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Polarization-resolved pump–probe spectroscopy with high harmonics

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Abstract. High harmonic generation in gases can be used as a probe of the electronic structure of the emitting medium, with attosecond temporal resolution and angström spatial resolution. The prospect of measuring molecular dynamics by pump–probe spectroscopy with such precision is attracting a lot of interest. An important issue in pump–probe spectroscopy lies in the ability to detect small signals: the detected signal can be easily dominated by the contributions from non-excited molecules or from a carrier gas. In this paper, we demonstrate that polarization-resolved pump–probe spectroscopy can be used to overcome this issue. We study high harmonic generation from rotationally excited molecules. We show that by measuring the harmonic field that is generated orthogonally to the driving laser field, the contrast in the detection of alignment revivals in nitrogen can be increased by a factor 4. We use this configuration to measure alignment revivals in an argon–nitrogen mixture, in which the total harmonic signal is dominated by the contributions from argon.

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1. Introduction

High harmonic generation from molecules is a three step process [1, 2]. Firstly, part of the highest occupied molecular orbital (HOMO) tunnels out into the continuum under the influence of the strong laser field. This free electron wavepacket is then accelerated by the field. Lastly, it comes back to the vicinity of the parent ion, where it interferes with the part of the HOMO that remained bound. The interference of the propagating free electron wavepacket and the HOMO leads to an oscillation of the electron density, resulting in the emission of a burst of light. This process is periodic and leads to the generation of a train of attosecond pulses separated by half the driving laser period [3, 4]. A single attosecond pulse can be isolated by using single cycle driving pulses [5, 6] or polarization gating techniques [7, 8].

The spectrum of the emitted light is determined by the two interfering components: the free electron wavepacket and the HOMO. The characteristics of the free electron wavepacket mainly depend on the propagation into the continuum, i.e. on the laser field intensity [9, 10]. The typical de Broglie wavelength of the recolliding electrons is in the angström domain. Thus, the harmonic signal is a very accurate probe of the HOMO. This property was recently used to perform the tomographic reconstruction of the HOMO of N_2 [11]. By extending such measurements to the case of molecular dynamics, it would be possible to follow the evolution of electron wavefunctions in chemical reactions.

Recent experiments have shown that the high harmonic signal could be used to encode rotational [11]–[13] and vibrational [14]–[16] molecular dynamics. The extension to more complex processes such as electronic excitations and photochemical dynamics will face the problem of the contrast in the measurements, especially for high temporal resolutions. In the case of a low cross-section excitation process, the harmonic signal will be dominated by the contributions from non-excited molecules. Furthermore, a carrier gas is often used in experiments and it can also create a strong background signal. In order to extract the contribution of excited molecules from the background, different techniques have been developed and are extensively used in conventional femtosecond pump–probe spectroscopy [17, 18]. One solution is transient grating spectroscopy, which has recently been transposed to high harmonic generation [19]. In the following, we show that polarization-resolved pump–probe spectroscopy can be used to increase the contrast in the detection of the harmonic emission from excited molecules. We consider the particular case of rotational wavepackets, but this technique could be used with any excitation process leading to anisotropy of the generating medium.

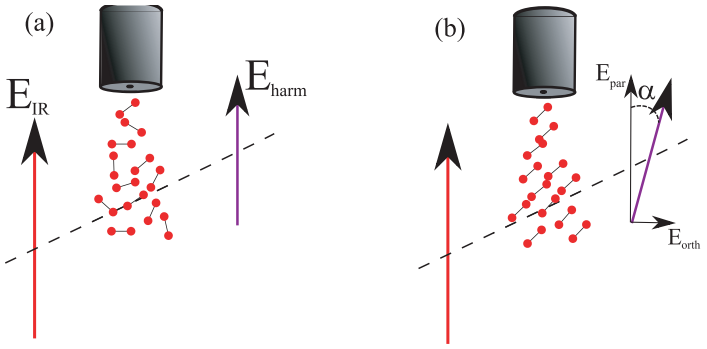


Figure 1. Principle of polarization-resolved pump–probe spectroscopy. When the generating medium is isotropic (a), the high harmonics are polarized parallel to the driving laser field. When anisotropy exists in the medium (b), the polarization of the high harmonics can be rotated with respect to the driving field by an angle α. The orthogonal polarization component is then non-zero.

