Molecular alignment allows low-order harmonic generation by circular light in a gas

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We experimentally investigate odd-order harmonic generation in molecular gases produced by circularly polarized laser fields. While forbidden in isotropic medium, this effect is allowed by symmetry breaking resulting from nonadiabatic laser-induced molecular alignment. The demonstration is provided by generating the third harmonic in CO_2 molecules. Attractive properties and challenging potential applications are discussed in the context of higher-order harmonic generation.

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I. INTRODUCTION

Nonlinear frequency up-conversion from prealigned molecular samples has been a subject of growing interest in the last decade. It has been shown for instance that high-order harmonic generation (HHG) from aligned molecules can provide access to tomographic imaging of molecular orbitals [1,2]. Molecular alignment has also been exploited for determining the phase of the high-order harmonics [3,4] or for controlling their polarization state with a variety of attractive applications [5,6]. The case of lower-order harmonics has also been investigated. Bartels and coworkers [7] have reported the influence of molecular alignment on third harmonic generation (THG) driven by linearly polarized laser fields. They have identified different types of THG processes and analyzed the alignment dependence of the phase matching.

This paper reports on the experimental study of THG produced by circularly polarized laser fields. The effect is demonstrated in CO_2 gas at room temperature and relatively low pressure. We should recall that circular light does not generate harmonics in isotropic media because of symmetry reasons [8]. We therefore take advantage of molecular alignment to break the symmetry of the gas medium. A short nonresonant laser pump pulse excites a rotational wave packet by driving a series of impulsive stimulated Raman transitions within the vibronic ground state of the molecule. The free evolution of the system after the pulse turnoff leads to periodic revivals of molecular alignment [9,10]. A short time-delayed probe pulse, circularly polarized, generates third-order harmonic radiation in the sample of aligned molecules. An extended control of the THG efficiency upon molecular alignment is observed. It is noticed that the signal evolves with the pump-probe delay as a combination of the rotational expectation values $\langle\cos^2\theta\rangle(t)$ and $\langle\cos^4\theta\rangle(t)$. The present method provides therefore a direct measurement of $\langle\cos^4\theta\rangle(t)$, a term generally involved in the description of high-order harmonic signals produced by aligned molecules [11–14]. The observation of this expectation value provides also richer information about the evolution of rotational wave packets, which could be exploited for probing collisions in dissipative media as suggested in Ref. [15]. The method features additional attractive properties. We show in particular that the polarization of the THG radiation varies with the degree of alignment and that circularly polarized field can be produced from prealigned molecules. One can therefore envision that the extension of the method to HHG could allow production of VUV or XUV radiation with elliptic or circular polarization that would be highly desirable for instance in chiral recognition [16–20]. Finally, the standard rescattering model [21] is considered to be inadequate to explain the generation of high-order harmonics by circular light so that the underlying mechanism could shed light on appealing new physics as predicted in Refs. [22,23].

II. EXPERIMENTAL SETUP

The main features of the experimental setup are depicted in Fig. 1. A Ti:sapphire chirped pulse amplifier delivers 5 mJ pulses of 90 fs duration around 800 nm at 100 Hz repetition rate. The output beam is split in two parts to produce the pump and probe beams. The relative delay τ between them is adjusted via a motorized translation stage. The two beams are focused and crossed at small angle ($\approx 4^\circ$) in a static cell filled with CO_2 at low pressure (less than 0.1 bar). The THG radiation, filtered from the fundamental radiation by means of a bandpass filter and two dielectric mirrors at 266 nm, is detected by a photomultiplier. The probe field is circularly polarized by means of a zero-order quarter-wave plate. Special attention is paid to avoid any detrimental harmonic signal associated to residual ellipticity by carefully tilting the quarter-wave plate around its neutral axes such as to minimize the THG when the pump field is off. The pump field is linearly polarized along the vertical z axis and the THG is expected to have field components along the y and z directions (Fig. 1). In order to detect each component independently, we use a half-wave plate at 266 nm (produced by a Berek compensator) in conjunction with a glass plate set at Brewster angle. The latter selects the vertical polarization for the detection while the half-wave plate allows an overall rotation of the third harmonic field at the exit of the cell. This scheme allows measurement of the harmonic signals $S_y^{3\omega}$ and $S_z^{3\omega}$ produced perpendicularly and along the aligning pulse polarization, respectively. We have checked that the signal produced by rotating the polarization of the THG through this procedure is equivalent to the one obtained by rotating the pump polarization axis.

