Angular Dependence of High-order Harmonic Generation from Nonadiabatically Aligned Molecules

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We measured the dependence of high-order harmonic generation (HHG) on the angle \( \alpha \) between polarization directions of high-intensity femtosecond laser pulses in the pump and probe experiment. The experimental results of \( \text{N}_2 \) and \( \text{O}_2 \) are compared with the calculated ones using the theory developed recently to illustrate the characteristic properties of HHG from aligned \( \text{N}_2 \) and \( \text{O}_2 \), and then the excellent agreement is obtained. It is also shown that the observed \( \alpha \)-dependent harmonic signal is strongly influenced by the degree of alignment of molecules and is not identical to the harmonic distribution calculated as a function of the angle between the field direction and the molecular axis.

**Key Words:** High order harmonic generation, Molecular alignment, Femtosecond laser pulse, Angular dependence

1. Introduction

An intense ultrashort laser pulse is able to coherently align molecules in gas phase. When the pulse duration is shorter than the rotational period of a molecule, the transient alignment of molecules is induced by the formation of a rotational wave packet after the interaction between the laser pulse and molecules. The molecular alignment occurs recurrently as long as relaxation processes of the wave packet can be ignored. There have been considerable interests in this field-free molecular alignment, because it provides a promising and versatile way to control molecules with an external optical field in applications to photochemistry and/or molecular engineering.\(^{1,2}\)

Recently we reported that the temporal evolution of the field-free dynamics of molecular alignment can be observed using high-order harmonic generation (HHG) at a high sensitivity.\(^{4,5}\) This demonstrated that one can control the HHG process with aligned molecules and also examine the molecular structure by observing the nonlinear optical response of aligned molecules. Then much attention was focused on the HHG in the experimental studies\(^{6-10}\) as well as theoretical\(^{11-16}\) in a variety of fields of molecular science.

It has been observed so far that the HHG from aligned molecules depends on the angle between the molecular axis and the laser field direction\(^{5,6,8,10,13}\). This indicates that the nonlinear optical response of a molecule is strongly affected by the angular distribution of the highest occupied molecular orbital (HOMO) and/or the electron distribution in a molecule. However, the physical property is not understood well due to the lack of the theory to describe the angle-dependent interaction process.

In the present work, we measured the HHG efficiency for \( \text{N}_2 \) and \( \text{O}_2 \) molecules as a function of the angle between the laser polarization directions in the pump and probe experiment. The results are compared with those calculated with the recently developed theory\(^{15,16}\) to demonstrate the validity of the theory and to see the effects of the HOMO symmetry or the molecular structure on the HHG.

2. Theory

Let us define the orientation of a molecular axis by a polar angle \( \theta \) and an azimuth angle \( \phi \). In the pump and probe experiment, nonresonant linearly polarized pump and probe fs laser pulses are considered to be collinearly incident on the molecule along the \( y \) direction. The pump field \( \mathbf{E}_1 \) is fixed along the \( z \) direction, and the probe field \( \mathbf{E}_2 \) makes an angle \( \alpha \) with respect to the \( z \) axis and the relative angle \( \theta' \) to the molecular axis. The pump pulse nonadiabatically forms a rotational wave packet to align molecules, and the probe pulse delayed by a time \( \Delta t \) from the pump generates high-order harmonic radiation from the field-free aligned molecules.

The rotational wave packet evolving from the initial state \( |J_0 M_0> \) is described as

\[
|\Phi_{J_0 M_0}(t)\rangle = \sum_{n} C_{J_0 M_0}^{M_n}(t) |J M_n> \exp\left(-i\frac{E_i}{\hbar} t\right),
\]

where \( |J M_n> \) is the rotational state having the eigenenergy \( E_j \) with the rotational quantum number \( J \) and its projection \( M_n \). The coefficients \( C_{J_0 M_0}^{M_n}(t) \) are determined by solving the Schrödinger equation for the rotational motion, and it remains constant after the interaction between the pump pulse and molecules\(^{17,18}\)