2. Principle

In this paper, we study rotational excitation of molecular samples with high harmonic generation. Rotational wavepackets can be excited by focusing a femtosecond laser pulse at a few 10^{13} W cm^{-2} in a gas sample [20, 21]. A coherent superposition of rotational states is then populated. The molecular alignment distribution presents a characteristic temporal evolution: the molecules are aligned along the pump-laser polarization every half-rotational period of the considered molecule [22]. Since the harmonic generation process is sensitive to the alignment of the molecule with respect to the laser polarization, revivals of molecular alignment can be probed by monitoring the high harmonic signal produced in the rotationally excited gas sample [11]–[13].

In previous pump–probe studies, the revivals of molecular alignment were detected by measuring the total harmonic intensity. In the following, we show that the contrast can be significantly enhanced by performing polarization-resolved measurements. The principle of our measurement is described in figure 1. In an isotropic medium, the high harmonics generated by a linearly polarized laser pulse are polarized parallel to the laser polarization (figure 1(a)). If anisotropy exists in the medium, for example, a particular molecular alignment, then an orthogonal polarization component can be generated (figure 1(b)). Thus, measuring the orthogonal polarization of the harmonic light provides a sensitive way of probing any anisotropy of the generating medium.

The experiment was performed on two laser systems: the 1 kHz Ti:sapphire AURORE laser facility from CELIA, which provides 35 fs and 9 mJ pulses at 800 nm, and the 20 Hz Ti:sapphire LUCA laser from CEA which delivers 50 fs and 50 mJ pulses. Our experimental set-up is shown in figure 2. A two-arm interferometer splits the incoming laser pulse in two: one part for molecular alignment (pump pulse) and one for harmonic generation (probe pulse). The two pulses can be delayed by a motorized translation stage placed in the probe arm.

A zero-order half waveplate hwp1 (aligning waveplate) is placed in the pump arm, allowing control of the alignment direction of the molecules in the generating medium. A rotation of $\theta/2$ of hwp1 leads to a rotation of θ of the pump polarization axis, i.e. a rotation of θ between the alignment direction of the molecules and the polarization of the probe pulse.

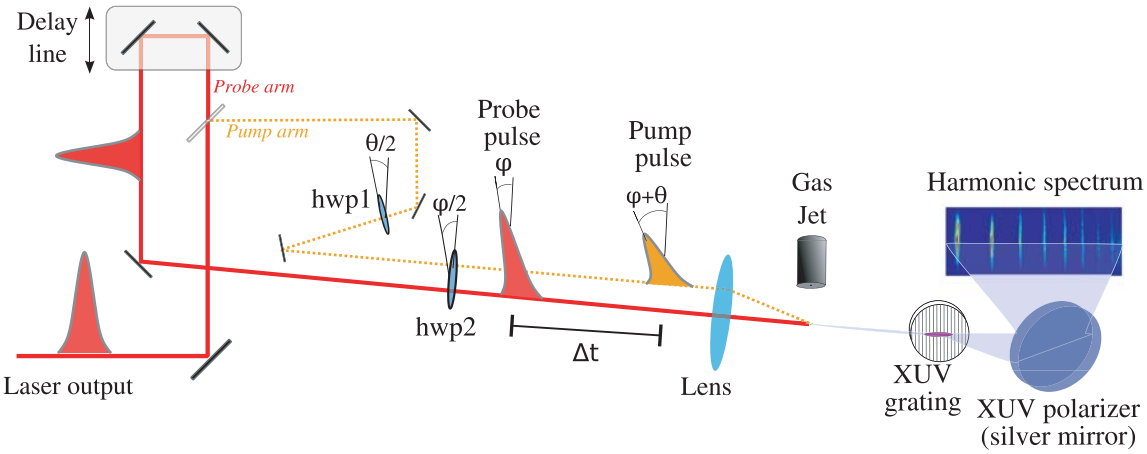


Figure 2. Experimental set-up (see text).

