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Quantum control of ground-state rotational coherence in a linear molecule

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We present an experimental and theoretical investigation of the quantum control of ground-state rotational coherence in a linear molecule. A sequence of two temporally separated laser pulses creates a rotational superposition state in CO_2 whose evolution is monitored through a polarization technique. We study the influence of the phase difference between the two pulses. We show that the overlapping of the two wave packets, produced by each pulse, gives rise to quantum interference that affects the orientational anisotropy of the sample. Because of the large number of coherently excited levels, the interference produces well-separated temporal structures, whose magnitude can be controlled through the relative delay of the two pulses.

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Quantum control of chemical reactions has recently become a fascinating topic. In order to achieve an active control over defined reaction channels, a molecular system is manipulated through its coherent interaction with laser light. Based on a broad range of quantum interference effects, quantum control allows for selective modulation of an outcome pathway in a multiproduct system.

Several control schemes are now available in order to complete this task, all taking benefit of the specific properties of the radiation field. Tailoring of a femtosecond laser pulse by the temporal manipulation of both phase and field amplitude is now technologically achievable. It can be employed in order to maximize a specific product yield in a chemical reaction by properly adjusting the electric field to the quantum system. A very elegant optimization procedure, based on a feedback controlled pulse shaper, has been used very recently to optimize the branching ratio in the dissociation process of different organometallic molecules [1]. Another class of control schemes, the so-called ‘‘phase-sensitive coherent control’’ [2], makes use of two different phase-related excitation fields, both connecting a common initial state to the same or opposite parity final state. The final-state population is then controlled through the manipulation of the phase difference between the two coherent fields. This technique has been successfully applied to molecules [3] as well as to atomic systems [2]. Laser-induced continuum structure [4,5] (LICS) is a somewhat different control scheme. It also involves the interaction of two electromagnetic fields but does not have the stringent requirement of having a constant phase relation between them. In this technique the two fields establish different pathways that connect two bounds states to a same continuum. Quantum-mechanical interference between these pathways mainly depends on the detuning frequency and laser intensities, which are the control parameters. Control of products can, in principle, be achieved in LICS whenever different energetically degenerate continua are coupled [6,7].

An alternative and complementary type of control has received widespread attention in recent years [8]. In this method, two identical laser pulses are applied to a quantum system at different times. The first pulse produces a coherent superposition state (a wave packet) whose phase evolution is determined by the energy difference between the individual states. After a certain delay, the second pulse is applied producing a second superposition state as well, but phase mismatched with respect to the first one. The two wave packets undergo a Ramsey-type interference, which can be observed by probing the final-state population in the time-delay domain of the two pulses. This two-pulse technique has been successfully applied to Rydberg [9–12], fine-structure [13,14], and vibrational wave packets [8,15].

The present work reports the observation of quantum manipulation of rotational coherence based on this two-pulse coherent control technique. A ground-state rotational superposition is prepared through a nonresonant stimulated Raman excitation by a linearly polarized femtosecond pump pulse. By using a polarization technique, a delayed femtosecond pulse probes the resulting transient alignment. This technique has been employed in the study of rotational coherence of small molecules [16]. In this work a two-pulse sequence prepared in a Mach-Zehnder interferometer is employed for the pump process. We show that the rotational coherence prepared by each pulse produces a quantum interference whose effect is observable in the time domain. By changing the pump-pump delay, the relative phase of the two superposition states can be adjusted so as to control the resulting rotational wave packet.

For convenience, we begin by recalling the expressions used in the description of the orientational anisotropy induced by a short laser pulse passing through a gas sample of linear molecules. At time $t=0$ a molecule is exposed to a short linearly polarized laser pump pulse whose complex electric field can be written as

$$E_{\mathrm{pump}}(t)=\mathcal{E}_{\mathrm{pump}}(t)\exp(-i\omega_{\mathrm{pump}}t), \tag{1}$$

where $\mathcal{E}_{\mathrm{pump}}(t)$ is the slowly varying amplitude and ω_{pump} is the carrier frequency.

