

## Revival Structures of Linear Molecules in a Field-Free Alignment Condition as Probed by High-Order Harmonic Generation

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Revival structures (rotational coherence) of three linear molecules ( $N_2$ ,  $O_2$ , and  $CO_2$ ) in a field-free alignment condition have been investigated using high-order harmonic generation. The harmonic yields of these molecules were measured in a pump-probe manner by using a weak femtosecond (fs) laser pulse for field-free alignment of molecules and another intense fs laser pulse for harmonic generation. The harmonic intensities from 23rd to 29th order with respect to the time delay between the pump and the probe pulses showed revival structures in the condition of a field-free alignment of molecules. While the revival structure of a  $N_2$  molecule had one-fourth the period of the full revival time and different degrees of modulation among different fractional revival times, the revival structures of  $O_2$  and  $CO_2$  molecules showed one-eighth the periods of the full revival time and similar degrees of modulation among all fractional revival times. The revival structures could be interpreted in terms of the nature of the highest occupied molecular orbital and the total nuclear spin.

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### I. INTRODUCTION

Interaction of intense laser fields with atoms or molecules generates high-order harmonics [1–4]. High-order harmonic generation (HHG) has been a major topic of strong-field physics due to its potential as an extreme ultraviolet (XUV) source and to the generation of attosecond pulses [5]. While the HHG process from atoms [5] has been intensively studied, HHG from molecules has not received much attention until recently, in part due to molecular systems being more complicated than atomic systems. Particularly, the evidence for quantum interference of electron de Broglie waves [6] and the possibility of revealing the molecular geometry [7] have been demonstrated by measuring HHG from molecules. In these studies, the field-free alignment of molecules using a rotational wave packet was an important tool for applications of HHG from molecules because

it showed the ability of intense laser pulses to control molecular alignment [8]. To understand the field-free alignment of molecules further, we need to study the interaction between molecules and an intense laser electric field [9–11] and the quantum phenomena associated with rotational wave-packet dynamics [12].

The alignment of molecules along a linearly polarized laser electric field can be of two types - adiabatic and nonadiabatic (field-free) [9]. In the adiabatic alignment, molecules can exhibit a classical rotational motion in the presence of a weak, but temporally-long, aligning laser field. The dipole induced due to the interaction between the laser field and molecules causes molecules to align in the direction of the laser polarization. Field-free molecular alignment is a fundamentally different process, in which rotational wave packets of molecules created by applying an intense femtosecond laser pulse can dynamically rotate their molecular axes after the laser pulse under a field-free condition. Molecules repeatedly align at the periods of a certain revival time. In contrast to adiabatic alignment, field-free alignment is a purely quantum effect, and its process is more complex and peculiar.

In this paper, we report on the revival structures

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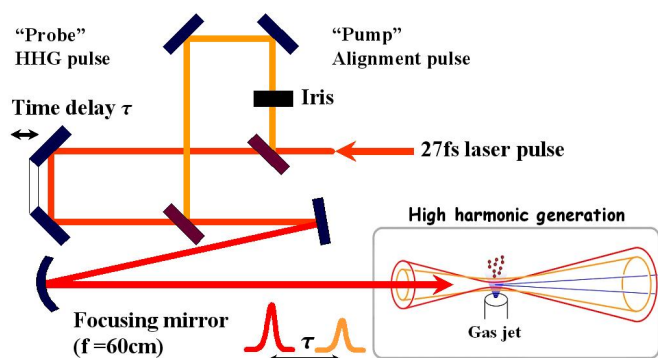


Fig. 1. Schematic of the pump-probe experimental setup for harmonic generation from aligned molecules.

of three linear molecules ( $N_2$ ,  $O_2$ , and  $CO_2$ ) observed from HHG induced by femtosecond laser pulses under field-free alignment condition. The high-order harmonic yields of these molecules are measured in a pump-probe manner: a weak first pulse is used to trigger field-free time-dependent dynamic alignment of molecules, and a second intense laser pulse produces high-order harmonics at a specific time-delay between the aligning and the harmonic-generating laser pulses. The revival structure contains information on the orientations of molecular axes and can be directly observed with an imaging technique, such as a Coulomb explosion [13,14]. It can also be observed in the evolution of the harmonic intensity because it is sensitive to the molecular orientation with respect to the laser field. The harmonic intensities from the 23rd to the 29th orders with respect to the time delay between the pump and the probe pulses were measured to investigate revival structures in the field-free alignment condition of molecules. Experimental findings in this work show that the characteristics of revival structures of molecules strongly depend on the molecular properties.