At the output of the interferometer the two beams are parallel and separated by 15 mm. They pass through a second zero-order broadband half waveplate hwp2. This 'analyzing' waveplate is used to rotate the polarization of the two pulses by the same angle φ, which is equivalent to rotating the whole experimental chamber.

The two outcoming beams are then focused by a 500 mm lens into a pulsed gas jet with a backing pressure of 2 bar. The probe beam is on-axis and generates high-order harmonics. The pump beam is tilted by 30 mrad with respect to the axis of the probe beam and thus to the axis of the vacuum chamber. This ensures that the high harmonics that it may generate will not reach the detector.

The harmonic spectrum generated by the probe pulse is measured by an XUV spectrometer consisting of a grazing incidence grating and a set of dual microchannel plates in front of a phosphor screen. The signal emitted by the phosphor screen is recorded by an 8-bit CCD camera. A typical spectrally resolved far field harmonic profile is presented in figure 2, showing harmonics 21–35 generated in N_2.

In order to analyze the polarization of the generated high-order harmonics, we placed a silver mirror with no protective coating at 45° incidence between the grating and the microchannel plates [23]. This silver mirror acts as a polarizer: at this incidence, the ratio between the XUV reflectivity for S ($\varphi = 0°$) and P ($\varphi = 90°$) polarizations, i.e. its extinction ratio, is about 30. This mirror cannot be rotated which justifies the use of hwp2 to change the axis of the detected polarization.

Figure 3 shows the calibration of our polarizer. The harmonic 21 signal generated in argon is monitored as a function of the angle of the analyzing waveplate. The signal follows a $\cos^2(\varphi)$ modulation, characteristic of Malus' law. In the general case of an imperfect polarizer with extinction ratio A and XUV light polarized at an angle α from the probe laser pulse, the measured intensity follows:

$$I = I_0 \left(\cos^2(\varphi - \alpha) + \frac{1}{A} \sin^2(\varphi - \alpha) \right). \tag{1}$$

Here, the generating medium (argon) is isotropic, so that $\alpha = 0°$ (figure 1(a)). A fit of the experimental data allows us to determine the orientations of the analyzing waveplate that

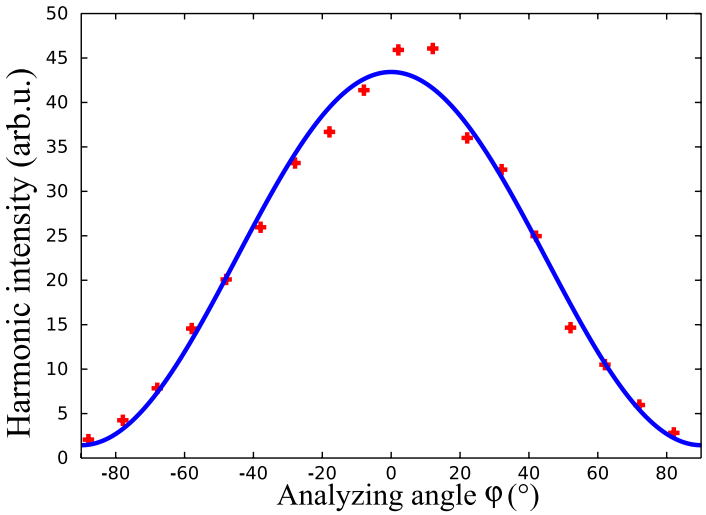


Figure 3. Evolution of the harmonic 21 intensity generated in argon as a function of the orientation of the analyzing waveplate $\varphi/2$. The red crosses are the experimental data points. The blue line is a fit using equation (1) which is used to calibrate the polarizer.

minimize and maximize the signal. They correspond to P and S polarizations, respectively. The measured extinction ratio of our polarizer is about 30 at this wavelength.