III. RESULTS AND DISCUSSION

Typical signals recorded at 0.07 bar are depicted in Figs. 2(a) and 2(b). As shown, the signal to noise ratio is very good in spite of the relatively low pressure indicating that the present technique can be seen as a valuable versatile method for measuring alignment. Besides the usual CO_2 transient

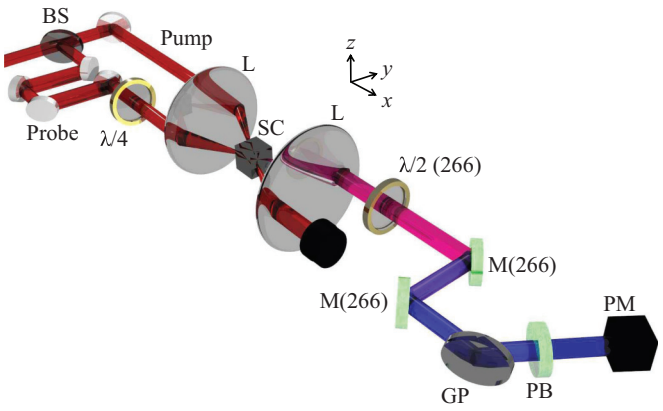

FIG. 1. (Color online) Experimental setup. BS: beam splitter, L: lenses ($f = 150$ mm), SC: static cell, $\lambda/4$: quarter-wave plate at 800 nm, $\lambda/2$ (266): half-wave plate at 266 nm, M(266): mirrors coated for maximizing the reflection at 266 nm, GP: glass plate at Brewster angle, PB: pass-band filter (250-280 nm), PM: photomultiplier.

revivals produced around 10.7 and 21.4 ps (i.e., around $nT_r/4$, with $T_r = 42.7$ ps the classical rotational period of the molecule [10]), the signal features additional tiny peaks around $(2n+1)T_r/8$ (i.e., 5.3 and 16.0 ps). In order to interpret the signal, the dependency of the THG upon molecular alignment is described with perturbation theory. We consider for the calculation a pump pulse polarized along the z axis. The probe field is assumed to have a purely circular polarization in the

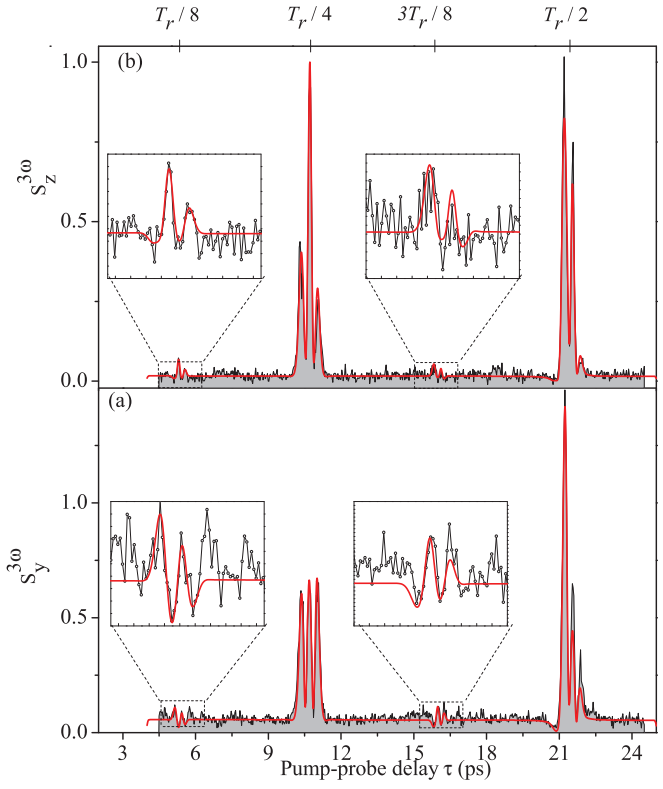

FIG. 2. (Color online) CO_2 harmonic signals (black lines with symbols) measured with a polarization along the y axis (a) and z axis (b) together with the simulation (red lines). Experimental conditions: pump energy 150 μJ, probe energy 50 μJ and pressure 0.07 bar.

