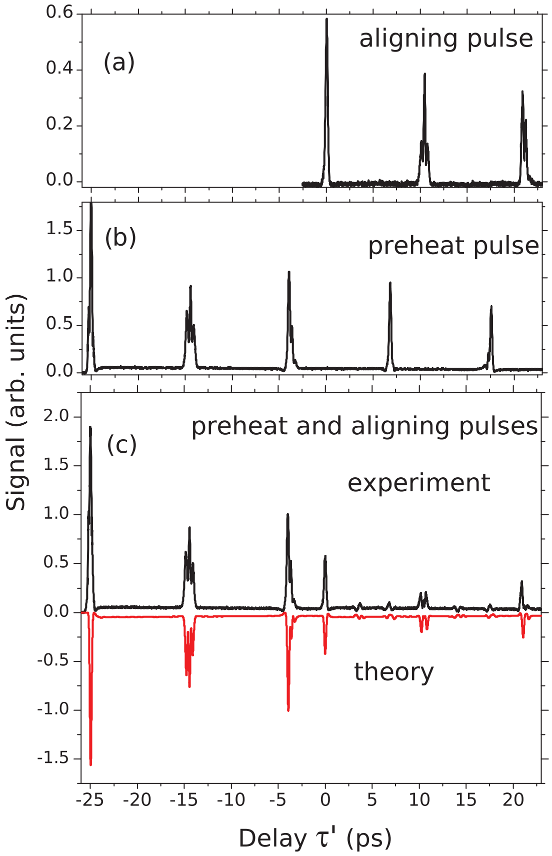

FIG. 2. (Color online) Experimentally obtained homodyne signals as a function of the delay τ' between the aligning and the probe pulses (a) when the preheat pulse is switched off, (b) when the aligning pulse is switched off, and (c) when both preheat and aligning pulses are switched on. In (c) the experimental result is shown together with the corresponding simulation, and the time delay between the preheat and aligning pulses is set to 25 ps.

does not apply, as is obvious from Fig. 2, because the system, prepared by the preheat pulse, is greatly modified as compared with its initial thermal distribution when it experiences the aligning pulse. Indeed, not only are the preheat and aligning revivals modified, but there is also a third series of revival transients with the first of them appearing at a time equal to the delay between the launch of the aligning pulse and the second revival of the preheat pulse, 3.8 ps. The periodicity of these transients, already observed in [24], is the same as that of the ones produced by the isolated pulses. As mentioned above, we see that the rotational wave packet created by the preheat pulse is significantly affected by the launch of the aligning pulse, and vice versa, embedding these changes in the shape and the amplitude of the revival transients. Specifically the transients corresponding to the preheat pulse at delays equal to $3T_r/4$ and T_r are significantly suppressed in terms of amplitude, by almost one order of magnitude, and their shape is also substantially changed. In addition the transients at delays initially corresponding to the aligning pulse also suffer significant modifications, mainly in their shape rather than in their amplitude, at least for the specific delay between the aligning and the preheat pulse. It is the information encoded in these transients that we used in order to study the dissipation of the rotational wave packets created by the preheat pulse.

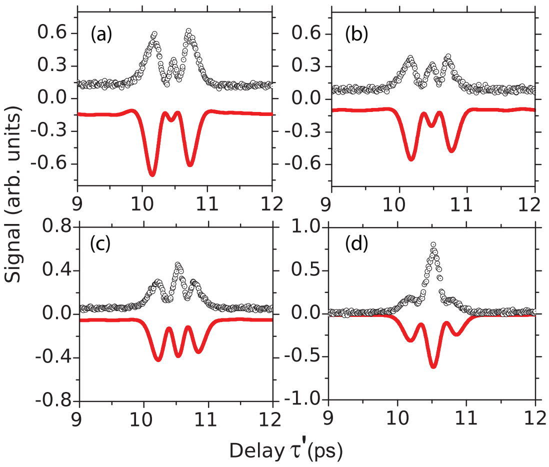

FIG. 3. (Color online) Comparisons between theoretical and experimental traces of the quarter revival transient for different delays τ between the aligning and the preheat pulses. The estimated intensities are 23 and 42 $\mathrm{TW/cm^2}$, respectively. (a) $\tau = 25$ ps, (b) $\tau = 46$ ps, (c) $\tau = 110$ ps, and (d) $\tau = 293$ ps.

The launch of the preheat pulse suddenly increases the rotational energy, bringing the system out of thermal equilibrium. According to theoretical calculations [18], several decay processes are involved in the collisional dissipation of a gas sample (pure CO_2) that has been irradiated by a laser pulse. Indeed, while local equilibrium of rotational energy (related to the alignment transients) is achieved in about 150 ps, the randomization of the rotational angular momentum orientation (related to the permanent component) takes two times longer. Furthermore, the thermalization between rotation and translation requires about 500 ps. Thus, by varying the delay between the preheat and the aligning pulses and recording for each delay the corresponding birefringence trace due to the latter, one can follow the various and subtle effects of rotation-rotation and rotation-translation transfers, providing a stringent test of theoretical predictions.