3. Polarization state of high harmonics from aligned nitrogen molecules

The polarization state of high harmonics in aligned molecules was recently measured [24], showing that when molecules are not parallel or perpendicular to the driving laser field the direction of the harmonic polarization can be tilted with respect to that of the probe laser. We have repeated these measurements in nitrogen with our experimental set-up.

We set the pump–probe delay to 4.1 ps (close to the half-rotational period of N_2) to maximize the degree of molecular alignment in the gas jet. For a given orientation of the aligning waveplate, we measure the harmonic intensity as a function of the orientation of the analyzing waveplate. A fit of the experimental data (similar to that shown in figure 3) allows us to extract the angle α, i.e. the direction of the harmonic polarization. We repeat this procedure for 15 orientations of the alignment waveplate, from -52.5° to 52.5°, which corresponds to molecular alignments from -105° to 105°

Figure 4 shows a polar plot of the experimental results. The radial dimension is the harmonic order, from 19 to 33. The polar angle is the molecular alignment angle θ with respect to the probe laser field. The colormap encodes the angle α between the harmonic polarization direction and the probe laser polarization. This picture is in qualitative agreement with previous experiments [24], even though the angles between the harmonic and laser polarizations are smaller in our measurements (between -2.5° and 2.5°). A remarkable feature appears when molecules are aligned around 30°: the polarization angle α changes sign from positive (red) to negative (blue) values. Around harmonic 25 the polarization angle is zero, which means that the harmonics are polarized parallel to the probe pulse polarization: the orthogonal component of the harmonic dipole is zero.

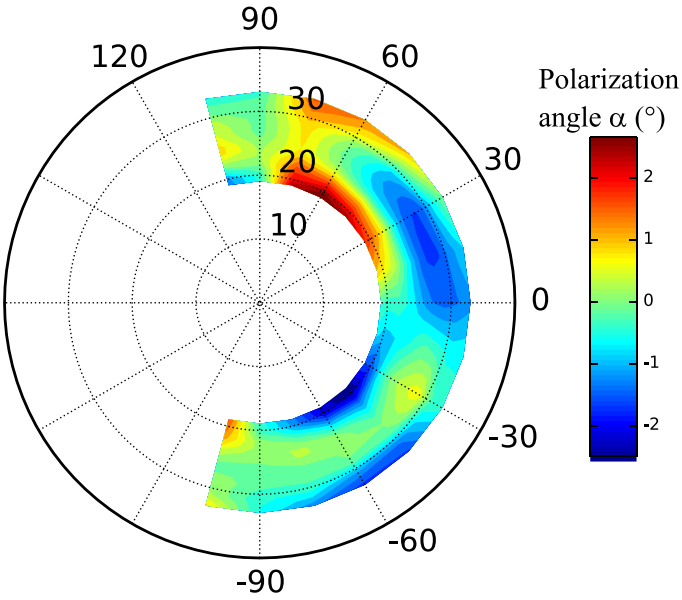


Figure 4. Polarimetry of high harmonic generation in aligned N_2. The colormap shows the angle α between the laser polarization and the harmonic polarization, in degrees. The radial direction is the harmonic order, from 19 to 33. The polar coordinate corresponds to the molecular alignment angle θ with respect to the probe laser field ($\theta = 0^\circ$ is along the horizontal direction).