(y,z) plane and a temporal field envelope $\varepsilon(t)$ so that $\vec{E}_{\rm pr} = 0$, $\varepsilon(t-\tau)$, $\pm i\varepsilon(t-\tau)$]. For a linear molecule, it can be shown that the components $\alpha = y,z$ of the induced dipole moment operator responsible for THG writes as

$$\mu_\alpha^{3\omega}(t) = c_{2\alpha}(\langle\cos^2\theta\rangle(t) - 1/3)\varepsilon(t-\tau)^3 + c_{4\alpha}(\langle\cos^4\theta\rangle(t) - 1/5)\varepsilon(t-\tau)^3, \quad (1)$$

with

$$\begin{aligned} c_{2y} &= -9/4\gamma_{ZZZZ} - 9/4\gamma_{XXYY} + 9\gamma_{XXZZ}, \\ c_{4y} &= 15/8\gamma_{ZZZZ} + 45/8\gamma_{XXYY} - 45/4\gamma_{XXZZ}, \\ c_{2z} &= \pm i(3/2\gamma_{ZZZZ} + 9\gamma_{XXYY} - 27/2\gamma_{XXZZ}), \\ c_{4z} &= \pm i(-5/2\gamma_{ZZZZ} - 15/2\gamma_{XXYY} + 15\gamma_{XXZZ}), \end{aligned} \quad (2)$$

and where γ_{IJKL} denotes the components of the second hyperpolarizability tensor in the molecular frame (X, Y, Z) with values given in Ref. [24]. The expectation values $\langle\cos^2\theta\rangle(t)$ and $\langle\cos^4\theta\rangle(t)$ are calculated by solving the time-dependent Schrödinger equation [10].

The signal detected by the photomultiplier as a function of the pump-probe delay τ is directly proportional to the complex modulus of the dipole moment:

$$S_\alpha^{3\omega}(\tau) \propto \int_{-\infty}^{\infty} \left|\mu_\alpha^{3\omega}(t)\right|^2 dt. \quad (3)$$

As discussed in Ref. [7], a part of the produced THG results from a mix of y and z field components as in a type-II conversion process. The phase mismatch depends in this case on the degree of alignment and varies with the pump-probe delay, which significantly complicates the analysis of the THG signal. However, a simple estimation shows that this effect can be neglected for the pressure investigated in the present work. This is confirmed by the simulations shown in red lines in Figs. 2(a) and 2(b) that reproduce fairly well the experimental data. We emphasize that, besides the temporal shape, the relative amplitudes between $S_y^{3\omega}$ and $S_z^{3\omega}$ are also well reproduced. The expectation values $\langle\cos^2\theta\rangle(\tau)$ and $\langle\cos^4\theta\rangle(\tau)$ are depicted in Fig. 3. As shown, both terms contribute to the large THG signal at the $nT_r/4$ revivals. However, the similitude between their temporal shapes prevents any clear disentanglement of their respective contributions. The small transients around $(2n+1)T_r/8$, resulting from coherences excited between J and $J+4$ rotational states, are in turn solely related to $\langle\cos^4\theta\rangle(\tau)$. Their observation provides therefore a clear experimental evidence of this term [11]. The accuracy of the simulations displayed in Fig. 2, including background and relative amplitude of $S_y^{3\omega}$ and $S_z^{3\omega}$, provides a stringent test for the determination of $\langle\cos^4\theta\rangle$. This is relevant considering the role played by this term in the production of high-order harmonics in several molecular systems [11–14]. Measurements conducted at various pump intensities and in the O_2 molecule allowed us to draw similar conclusions. It should be pointed out that the signals $S_y^{3\omega}$ and $S_z^{3\omega}$ produced at $(2n+1)T_r/8$ display almost opposite variations with respect to the baseline so that these small revivals would be hardly detectable without a polarization analysis. In this case, the sum of the two THG field components would indeed lead to a significant cancellation of the signal at $(2n+1)T_r/8$