## II. EXPERIMENTAL CONFIGURATION

HHG from aligned linear molecules was performed in a pump-probe geometry. In our experimental setup shown in Fig. 1, the output from a femtosecond chirped-pulse-amplification Ti:sapphire laser operating at 10 Hz was split into two beams, used as pump and probe pulses, in the configuration of a Michelson-type interferometer. The laser output had a pulse width of 27 fs and a spectral bandwidth of 42 nm centered at 820 nm. The time delay between the two pulses was controlled by adjusting the path length of one arm. The beam splitter divided the incident laser pulse into two pulses of equal intensities. For the pump pulse, an iris was used to control its intensity. The resulting pump pulse was used to create rotational wave packets and to induce field-free molecular alignment. A probe pulse with a time delay with respect to

the pump pulse generated harmonics from the molecules. The two pulses were recombined collinearly with parallel polarizations. The two laser pulses were focused together into a gas jet by using a spherical mirror ( $f = 600$  mm). A jet of molecules was produced by using a 500- $\mu$ m-diameter nozzle (General Valve) with a backing pressure of 1.5 atm. The molecular gas jet perpendicularly intersected the laser pulses. HHG occurred within the intersecting volume of aligned molecules because the aligning beam had a larger beam waist due to a smaller f-number. The emitted harmonics were detected using a flat-field extreme ultraviolet (XUV) spectrometer equipped with a back-illuminated X-ray charge-coupled device (CCD; Princeton Instruments). This XUV spectrometer could monitor several harmonics simultaneously, which was advantageous compared to a monochromator that can detect one harmonic at a time. Typically 100 shots were accumulated on the CCD camera to obtain one image. Harmonic spectra without the pump pulse were continually monitored and subtracted from those obtained with laser pulses in order to compensate for the drift of laser conditions.

## III. CHARACTERISTICS OF REVIVAL STRUCTURE

The field-free alignment technique used for molecular alignment is essential to investigate the revival structure of molecules. A sufficiently short and intense pulse gives a ‘kick’ to molecules [9] and induces a sudden alignment. In this process, a rotational wave packet (coherent superposition of rotational states) of a molecule is excited, which rotates freely with regular recurrence of the original aligned distribution due to the nature of rotational states. As time goes on, the wave packet eventually begins to rephase. When the accumulated phase of each state reaches multiples of  $2\pi$ , the molecular alignment is reproduced. These phenomena are well known as the full revival of molecular alignment or rotational coherence. Within the full revival time, fractional revivals in which the wave packet partially rephases can occur. To characterize the degree of alignment and the revival structure as functions of the time delay between pump and probe laser pulses, we measured and analyzed the high-order harmonic intensities from the 23rd to the 29th order from linear molecules.

We first investigated harmonic spectra with different laser chirps by changing the distance between the compression gratings. The harmonic spectra obtained by varying the laser chirp from negatively chirped 54 fs to positively chirped 85 fs are shown in Fig. 2. For the chirp-free 27 fs case, the harmonic spectrum exhibits a double-peaked structure that typically comes from the contributions of the short and the long trajectories. In the case of the negatively chirped 54 fs pulse, the harmonic spectrum is broader than it is in

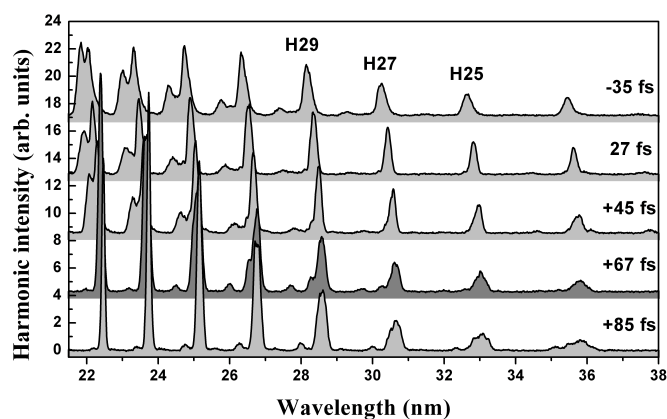


Fig. 2. High-order harmonic spectra from  $N_2$  molecules obtained by varying the laser chirp. The chirp-free pulse duration was 27 fs. '+' and '-' in front of pulse duration mean positively chirped and negatively chirped pulses, respectively.