At intermediate alignment, except around H25, the harmonic dipole has a non-zero orthogonal component. Our polarization resolved measurements are based on the detection of this component. We will focus on the region of the spectrum where the orthogonal component is maximum, i.e. on harmonics 19 and 21. In the case presented in figure 4, the angle α is about 2° and the orthogonal component is very small. This is certainly due to a poor degree of alignment in the experiment. The quality of alignment is very sensitive to the rotational temperature in the gas jet. This temperature can be decreased by adjusting the backing pressure, the nozzle aperture, and the distance between the laser focus and the nozzle. In figure 5, we present the evolution of the harmonic signal detected when $\varphi = 90^\circ$ (referred to as orthogonal signal) as a function of molecular alignment angle θ for harmonic 21, for optimized molecular alignment conditions. The orthogonal signal is maximum when molecules are aligned around 45° from the laser polarization. Therefore, we chose molecular alignments in this range for the polarization-resolved pump–probe spectroscopy. We estimate that in this case the harmonics polarization is around 18° from the laser polarization (the derivation of this value is given in the following section).

4. Pump–probe measurements in pure N_2

In order to illustrate the principle of polarization-resolved spectroscopy, we have performed a pump–probe study of high harmonic generation in rotationally excited nitrogen molecules. The evolution of the molecular alignment distribution around the half revival of N_2 is well known: the molecules are aligned parallel to the pump-laser polarization slightly before the half revival

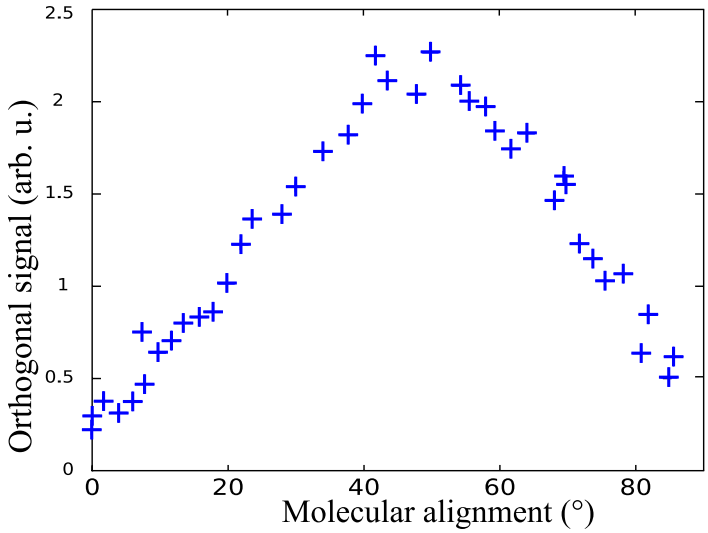


Figure 5. Evolution of the harmonic 21 orthogonal signal ($\varphi = 90°$) as a function of the molecular alignment angle θ.

and anti-aligned slightly after [22]. In addition, the pump pulse induces a slight permanent molecular alignment along its polarization, known as incoherent alignment.

We compare two situations. In what we refer to as the 'conventional situation', the pump and probe pulses have parallel polarization. The analyzing waveplate is set to maximize the reflection on the polarizer (S polarization). This configuration is very close to what would be obtained without any polarizer, since the parallel component of the harmonic field is always dominant. The evolution of the harmonic 21 signal with the pump–probe delay Δt is shown in figure 6(a). The average value of the signal between $\Delta t = 3.4$ ps and $\Delta t = 3.6$ ps is normalized to 1. In this range of delay the molecular alignment distribution is almost isotropic because the permanent alignment is weak at this pump intensity ($\langle \cos^2 \theta \rangle = 0.35$ while it is 0.33 for an isotropic distribution [19, 22]). The harmonic signal is maximum at $\Delta t = 4.1$ ps, when the molecules are aligned parallel to the laser polarization, and minimum at $\Delta t = 4.3$ ps, when the molecules are anti-aligned. The contrast in the detection of the alignment revival, defined as the ratio between the signal off and on the revival, is 2 (which is similar to what has been reported in other experiments).