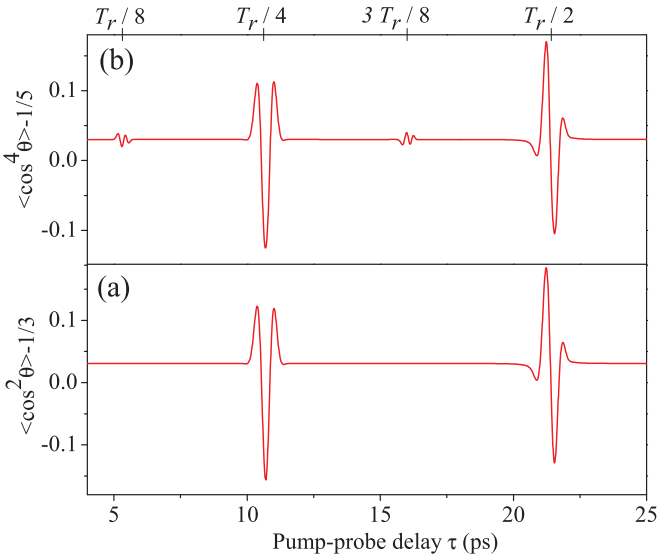

FIG. 3. (Color online) Expectation values $\langle\cos^2\theta\rangle(\tau)$ and $\langle\cos^4\theta\rangle(\tau)$ for a pump intensity of 55 TW/cm^2 corresponding to Fig. 2.

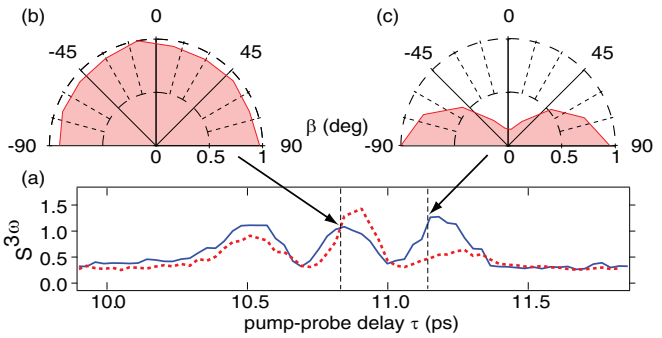

FIG. 4. (Color online) (a) THG signals $S_y^{3\omega}$ and $S_z^{3\omega}$ recorded along the y axis (blue line) and the z axis (red dashed line), respectively. Upper panels (b) and (c) depict the polarization analysis for the two specific delays indicated by arrows, β being the angle between the detected THG polarization and z (see text).

that would prevent the determination of $\langle\cos^4\theta\rangle(\tau)$. Another criterion for the observation of $\langle\cos^4\theta\rangle(\tau)$ refers to the molecular density. At high molecular density, the probe beam suffers from depolarization as it propagates through a sample of aligned molecules. The induced birefringence resulting from molecular alignment is proportional to $\langle\cos^2\theta\rangle(t)$ [10] so that depolarization mainly occurs at $nT_r/4$. The weak depolarization of the probe contributes to a large enhancement of the THG since frequency conversion by elliptic polarization is not forbidden in isotropic medium. The corresponding enhancement can reach a factor of 100 at 1 bar according to our calculation. In these conditions, the tiny peaks around $(2n+1)T_r/8$ that do not benefit from this increase are not detectable any more. This feature has been experimentally verified and is a subject for future work. We emphasize that an increase of the angle between pump and probe beams can prevent the effect of depolarization. In this case, the probe pulse will interact with the sample of aligned molecules only at the laser focus where THG is produced.