Using the HOMO and Volkov wavefunctions, the expectation value of the dipole operator can be evaluated from Eq. (1), and then the HHG operator \( T^{(n)}(\theta, \phi, \alpha) \) is defined by using the expectation value.\(^{11}\) Using \( T^{(n)} \), the \( n \)-th harmonic signal from aligned molecules is given as\(^{15,16}\)

\[
S^{(n)}(\lambda; \alpha) = \sum_{\lambda'} \rho(J_0) |\Phi_{J_0}(\Delta \tau)\rangle T^{(n)}(\theta, \phi, \alpha) \langle \Phi_{J_0}(\Delta \tau)| \delta(\lambda - \lambda')(\lambda)| \lambda'\rangle
\]

The Boltzmann average over the rotational temperature \( T_{\text{rot}} \) is taken into account in \( \rho(J_0) \).

At \( \alpha = 0^\circ \), the dynamic HHG signal for \( \text{N}_2 \) is derived from Eq. (2):

\[
S^{(n)}(\lambda; 0) = \rho(\lambda) + \rho(\lambda) + \rho(\lambda) + \rho(\lambda) + \rho(\lambda) + \rho(\lambda)
\]

(3)
and similarly the signal of O\textsubscript{2} is written as

\[ S^{(N)}(\Delta, \alpha) = a_1\cos^2 \alpha \cos \Delta + a_2\sin^2 \alpha \cos \Delta, \]

where the inner and outer brackets in \langle \langle \cos^2 \theta \rangle \rangle stand for the expectation value calculated by Eq. (1) and for the Boltzmann distribution, respectively, and the coefficients \(a_1\) and \(a_2\) are related to \(T^{\text{rot}}\).

Setting \(\theta = 0\) in Eqs. (3) and (4) we obtain the harmonic signal of the probe pulse. Substituting the relation, \(\cos \theta = \cos \alpha \pm \sin \alpha \cos \alpha\), into Eq. (3) and taking only the first and second terms on the right-hand side, we approximate the \(\alpha\)-dependent harmonic signal in N\textsubscript{2}:

\[ S^{(N)}(\Delta, \alpha) = p_1 + p_2 \frac{1}{2} \sin^2 \alpha + \cos \alpha - \frac{1}{2} \sin^2 \alpha \langle \langle \cos \theta \rangle \rangle_{\Delta}, \]

(5)

Similarly, the main term for O\textsubscript{2} is derived from the first term of Eq. (4):

\[ S^{(O)}(\Delta, \alpha) = a_1(\Delta) + b(\alpha) + C(\alpha) \langle \langle \cos \theta \rangle \rangle_{\Delta}, \]

(6)

where \(A(\alpha) \sim F(\alpha)\) are the functions of \(\alpha\).

Equations (3) – (6) as functions of \(\theta\) and \(\alpha\) provide the harmonic signal per molecule, taking into account the statistical average of harmonic emission probabilities for an ensemble of molecules.\(^{10,45}\) Here we measured the harmonic signal for different \(\alpha\) and compared the results with those calculated using the theory, noting the difference between the physical meanings of \(\theta\) and \(\alpha\).

3. Experiment

The experimental setup used was the same as in our recent work.\(^{4,5}\) Briefly, the pump pulse \(E_1\) and the probe pulse \(E_2\) were produced with a Ti:sapphire laser chirped-pulse amplification system operating at a repetition rate of 10 Hz. The maximum output pulse energy is 40 mJ in 40 fs at 800 nm, producing a peak power of 1 TW. After a time delay \(\Delta t\) was produced between \(E_1\) and \(E_2\), the two pulses were recombined collinearly and focused with a 500 mm focal-length lens into a pulsed molecular gas jet. The interaction length in the gas jet was ~1 mm. The \(n\)-th harmonic radiation was detected by an electron multiplier mounted on a vacuum ultraviolet monochromator, and the signal was processed by a boxcar averager, converted to the digital signal with an A/D converter and stored on a personal computer. The probe pulse polarization was fixed to the direction along the entrance slit of the monochromator to maintain a constant diffraction efficiency,\(^{10}\) while the pump polarization was rotated.