the chirp-free case. On the other hand, the harmonic spectra are sharper with positively chirped pulses, giving the sharpest harmonics with the positively chirped 67 fs pulse. At relatively low laser intensity ( $\leq 10^{14}$  W/cm<sup>2</sup>), dominant harmonic chirp comes from the negative harmonic chirp formed in the leading edge of a rapidly increasing laser field. Thus, high-order harmonics became spectrally sharp and strong when the positively chirped laser pulse compensated for the negative harmonic chirp. Consequently, for pump and probe experiments, positively chirped 67 fs pulses were used with intensities of  $4 \times 10^{13}$  W/cm<sup>2</sup> and  $1 \times 10^{14}$  W/cm<sup>2</sup> for the aligning and the harmonic-generation pulses, respectively.

For the investigation of the revival structures of the rotational wave packets in the three linear molecules  $N_2$ ,  $O_2$ , and  $CO_2$ , the intensity ratios between harmonics taken with and without the aligning pulse were measured for a range of the time delays between the aligning and the harmonic-generation pulses. The progression of the intensity ratios of the 23rd – 29th order harmonics from  $N_2$  molecules with respect to the time delay between the pump and the probe pulses is shown in Fig. 3. The inset in Fig. 3 shows the revival structure of the 29th harmonic for three periods. The intensity ratio just before  $t = 0$  drops rapidly due most likely to destructive interference between the pump and the probe pulses. Just after  $t = 0$ , the aligning pulse creates a rotational wave packet, which exhibits maximum field-free alignment at  $t = 0.13$  ps. The harmonic intensity ratio progression repeats after a full revival time ( $T = 8.4$  ps). The intensity ratio modulates at a period  $\approx 2$  ps, a quarter of the full revival time. The time duration between the maximum and the minimum peaks of the intensity ratio at the fractional revival time is  $\approx 0.4$  ps. During this time, the orientation of the molecular axis changes by 90 degrees; the rotational wave packet of molecules aligns in a direction parallel or perpendicular to the laser polarization axis. Intuitively, the free electron tunneling through the

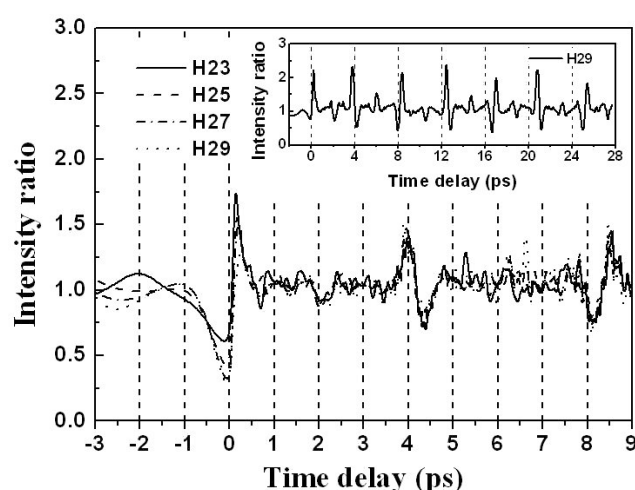


Fig. 3. Progression of the 23rd – 29th harmonic intensity ratios with and without the pump pulse from  $N_2$  molecules with respect to the time delay between the pump ( $4 \times 10^{13}$  W/cm<sup>2</sup>, +67 fs) and probe pulses ( $1 \times 10^{14}$  W/cm<sup>2</sup>, +67 fs). The inset shows the revival structure of the 29th harmonic for three periods.

potential barrier of a molecule has the highest (lowest) probability of returning to the nucleus of the molecule when the molecular axis is parallel (perpendicular) to the laser polarization. In explosion experiments done for molecular imaging, the ion distribution of molecules at a fractional revival time shows an agreement with such a phenomenon [15,16]. The degrees of modulation at 4 ps and 8 ps in Fig. 3 are much stronger than those at 2 ps and 6 ps. Revival structures in the vicinity of  $T/4$  and  $T/2$  have reverse amplitudes of those in the vicinity of  $3T/4$  and  $T$ . For example, at  $T/2$ , an up-down temporal trend appears whereas near the time delay  $T$ , a down-up trend turns up. Thus, the fractional revival structures exhibit inverse symmetry with a half period of the full revival time.