It is worth mentioning that the present measurements do not involve any significant contribution of plasma-enhanced THG. Recently, enhancement of THG by preionizing a gas medium with a pump laser pulse has been reported. Two different interpretations have been proposed, both related to the plasma left out by the pump pulse. The first one [25] argues for an effective plasma-enhanced third-order optical susceptibility, while the second one [26] invokes a reduction of the interaction length through a propagation effect, which limits the partial THG cancellation due to the Gouy phase. In both cases, the plasma-enhanced THG would result in a substantial background at positive pump-probe delays that would obscure the analysis of THG signal. This has been confirmed by producing the THG with a probe linearly polarized. However, it can be shown that circular polarization does not allow plasma-enhanced THG in a centrosymmetric medium so that this effect is assumed to be marginal for the moderate molecular alignment achieved in the present study.

Another interesting prospect is related to the control of the THG ellipticity, with the possibility of producing a THG field with circular polarization as ultimate goal. According to Eqs. (1)–(3), the harmonic fields along the y and z axis are produced in phase quadrature, resulting in an elliptic field in most cases. However, depending on the time delay τ, the THG field amplitudes along y and z are differently modulated by the $\langle\cos^2\theta\rangle(\tau)$ and $\langle\cos^4\theta\rangle(\tau)$ terms as shown by the measurements presented in Fig. 4(a). For certain values of τ, equal amplitude components can be observed meeting therefore the requirements for the generation of circularly polarized THG.

We have analyzed the THG field polarization for the delay $\tau = 10.8$ ps satisfying this condition and indicated by the left arrow in Fig. 4(a). Figure 4(b) depicts the signal obtained by inducing an overall rotation β of the THG field at the exit of the cell with the half-wave plate. As observed, the measured signal does not exhibit any significant variation with β bearing out the circular polarization of the produced THG field. In contrast, the polarization analysis performed at a delay $\tau = 11.2$ ps, where pronounced difference between $S_y^{3\omega}$ and $S_z^{3\omega}$ are observed, displays large variations [Fig. 4(c)] revealing the significant ellipticity of the THG field. Production of a circularly polarized harmonic field is an important issue, especially in the context of HHG with applications in ultrafast spin dynamics, nanolithography, and magnetic circular dichromism. Extension of the present technique to HHG provides an alternative approach to other existing methods [16–20].

IV. SUMMARY AND CONCLUSION

In conclusion, optical harmonic generation has been produced in a molecular gas with a circularly polarized laser field. The conversion process is made feasible by breaking the symmetry of the gas medium through nonadiabatic laser-induced molecular alignment. Although the effect is demonstrated using third-harmonic generation, it can be straightforwardly applied to higher-order harmonics. Experimental conditions allowing THG observation are discussed. Besides a simple

way to measure the alignment, the method features several attractive properties. First, it provides a direct measurement of the expectation value $\langle\cos^4\theta\rangle(t)$. This term plays a key role in HHG signals produced by aligned molecules but its measurement also features a broad range of additional applications. For instance, the expectation value $\langle\cos^2\theta\rangle(t)$ is proportional to the second moment of the rotational distribution while the complete rotational distribution implies all moments. In this regard, measurement of higher-order rotational expectation values offers potential for rotational wave-packet imaging [27] or for probing dissipative media [15] by providing information that is not revealed by $\langle\cos^2\theta\rangle(t)$. Second, the simulations of Fig. 2 have been performed using the components of the second hyperpolarizability tensor given in Ref. [24]. Our analysis has revealed a noticeable sensitivity of the model with respect to this set of elements. Other values found in the literature did not allow us to reach a satisfactory agreement for $S_y^{3\omega}$ together with $S_z^{3\omega}$, including the relative amplitude between them. Measurement of the hyperpolarizability components and in particular of the off-diagonal ones (i.e., γ_{XXZZ}) is known to be a tricky task. We believe that the present method could be very helpful in this issue and should be considered as a future prospect of our work. Third, the technique enables the production of circularly polarized harmonics. Extension of the method to HHG could allow production of elliptically or circularly polarized fields, which represents a subject of active research [16–20]. Finally, HHG in aligned molecules by circularly polarized pulses could significantly differ from the well-known recollision model [21] and thus reveals particular physical mechanisms [23]. Unforeseen dynamics are predicted with, for instance, harmonic spectra revealing two distinguishable plateaus [22]. The present work provides the guidelines for such forthcoming experiments.

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