4. Results and Discussion

4.1 N\textsubscript{2} molecule

Figure 1 shows the time-dependent 19th harmonic signal observed for N\textsubscript{2} as a function of \(\Delta t\) for \(\alpha = 0^\circ\) and the 19th harmonic signal \(S^{(N)}(\Delta)\) calculated by the leading term \(p_1 \langle \langle \cos^2 \theta \rangle \rangle_{\Delta}\) in Eq. (3) under the same condition as the experiment. In the calculation for N\textsubscript{2}, we used the rotational constant \(B = 1.99 \text{ cm}^{-1}\), from which a revival period \(T_{\text{rev}} = 1/(2Bc)\) is calculated to be 8.3 ps, and a constant value of \(p_1\) so as to fit the result to the experimental. The rotational temperature was set at \(T_{\text{rot}} = 100 \text{ K}\), since this value reproduced the frequency spectrum of \(S^{(N)}(\Delta)\) having the peak at the same \(\Delta\) as that in the experimental. As shown in Fig.1, the leading term \(p_1 \langle \langle \cos^2 \theta \rangle \rangle_{\Delta}\) in Eq. (3) can reproduce well the time-dependent 19th harmonic signal. This corresponds to the fact that the temporal change in \(\eta\) is in accordance with the time-dependent harmonic signal of N\textsubscript{2}.\(^{4,5,9}\)

In Fig.2(a) we show the time-dependent 19th harmonic signals observed around \(\Delta t = T_{\text{rev}}/2\) at different angles \(\alpha\). As \(\alpha\) increases from \(\alpha = 0^\circ\), the modulation at \(\Delta t \sim T_{\text{rev}}/2\) decreases and almost disappears at \(\alpha \sim 55^\circ\). With a further increase in \(\alpha\), the signal modulation is inverted in phase and monotonously increases to be peaked at \(\alpha = 90^\circ\).

In Fig.2(b) the signal modulations \(S_1 - S_0\) (solid circle) and \(S_2 - S_0\) (open circle) are plotted as a function of \(\alpha\), which are derived from the result shown in Fig.2(a), where \(S_1\) and \(S_2\) are the maximum and the minimum of the harmonic signal at \(\Delta t \sim T_{\text{rev}}/2\), and \(S_0\) is the mean value of the background signal, as illustrated in the inset of Fig.2(b). Each point is the averaged value of data at \(\alpha\) and \(-\alpha\). In Fig.2(b), the solid and dotted lines represent the corresponding modulations calculated with Eq. (5), where \(p_2\) is given for reproducing the experimental result. The calculated results are in excellent agreement with the experimental ones. The maximum modulation signals are obtained by setting \(\sin \alpha = 0\), \(\cos \alpha = 1\) at \(\alpha = 0^\circ\) and \(\sin \alpha = 1\), \(\cos \alpha = 0\) at \(\alpha = 90^\circ\). Furthermore, it is noted that the calculated signal phase is also reversed at \(\alpha \sim 55^\circ\). These characteristic features of HHG in aligned N\textsubscript{2} molecules are reproduced with only the leading term in Eq.(3).

Thus, the present results for aligned N\textsubscript{2} molecules demonstrate the validity of Eq.(5) to confirm that the harmonic yield is maximized (minimized) with the field parallel (perpendicular) to the molecular axis, as discussed in the previous works.\(^{4,7,11,12}\)

4.2 O\textsubscript{2} molecules

Figure 3 shows the time-dependent 19th harmonic signal observed for O\textsubscript{2} as a function of \(\alpha = 0^\circ\) and the signal calculated by the leading term \(q_1 \langle \langle \cos^2 \theta \rangle \rangle_{\Delta}\) in Eq. (4) under the same condition as in the experiment. The calculation was performed in the same way as for N\textsubscript{2}, where \(T_{\text{rot}} = 200 \text{ K}\) and \(B = 1.44 \text{ cm}^{-1}\) were used for O\textsubscript{2}. The calculated result is in good agreement with the experimental one. It has empirically been known so far that the time-dependent
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While of the asymptotic wavefunctions of HOMO $20)$ and the electron density distribution of the orbital of O$_2$ are quite different from that of the $\sigma_g$ of N$_2$, and then the theory predicts that the angle-dependent HHG almost follows the electron distribution of the HOMO. However, the $\alpha$-dependent harmonic signals observed for aligned O$_2$ molecules are very similar to those for N$_2$, as seen in Figs. 2 and 4.