In Fig. 3 a series of experimental traces of the first $T_r/4$ revival of the aligning pulse compared with their equivalent theoretical ones is presented for different delays between the preheat and the aligning pulses. As we see, each transient is comprised of three peaks. The middle one corresponds to the delocalization of the molecules in a plane perpendicular to the laser polarization axis while, for the other two peaks the molecules are aligned along the direction of the field. The increase of the delay between the aligning and preheat pulses results in the decrease of the amplitude of the side peaks and increase of the amplitude of the middle one. In a simplified approach this behavior can be understood if we take into account the remaining contribution of the permanent component of the alignment due to the preheat pulse. For small delays between the aligning and the preheat pulses this contribution significantly modifies the shape of the acquired traces by favoring the alignment and opposing the planar delocalization peak. As the relaxation of the sample proceeds and equilibrium among different degrees of freedom

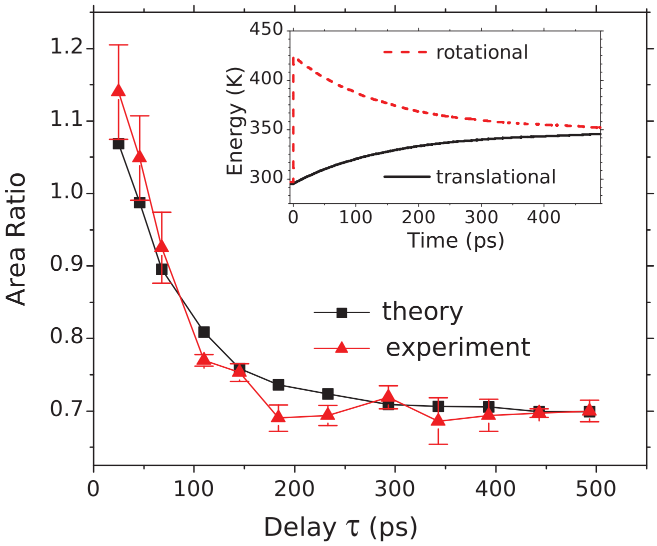

FIG. 4. (Color online) Dependence of the integrated areas of the quarter revival transients on the delay τ, between the preheat and the aligning pulses. The squares are theoretical results and the triangles experimental ones. The estimated intensities of the preheat and the aligning pulses are 42 and 23 TW/cm^2, respectively.

is approached, the shape of the revival transients resembles more the one recorded when the preheat pulse is switched off. However, as we have shown and analyzed in a previous publication [19], significant changes in the experimental traces obtained with and without the presence of the preheat pulse are still observed when the gas sample is thermalized. These changes are due to the increase of the sample's temperature and manifest in Fig. 4 by the fact that the asymptotic value for large delays is not unity.

Specifically, in the latter we present the evolution, with the preheat-aligning delay, of the ratio of the areas of the first aligning transient obtained with and without the preheat pulse. For a time interval of 500 ps we track the consequences of the various relaxation mechanisms taking place in the gas sample after its irradiation with a femtosecond laser pulse. Figure 4 (and Fig. 3) show that the experimental findings are reproduced quite well by the theoretical calculations, providing an additional and severe test of the RCMDS approach, showing its ability to describe the collisional dissipation dynamics of laser-induced molecular alignment. Note that the ratio of the integrated areas decreases as the delay between preheat and aligning pulse increases. This indicates the significant contribution of the permanent component of the alignment of the preheat pulse for short delays, and the fact that a heated gas is probed for long delays. Finally the inset of Fig. 4 depicts the predicted evolution of the average rotational and translational energies under the current experimental conditions. It is important to recall that the time-delay evolution of values plotted in Fig. 4 results for the conjugative effects of various collision-induced relaxation mechanisms: the exchanges of populations between rotational states J, the randomization of the angular momentum orientation (i.e., of M/J), and the exchanges between rotation and translation. As shown in [18] all these have their proper time scales that are different, but not different enough to enable attributing the measured (and calculated) values in Fig. 4 to a single process. Although the measurements thus do not enable the retrieval of a clearly attributable time constant, they can nevertheless be used for stringent tests of theoretical approaches. From this point of view, note that, since the quantum approaches of [16–18] disregard rotation-translation exchanges, they are not adapted for the modeling of the present experiments.

IV. CONCLUSION

In the above we have shown how field-free laser-induced molecular alignment can be used as a valuable tool for probing relaxation dynamics in dissipative environments. Irradiating a gas sample, at ambient pressure and temperature conditions, with an intense femtosecond laser pulse (preheat pulse) we impulsively increase the rotational energy of the system. Due to intermolecular collisions this energy is partitioned between the colliding partners by means of rotation-rotation and rotation-translation transfers, increasing their kinetic energy until thermalization. By sending a second delayed laser pulse (aligning pulse) and aligning the already preheated molecules, we observe that the corresponding revival transients are severely changed when compared to the case where the preheat pulse is switched off. These changes, embedded on the shape and the magnitude of the transients, strongly depend on the delay between the aligning and the preheat pulses. Thus, by varying the aforementioned delay and recording the molecular response we track the relaxation of the gas sample until the rotational and translational degrees of freedom reach equilibrium. The recorded traces are used for a test for the predictions of molecular dynamics simulations, showing a good agreement between theory and experiments. This further confirms the validity of the RCMDS approach and shows that it can be used to extended the time scales describing the molecular response in dissipative media.

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