In the second part of the experiment, we perform polarization-resolved spectroscopy. We rotate the aligning waveplate by 20°, so that the pump-pulse polarization is at 40° to the probe pulse polarization. In this configuration an orthogonal polarization component of the harmonic field can be generated by the molecules that are aligned. In order to detect this orthogonal signal, we rotate the analyzing waveplate by 45° ($\varphi = 90°$) so that the probe pulse is P polarized on the polarizer. The evolution of the harmonic intensity as a function of delay is shown in figure 6(a). The signal is normalized to one away from the revival. Before this normalization, the harmonic intensity is 30 times lower in this configuration than in the conventional configuration. When the molecules are aligned ($\Delta t = 4.1$ ps), the orthogonal polarization of the harmonic field goes through a maximum. The contrast in the detection of the molecular alignment is here 8: the implementation of polarization-resolved spectroscopy allows us to enhance the sensitivity by a factor 4. The contrast is set by the extinction ratio of the polarizer and could be further enhanced by increasing this extinction ratio.

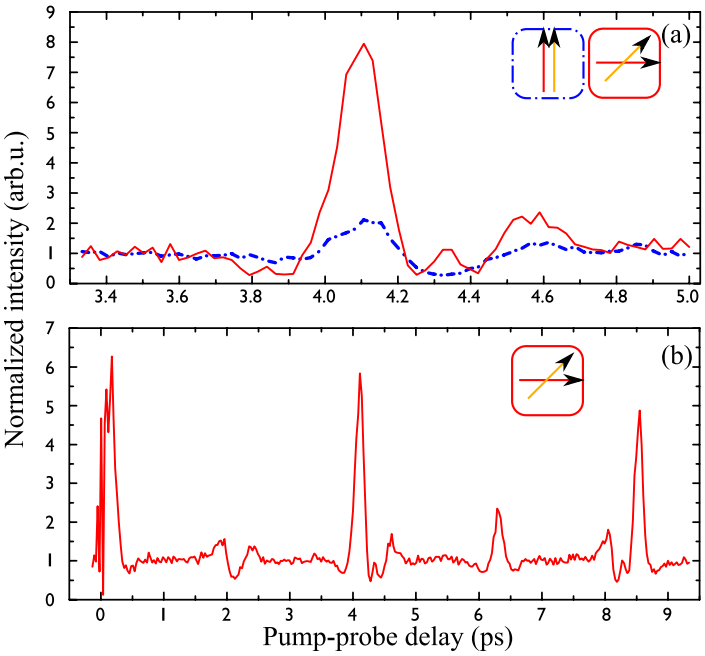


Figure 6. Pump–probe scans in N_2, with a pump intensity of $5 \times 10^{13}\,\mathrm{W\,cm^{-2}}$ and a probe intensity of $1.2 \times 10^{14}\,\mathrm{W \cdot cm^{-2}}$. (a) Evolution of the H21 signal as a function of pump–probe delay in two configurations. Conventional configuration (blue): the pump and probe pulse polarizations are parallel and the analyzing waveplate is rotated to maximize the reflection on the polarizer (S polarization). Polarization-resolved spectroscopy (red): the pump-pulse polarization is rotated by 40° with respect to the probe. The analyzing waveplate is rotated so that the probe pulse is P polarized on the polarizer. (b) Evolution of the H19 intensity as a function of pump–probe delay over a full-rotational period of N_2, in the polarization resolved spectroscopy configuration.

We can estimate the polarization angle α of harmonic 21 at the revival with respect to the probe pulse polarization by deriving the ratio of intensities on and off the revival $C = I_{\mathrm{on}}/I_{\mathrm{off}}$ from Malus' law (equation (1)). Off the revival, $I_{0,\mathrm{off}}$ is normalized to 1 and $\alpha = 0°$, i.e. $I_{\mathrm{off}} = 1/A$. On the revival, we observed in the 'conventional situation' that the total harmonic signal is doubled: $I_{0,\mathrm{on}} = 2$. Hence $C = 2A(\cos^2(90° - \alpha) + \frac{1}{A}\sin^2(90° - \alpha))$, yielding $\alpha \approx 18°$ for $A = 30$ and the observed contrast of $C = 8$.