The full revival time of a molecule can be estimated from the formula  $T = 1/(2B_0c)$ , where  $B_0$  is the ground-state rotational constant and  $c$  is the speed of light. The rotational constant is inversely proportional to the moment of inertia, which corresponds to effective mass times the distance between atoms in a diatomic molecule. According to the formula, a molecule rotates more slowly when it has a smaller rotational constant. In other words, a larger molecule has a longer revival time. For  $N_2$ ,  $B_0 = 1.99$  cm<sup>-1</sup>, for  $O_2$ ,  $B_0 = 1.44$  cm<sup>-1</sup>, and for  $CO_2$ ,  $B_0 = 0.39$  cm<sup>-1</sup>. Thus, the full revival times of  $O_2$  and  $CO_2$  are 11.6 ps, and 42.7 ps, respectively. The full revival times of  $O_2$  (11.5 ps) and  $CO_2$  (43 ps) as measured from Figs. 4 and 5, respectively, show good agreement with the calculated full revival times.

The revival structure of  $O_2$  molecules with respect to the time delay is shown in Fig. 4. Compared to that of  $N_2$  molecules, the revival structure has distinct differences in the number of fractional revivals within a full re-

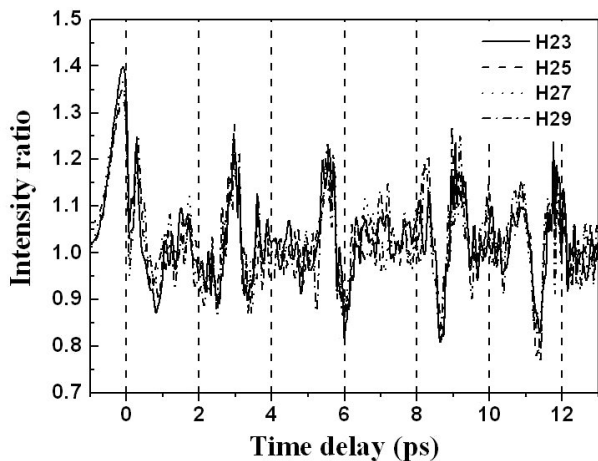


Fig. 4. Progression of the 23rd – 29th harmonic intensity ratios with and without the pump pulse from  $O_2$  molecules with respect to the time delay between the pump ( $4 \times 10^{13}$  W/cm<sup>2</sup>, +67 fs) and probe pulses ( $1 \times 10^{14}$  W/cm<sup>2</sup>, +67 fs).

vival time and in the degree of modulation near a quarter of the full revival time. That is, the number of fractional revivals in a full revival time is 8 in  $O_2$  whereas it is 4 in  $N_2$ , and the degree of modulation is stronger near a quarter of the full revival time in  $O_2$  whereas it is stronger at half the full revival time in  $N_2$ . In the following, we discuss the potential origins for these differences.

First, the highest occupied molecular orbital (HOMO) of  $O_2$  molecules is the  $\pi_g$  orbital, but HOMO of  $N_2$  molecules is the  $\sigma_g$  orbital. While the  $\pi_g$  orbital is anti-bonding and has  $\pi/2$  rotational symmetry in space, the  $\sigma_g$  is bonding and has  $\pi$  rotational symmetry. The HOMO affects the number of fractional revivals within the full revival time. For  $O_2$  molecules, fractional revivals occur with one-eighth the period of the full revival time, but the degrees of modulation at  $T/8$ ,  $3T/8$ ,  $5T/8$  and  $7T/8$  are much smaller than they are at the other fractional revival times. As we stated above, for  $N_2$  molecules, fractional revivals occur four times within a full revival time. Another origin for this different number of fractional revivals between  $N_2$  and  $O_2$  molecules can be attributed to the total nuclear spin of the molecules [15].  $N_2$  molecules can take values of 0, 1, and 2 for the total nuclear spin, but  $O_2$  molecules can have only 0, which determines the possible rotational wave number  $J$  of the states that rephase partially. In comparison with  $N_2$  molecules, the degree of modulation of  $O_2$  at  $T/4$  and  $3T/4$  is similar to that of the  $T/2$  and  $T$  revivals. The behavior in which the degree of modulation at  $T/8$  is much smaller than that at  $T/4$  corresponds to different quantum-mechanical states of alignment at the two fractional revivals. In the case of  $CO_2$ , the evolution of the harmonic intensity with respect to the time delay, shown in Fig. 5, is similar to that of  $O_2$  except for the intensity ratio. The alignment process of a  $CO_2$  molecule can be comparable to that of  $O_2$  since the HOMO of a  $CO_2$