The nonresonant stimulated Raman excitation of the medium creates an orientational anisotropy that is observable by measuring the polarization rotation of the electric-field probe

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*Electronic address: faucher@satie.u-bourgogne.fr beam. The latter is a replica from the same laser beam as the one used for the pump process except for its linear polarization, which is initially rotated by 45° with respect to the pump beam. Assuming that the system is probed at time t greater than the pump pulse width Δ_p, the complex amplitude of the electric-field signal at time t can be obtained by solving the wave equations. For linear molecules and a nonresonant stimulated Raman interaction, the solution can be written [17]

$$\varepsilon_S(t) \propto \varepsilon_d(t)\,\mathrm{Im}\left(\sum_J T_J \int_{-\infty}^{+\infty} \left| E_{\mathrm{pump}}(t') \right|^2 \times \exp[-i\omega_J(t-t')]\,dt' \right). \tag{2}$$

In this last expression, T_J represents the nonlinear response of the medium that depends on the rotational quantum number J and ω_J is the Raman frequency. ε_d is the probe field.

Expression (2) describes a coherent ground-state superposition completed by the pump pulse. More specifically, the probe field is expanded as a linear combination of Fourier components pondered by a factor T_J. Because the Raman coupling induced by the pump is a two-photon process, the signal is proportional to the Fourier transform of the squared modulus of the pump field, the former being calculated at the Raman transition frequency ω_J. This implies that the transitions contributing to the signal are those having frequency ω_J within the convoluted bandwidth of the pump electric field. The beating between the different frequencies produces recurrences in the probe time domain, whose periodicity T_0 is determined by the principal moment-of-inertia of the molecule [16]. From Eq. (2), one can calculate the averaged signal I measured by the detector

$$I \propto \int_{-\infty}^{+\infty} |\mathcal{E}_S(t)|^2\,dt. \tag{3}$$

We proceed further by deriving the analytical expression related to the quantum control of the coherent superposition state. We show that the time evolution of the system, coherently prepared by a pump pulse at time $t=0$, can be controlled by applying a second identical time delayed pump pulse. For convenience, this pulse is called the ''control'' pulse. The total pump field at frequency ω is now divided into two identical pulses, the primary and the control pulse

$$E_{\mathrm{pump}}(t') = E_p(t') + E_c(t'-\tau_c) \tag{4}$$

with an amplitude ratio of the two pulses defined as $r = |\varepsilon_c(0)|/|\varepsilon_p(0)|$.

To obtain the signal field resulting from the control process we then substitute in Eq. (2) E_{pump} by the new expression given in Eq. (4)

$$\varepsilon_S(t) \propto \varepsilon_d(t)\,\mathrm{Im}\left(\sum_J T_J \exp(-\omega_J t)\{A(\omega_J)[1+r^2 \times \exp(i\omega_J\tau_c)] + 2r\ \mathrm{Re}[B(\omega_J,\tau_c)\exp(-i\omega\tau_c)]\} \right), \tag{5}$$

where $A(\omega_J)$ is proportional to the Fourier transform of the laser intensity at the Raman frequency transition ω_J,

$$A(\omega_J) = \int_{-\infty}^{+\infty} |\mathcal{E}_p(t')|^2 \exp(i\omega_J t')\,dt' \tag{6}$$

and $B(\omega_J,\tau_c)$ is a quantity that contains the field correlation (first-order correlation) pondered by a slowly varying factor $\exp(i\omega_J t')$

$$B(\omega_J,\tau_c) = \int_{-\infty}^{+\infty} \mathcal{E}_p(t')\mathcal{E}_p^*(t'-\tau_c)\exp(i\omega_J t')\,dt'. \tag{7}$$

By first assuming that the control delay τ_c is larger than the laser pulse duration $\Delta\tau_p$, the $B(\omega_J,\tau_c)$ term can be neglected. In that case, Eq. (5) results in a similar expression to the one given in Eq. (2), except for the presence of a factor $[1+r^2\exp(i\omega_J\tau_c)]$ that depends on the control delay. This term accounts for the interference process occurring in the excitation of the rotational J levels by the delayed laser pulses. In other words, the evolution of the electric field (5) in time delay domain τ_c reflects the quantum interference occurring between the two rotational wave packets produced by each pulse. Since each rotational contribution is modulated at the transition frequency ω_J, interference occurs at time t whenever the control delay is set close to an integral number of the period T_0 defined previously, i.e., when the revivals of the two separate rotational wave packets coincide in time. The quantum interferences are then observable over a range $\Delta\tau_0$ that depends on the T_J factors (i.e., temperature and molecular parameters). When the primary and the control pulse slightly overlap in time ($\tau_c \sim \Delta\tau_p/2$), the quantity $B(\omega_J,\tau_c)$ modifies the signal by introducing a fast oscillating term that reflects the temporal coherence of the laser field. At the limit of very small delay ($\tau_c \ll \Delta\tau_p/2$), the signal is dominated by an optical interference reproducing the interferogram of the laser field.