The orthogonal signal presents a secondary maximum at $\Delta t = 4.3\,\mathrm{ps}$. This delay corresponds to the molecular anti-alignment. The molecules are then contained in a plane perpendicular to the pump-pulse polarization. These molecules can produce harmonic light polarized perpendicular to the probe pulse, which leads to a significant orthogonal harmonic signal.

Figure 6(b) presents a similar measurement for harmonic 19. The delay is, here, scanned over a full-rotational period of nitrogen. The orthogonal harmonic signal is peaked when the molecules are aligned around the full and half revivals. A significant modulation is also measured around quarter revivals, with a contrast that reaches 2 at the 3/4 revival. This shows that polarization-resolved pump–probe spectroscopy provides a sensitive characterization of the rotational wavepacket dynamics.

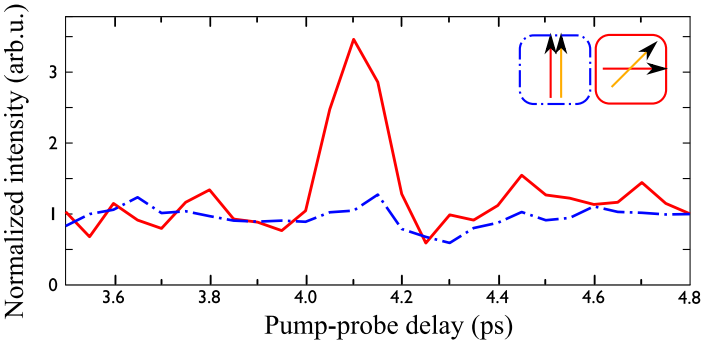


Figure 7. Pump-probe scans for H21 in a 50/50 mixture of argon and nitrogen, around the half revival of N_2. The blue line corresponds to the conventional configuration and the red line to the polarization-resolved configuration.

We have shown that polarization-resolved spectroscopy could be used to increase the contrast in the detection of alignment revivals in nitrogen. Performing complete polarimetric measurements as a function of the pump–probe delay would allow an additional contrast enhancement. Small variations of the polarization angle can be determined with a very high accuracy through the fits with the Malus' law (figure 4). Knowing the total harmonic signal, it is then possible to calculate the value of the orthogonal component of the harmonic field. In that case there is no background: the orthogonal component is zero if the polarization angle is zero. As soon as a small degree of molecular alignment exists, the polarization angle deviates and creates a non-zero orthogonal background. This method could be used to study subtle effects in the rotational wavepacket dynamics.

In the next section, we show that polarization-resolved pump–probe spectroscopy can be employed to detect revivals in a case where the total harmonic signal is dominated by a continuous background.

5. Detection of the alignment revival in an Ar–N_2 mixture

Polarization-resolved spectroscopy should be used to extract a signal generated by excited molecules from a strong background generated by non-excited molecules or by a carrier gas. In the particular case studied here, the rotational excitation is a very efficient process and the total harmonic signal is sufficient to detect the alignment revivals with a decent contrast. In order to study a less favorable case, we have performed a similar experiment in a mixture of argon and nitrogen.

The high harmonic signal generated in argon is typically about three times more important than the one produced in nitrogen under the same experimental conditions. In a 50/50 mixture, we expect the harmonic yield to be dominated by argon. Figure 7 (blue dashed-dotted line) shows the evolution of the harmonic 21 signal in the conventional configuration (parallel alignment and parallel polarization) as the delay is scanned around the half revival. The modulation of the harmonic signal induced by the evolution of the rotational wavepacket is hardly distinguishable. The red continuous line is the evolution of the orthogonal signal in the case of a pump polarization at 30° from the probe polarization. A clear maximum is observed at $\Delta t = 4.1$ ps. The polarization-resolved measurement allows us to detect the revival

of molecular alignment in the mixture with a contrast of 3.5, greatly improving the sensitivity of the measurement.