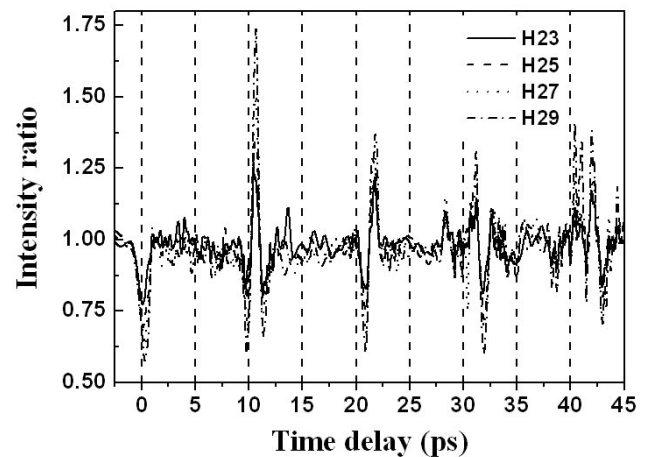


Fig. 5. Progression of the 23rd – 29th harmonic intensity ratios with and without the pump pulse from  $CO_2$  molecules with respect to the time delay between the pump ( $4 \times 10^{13}$  W/cm<sup>2</sup>, +67 fs) and probe pulses ( $1 \times 10^{14}$  W/cm<sup>2</sup>, +67 fs).

molecule is dominated by two  $p$  orbitals of two O atoms.

For  $N_2$ , the intensity ratio around the time zero is modulated from 0.3 to 1.7. The modulation ratios of  $O_2$  and  $CO_2$  are smaller than that of  $N_2$ . This can be attributed to the ionization rate of the molecules. Since the HOMO of the  $N_2$  molecule is the  $\sigma_g$  orbital, it has a maximum electron density along the direction of the internuclear axis. The ionization rate is maximal when the molecular axis of the  $N_2$  molecule is aligned along the laser polarization direction [17]. For  $O_2$  and  $CO_2$ , the ionization rates are minimal when their molecular axes are aligned along the laser polarization because their HOMOs have a node in the direction of the molecular axis. At the peaks of the  $N_2$  revival structure, molecules are aligned parallel to the laser polarization. Thus, for  $N_2$ , the intensity ratio at fractional revival times changes very much from the minimum to the maximum when compared to those of  $O_2$  and  $CO_2$  molecules.

#### IV. CONCLUSIONS

We have investigated the progression of the harmonic intensities from the 23rd to the 29th orders with respect to the time delay between the aligning pulse and the harmonic-generation pulse for three linear molecules aligned by a field-free alignment technique. In the molecules, the modulation of the harmonic intensity at fractional revival times was clearly shown, but its tendency was different for different molecules. For  $N_2$ , the intensity modulation due to alignment occurred at one-fourth the period of the full revival time. The degree of modulation at half full revival time ( $T/2$ ) was stronger than that at  $T/4$  and  $3T/4$ . In the cases of  $O_2$  and  $CO_2$ , the intensity modulation had a period of  $T/8$ , and degrees of modulation at every quarter full revival time

were similar to each other. These differences in the intensity modulation were explained in terms of the molecular properties, such as the nature of the HOMO and molecule's total nuclear spin.

The revival structures of molecules probed by using high-order harmonics agree well with the molecular orientations and the angular distributions obtained by using Coulomb explosion experiments. The sensitivity and the modulation ratio from the high-order harmonics were as strong as those from other techniques. Thus, the method using HHG is well qualified to be an important tool for observing the revival structures of molecules.

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