To see the origin of this similarity, we calculated the square of the asymptotic wavefunctions of HOMO$^{29}$ and the $\theta$-dependent HHG signal from a single N$_2$ and O$_2$ molecule.

Theoretical studies have shown so far that the harmonic signal observed for O$_2$ is reproduced well by $<\sin^2\theta><\Delta \alpha>^{5,7,8}$ Equation (4) make the origin of this empirical law clear, since $<\cos^2\theta> = 1$ and $<\sin^2\theta> = 1$ in Eqs. (5) and (6) for a molecule. The results are shown in Fig. 5(a). For comparison, in Fig. 5(b) we plot the measured and calculated $\alpha$-dependent signal modulations $S_1 - S_0$ and $S_2 - S_0$ in polar coordinates, using the data shown in Figs. 2(b) and 4(b). As seen in Fig. 5(a), the electron density in a single N$_2$ and O$_2$ molecule is peaked in the direction of $\theta = 0^\circ$ and $\theta \sim 45^\circ$, respectively, and the angle-dependent harmonic signal is subject to the electron density distribution in a molecule.

For N$_2$ molecules, $S_1 - S_0$ are maximized and $S_2 - S_0$...
The degree of alignment estimated from the measurements is \( \eta = 0.55 \) at \( \Delta t = 4.10 \text{ ps} \) for the peak of \( S_1 \) and \( \eta = 0.22 \) at \( \Delta t = 4.33 \text{ ps} \) for the minimum of \( S_2 \). Considering \( \eta = 1/3 \) for randomly oriented molecules, the estimated values of \( \eta \) for \( N_2 \) suggest that the degree of alignment is rather weak. Nevertheless, the results shown in Fig.5(b) indicate that the \( \alpha \)-dependent harmonic generation from the partially-aligned \( N_2 \) is strongly dominated with the HOMO of a single molecule. This result for \( N_2 \) reconciles with the previous theoretical \(^{1,2} \) and experimental results. \(^{10} \)

For \( O_2 \), \( \eta \) was estimated to be \( \eta = 0.48 \) at \( \Delta t = 5.70 \text{ ps} \) for the \( S_1 \) peak and \( \eta = 0.23 \) at \( \Delta t = 5.91 \text{ ps} \) for the \( S_2 \) minimum. These values of \( \eta \) are comparable with those for \( N_2 \). However, the \( \alpha \)-dependent HHG observed for \( O_2 \) molecules is significantly different from the calculated result as a function of \( \theta \), as seen in Figs.5(a) and (b), and rather similar to that for \( N_2 \). The observed \( \alpha \)-dependence shows that the \emph{partially aligned} \( O_2 \) molecules contribute to the HHG in the direction of \( \alpha = 0^\circ \sim 20^\circ \). Then the node at \( \theta = 0^\circ \) in the electron density distribution of the HOMO of \( O_2 \) is greatly smeared in the harmonic signal by the convolution with the alignment distribution, as observed in the ionization experiment for aligned molecules. \(^{21} \) The present results suggest that the electron density distribution can be deduced by taking into account the alignment distribution in the observed \( \alpha \)-dependent harmonic signal.

5. Conclusion

We have experimentally and theoretically investigated the angle-dependent HHG from nonadiabatically aligned \( N_2 \) and \( O_2 \) molecules. The validity of the recently developed theory is demonstrated by comparing the experimental and calculated results. It is shown that the time-dependent harmonic signals can be reproduced by the leading terms in the theoretical expressions for the HHG from \( N_2 \) and \( O_2 \). The \( \theta \)-dependent HHG from a single molecule is dominated by the electron density distribution of the HOMO, while the \( \alpha \)-dependent signal observed is strongly influenced by the degree of molecular alignment. The \( \alpha \)- and \( \theta \)-dependent HHG from aligned molecules has been investigated for the first time, to our knowledge.

References