6. Conclusion

We have shown that polarization-resolved pump–probe spectroscopy could be used to study high harmonic generation from rotationally excited molecules. We have measured the state of polarization of high harmonics from aligned nitrogen molecules. We observe remarkable features, such as sign changes in the orthogonal component of the harmonic field. These features should be further analyzed, since the polarization of high harmonics was recently predicted to contain signatures of multielectron effects in the generation process [25].

In pump–probe scans, we have demonstrated an enhancement by a factor 4 of the contrast in the detection of alignment revivals in pure nitrogen. We have also shown that polarization-resolved measurements could be used to extract the signal from excited nitrogen molecules from a strong background generated by argon atoms. The contrast could be further enhanced by increasing the extinction ratio of our polarizer, e.g. by using several reflections on silver surfaces. The extension of this technique to other types of excitation is straightforward, as soon as the excited medium presents some anisotropy. This is thus an important step towards the investigation of molecular dynamics initiated by low cross-section processes.

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References

[1] Corkum P B 1993 *Phys. Rev. Lett.* **71** 1994
[2] Schafer K J, Yang B, DiMauro L F and Kulander K C 1993 *Phys. Rev. Lett.* **70** 1599
[3] Paul P M, Toma E S, Breger P, Mullot G, Augé F, Balcou Ph, Muller H G and Agostini P 2001 *Science* **292** 1689
[4] Mairesse Y *et al* 2003 *Science* **302** 1540
[5] Hentschel M *et al* 2001 *Nature* **414** 509
[6] Kienberger R *et al* 2004 *Nature* **427** 817
[7] Sola I J *et al* 2006 *Nat. Phys.* **2** 319
[8] Sansone G *et al* 2006 *Science* **314** 443
[9] Zeidler D, Bardon A B, Staudte A, Villeneuve D M, Dörner R and Corkum P B 2006 *J. Phys. B: At. Mol. Opt. Phys.* **39** L159
[10] Levesque J, Zeidler D, Marangos J P, Corkum P B and Villeneuve D M 2007 *Phys. Rev. Lett.* **98** 183903
[11] Itatani J, Levesque J, Zeidler D, Niikura H, Pépin H, Kieffer J C, Corkum P B and Villeneuve D M 2004 *Nature* **432** 867
[12] Kanai T, Minemoto S and Sakai H 2005 *Nature* **435** 470
[13] Vozzi C *et al* 2005 *Phys. Rev. Lett.* **95** 153902
[14] Lein M 2005 *Phys. Rev. Lett.* **94** 053004

[15] Baker S, Robinson J S, Haworth C A, Teng H, Smith R A, Chirila C C, Lein M, Tisch J W G and Marangos J P 2006 *Science* **312** 424
[16] Wagner N, Wuest A, Christov I, Popmintchev T, Zhou X, Murnane M and Kapteyn H 2006 *Proc. Natl Acad. Sci.* **103** 13279
[17] Levenson M D 1982 *Introduction to Nonlinear Laser Spectroscopy* (New York: Academic)
[18] Mukamel S 1995 *Principles of Nonlinear Optical Spectroscopy* (New York: Oxford University Press)
[19] Mairesse Y, Zeidler D, Dudovich N, Spanner M, Levesque J, Villeneuve D M and Corkum P B submitted
[20] Rosca-Pruna F and Vrakking M J J 2001 *Phys. Rev. Lett.* **87** 153902
[21] Stapelfeldt H and Seideman T 2003 *Rev. Mod. Phys.* **75** 543
[22] Dooley P W, Litvinyuk I V, Lee K F, Rayner D M, Spanner M, Villeneuve D M and Corkum P B 2003 *Phys. Rev.* A **68** 023406
[23] Antoine P, Carré B, L'Huillier A and Lewenstein M 1997 *Phys. Rev.* A **55** 1314
[24] Levesque J, Mairesse Y, Dudovich N, Pépin H, Kieffer J-C, Corkum P B and Villeneuve D M 2007 *Phys. Rev. Lett.* **99** 243001
[25] Zhao Z, Yuan J and Brabec T 2007 *Phys. Rev.* A **76** 031404