By assuming a real expression for the laser field amplitude (Fourier-transformed pulse) the expression (5) can be simplified to

$$\mathcal{E}_S(t) \propto \mathcal{E}_d(t) \sum_J T_J(A(\omega_J)\{\sin(\omega_J t) + r^2 \sin[\omega_J(t-\tau_c)]\} + 2rB(\omega_J,\tau_c)\sin(\omega_J t)\cos(\omega\tau_c)), \tag{8}$$

where the contribution from the two laser pulses are clearly separated. The $\sin(\omega_J t)$ term corresponds to the response of the system at time t, after excitation by the pump pulse. It is independent of τ_c and therefore produces a continuous component in the delay time domain. The second term, $\sin[\omega_J(t-\tau_c)]$, is due to a further excitation of the system by the

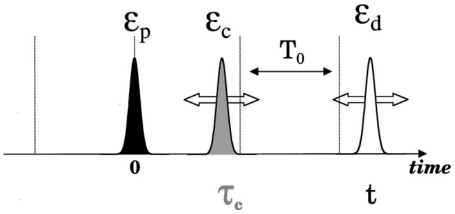

FIG. 1. Schematic representation of the pulse sequence used in the quantum control experiment.

delayed laser pulse. The combination of only these two terms defines the regime of pure quantum interference. The second line of Eq. (8) gives rise to the optical modulation of the signal at the laser frequency ω, through the $\cos(\omega\tau_c)$ term.

In order to simulate the intensity signal (3) averaged by the detector, the expression (8) has to be integrated numerically. The Fourier-transform amplitudes for the primary, the control, and the probe pulse will be assumed to have a pure Gaussian temporal envelope.

The present experiment is based on a chirped pulsed amplified Ti sapphire femtosecond laser. A Mach-Zehnder interferometer is employed to produce a control pulse as a delayed replica of the primary pump pulse issued from the laser amplifier. The linearly polarized pump and probe beams are overlapped at a small angle in a gas cell filled with CO_2 gas. The probe beam passes through two crossed polarizers, respectively located at the entrance and exit slot of the static cell. The probe beam, inside the cell, is polarized at 45° with respect to the pump laser field. The polarization signal is detected by a photomultiplier, sampled by a boxcar, and finally acquired by a computer card.

The pulse temporal sequence referred to in this work is sketched in Fig. 1. The primary pulse is centered at the origin of time. The control pulse can be tuned from negative to positive delay τ_c, relative to the primary pulse. During scanning of the control pulse, the system is probed at a fixed positive time, ensuring that the probe delay pulse t is set to a value larger than τ_c. The time interval T_0 is the recurrence period introduced previously. The dash lines depict the time occurrence of the transients produced by the primary pulse alone.

The time domain spectrum presented in Fig. 2(a) has been recorded for a probe delay t set at the occurrence of the primary pulse first recurrence $(t=T_0)$. The probe signal is depicted versus the control delay τ_c scanned over 70 ps. Each data point corresponds to an averaging of the signal over 25 laser shots. The numerical simulation [Fig. 2(b)] was computed from expressions (8) and (3). In the calculation, the pulse duration was set to 90 fs [full width at half maximum (FWHM)], as obtained from the autocorrelation trace of our laser. The r^2 factor was measured to be 1.3 at the exit of the Mach-Zehnder interferometer. The recorded spectrum clearly depicts the primary pulse signal modified by the control pulse signal. The baseline component corresponds to the primary pulse induced rotational coherence of the system probed at time t (see Fig. 1). It arises from the discrete summation of the first term of expression (8). The second term accounts for the contribution of the control pulse. The structures regularly spaced in time result from the quantum interference between the two coherent superposition states produced by each of the delayed pulses. The interference feature appears through the calculation of the square modulus of the whole expression (8) as defined in (3). The narrowness of the temporal structure results from the large number of rotational states (more that 30 at room temperature) coherently excited within the laser bandwidth. As shown from Fig. 2, the interference structures tend to decrease as the control delay increases. This is mainly due to collisonal (elastic and inelastic) coherence decay. It was taken into account in the theoretical model by including a constant linewidth γ_J (the thermally averaged value). The structure recorded around -10 ps results from the interference occurring between the first and second rotational recurrence produced by the primary and control pulse, respectively. Since these two recurrences have comparable amplitudes, the degree of modulation of the rotational coherence versus control delay is quite effective. In terms of molecular alignment, the anisotropy of the medium can be switched from maximum to a near-zero value (isotropy) within the 1.5-ps sweep of the control delay. It is worth noting that, considering that the theoretical model uses only one adjustable parameter (a scale factor), there is a reasonably good agreement between experiment and theory.

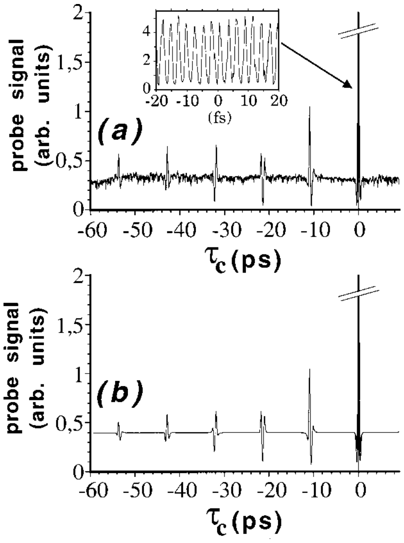

FIG. 2. (a) Polarization probe signal reflecting the CO_2 rotational coherence versus the control delay at room temperature $(P=1.7\,\text{bar})$. The equally spaced structures recorded at negative delay result from the quantum interference occurring between the two rotational wave packets produced by each laser pump pulse. The inset graph depicts the optical interference regime for which the signal exhibits a 2.6-fs periodic. (b) Numerical simulation.

The inset included in Fig. 2 shows the optical fringes recorded around the zero delay (zeroth recurrence) where the primary and control pulses overlap in time. For such a narrow delay range, all the terms appearing in expression (8) remain almost constant, except for the $\cos(\omega\tau_c)$ modulation term. A quantitative analysis of the total range signal can provide information on the laser beam properties, such as field amplitude and phase modulation (chirp) versus time. The advantage of using a transparent nonlinear medium is evident with respect to the characterization of infrared or

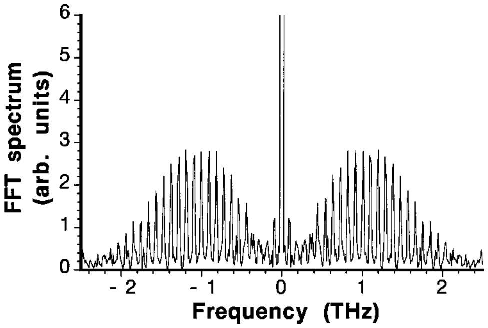

FIG. 3. Discrete Fourier transform of the temporal interferogram depicted in Fig. 2 (see text). The Raman transitions appear in the frequency domain with a resolution limited by the optical path-length difference of the interferometer (~ 60 ps).

far-UV coherent beams, produced though frequency conversion.

The spectrum of Fig. 2 can be translated to the frequency domain by a simple mathematical transformation. This has been done by calculating the discrete Fourier transform of the temporal interferogram (τ_c: $-60, -2$ ps), from which the structure arising at zero delay has been left out. The result is depicted in Fig. 3. The fast-Fourier-transform spectrum is symmetrical because only negative delays have been recorded in Fig. 2. The zero-frequency signal results from the base line signal produced by the primary pulse in the time delay spectrum. The equally spaced structures correspond to the difference between the spontaneous Raman transitions of CO_2, as they would be obtained in a frequency domain experiment. No absolute transition values are directly accessible because the information concerning the laser frequency is missing in all the time-domain structures of Fig. 2, except in the first transient.

In conclusion, we have demonstrated the possibility of controlling in a robust way the ground-state rotational coherence in a linear molecule. The effect under consideration has been studied in CO_2, through the observation of the transient alignment produced by two, time-delayed, short laser pulses. The spectra recorded in the time-delay domain show that the rotational wave packet can be manipulated by adjusting the time sequence of the two pulses. More precisely, we have shown that the anisotropy induced by the first laser pulse can be either enhanced or reduced to zero by the adjunction of the second laser pulse. An analytical model, based on perturbation theory and taking into account the laser characteristics and the molecular parameters, has been presented. The good agreement with the experimental data implies that information about the dynamics of the rotational wave packets can also be extracted using this method. Moreover, the process presented in this work can be applied for the control of coherence of high-lying states, using a resonant multiphoton ionization scheme instead of a stimulated Raman process. We believe that the ability of this technique to quantum manipulate molecular systems can greatly benefit in active control studies of chemical reaction.

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