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Retrieval of Angle-Dependent Strong-Field Ionization by Using High Harmonics Generated from Aligned N_2 Molecules

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We propose a method to retrieve the angle-dependent strong-field ionization of highest occupied molecular orbital (HOMO) from high-order harmonic generation (HHG) of aligned molecules. This method is based on the single-molecule quantitative rescattering model with known alignment distribution and photo-recombination cross sections of fixed-in-space molecules. With the macroscopic HHG of aligned N_2 molecules, we show that angle-dependent ionization of HOMO can be successfully retrieved at both low and high degrees of alignment. We then show that the error in the retrieved angular dependence of ionization becomes larger if the uncertainty in the alignment distribution is introduced in the retrieval procedure. We also examine that the retrieved ionization of HOMO is much deviated from the accurate one if the intensity of probe laser becomes higher such that inner HOMO-1 can contribute to HHG.

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Ionization is the first step for all strong-field phenomena when molecules are irradiated by an intense laser pulse. These phenomena include high-order harmonic generation (HHG),[1–15] high-energy above-threshold ionization (HATI),[16] nonsequential double ionization (NSDI),[17,18] laser-induced electron diffraction (LIED),[19–21] and so on. Molecular ionization can be used to image the molecular orbitals[22] and to probe nuclear and electronic dynamics with attosecond resolution.[1–6,23–33] It is essential to understand the molecular ionization, especially the angular dependence of ionization, since molecules in an intense laser field are expected to response differently depending on their orientations with respect to the laser. To measure the angular dependence of ionization experimentally, one can impulsively orient (or align) the isotropic molecules first by using a femtosecond laser pulse (pump laser) and then record the ionization yield due to another intense laser (called probe laser). The angular dependence of ionization can be de-convoluted from the yield as a function of the angle between the polarization axes of pump and probe laser pulses.[34] Other methods can also be employed for the same purpose, such as using Coulomb explosion to determine the alignment angle while recording the fragmented ions in coincidence, and measuring the angular dependence of fragmented ions in the nonsequential double ionization process.[35] The measured angle-dependent strong-field ionization agrees well with the theoretically predicted one for N_2 and O_2.[34] However, some discrepancies occur for CO_2 molecules reported in Ref. [34], where measured angular width of angle-dependent ionization is much narrower compared to various theoretical ones.[36–38] Very recently, Lam *et al.* retrieved the angle-dependent ionization of CO_2 molecules by using a time-domain measurement on an impulsively excited rotational wave packet.[39] Their fitting procedure performs well when molecules have a high degree of alignment, but it cannot give a convergent angular dependent ionization at a low degree of alignment. Although the topic of molecular ionization has been intensively studied both experimentally and theoretically, for better understanding of this process, it is still necessary to develop new approaches to accurately obtain the angular dependence of ionization from experimental measurements.

High-order harmonic generation (HHG) from laser-gas interaction has become an important ap-

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proach for probing ultrafast dynamics for nuclei and electrons,[1−6] reconstructing the shape of molecular orbitals by orbital tomography,[40] and generating attosecond pulses.[41−43] The HHG can be characterized by the classical three-step model. The valence electron is single ionized. Then, it is accelerated in the electric field and it gains the kinetic energy. When driven back and recombining with parent ion, it can emit a high-energy photon. Since ionization of molecules is the first step of HHG process, its angular dependence is also closely related to angle-dependent HHG yield. According to the quantitative rescattering (QRS) model,[44−46] in the molecular frame, single-molecule induced dipole moment by the laser field can be expressed as the product of angle-dependent ionization, complex returning electron wave packet and the angle-dependent complex recombination dipole moment between laser-free electron and target ion. Since returning electron wave packet only reflects the property of driving laser and it does not have the angle dependence, the QRS model can be further extended for transiently aligned molecules under pump-probe scheme to quantitatively relate ionization and HHG. It is naturally asked whether the HHG measurements with partially aligned molecules can be used to retrieve angular dependence of molecular ionization, which has not been addressed by others according to our knowledge.

In this Letter, our main goal is to propose a retrieval method for the angular dependence of strong-field ionization by using molecular high harmonics generated under the pump-probe scheme. We choose N_2 as our target molecule. The method is based on the QRS model for single-molecule HHG of highest occupied molecular orbital (HOMO). Assuming the alignment distribution of molecules is well known and only HOMO contributes to the HHG, the method is tested by using simulated single-molecule HHG and macroscopic HHG after propagation in the gas medium as the "input" data. Then, we investigate whether the accuracy of retrieved angular dependence of ionization for HOMO will be acceptable if we include the uncertainty of alignment degree or consider the interference between outmost orbital and inner orbitals. In the following, firstly we present the QRS model for single-molecule HHG and the theory for retrieving angle-dependent ionization. Then, we test the retrieval method and show the retrieved ionization results. Finally, a summary is given.

Theoretical Methods. We first introduce the quantitative rescattering model for a multiple-orbital molecular system. In the QRS model, for a single orbital molecular system, parallel or perpendicular component of the complex laser-induced dipole moment in the frequency domain is given by[44−46]

$$D^{||,\perp}(\omega,\theta,\phi) = N(\theta)^{1/2} W(\omega) d^{||,\perp}(\omega,\theta,\phi). \quad (1)$$

Here θ and ϕ are polar and azimuthal angles of the molecular axis in the frame attached to the probe field, which refers to a right-handed coordinate system with the polarization direction of the probe field as the z-axis and its propagation direction as the y-axis of the coordinate system, $N(\theta)$ is the angle-dependent ionization probability, $W(\omega)$ represents the recombining electron wave packet, which is the same for both components, and $d^{||,\perp}(\omega,\theta,\phi)$ is the parallel (or perpendicular) component of the photo-recombination (PR) transition dipole (complex in general). For convenience, $W(\omega)$ can be calculated as

$$W(\omega) = \frac{D^{||,\perp}_{\rm SFA}(\omega,\theta,\phi)}{N(\theta)^{1/2} d^{||,\perp}_{\rm SFA}(\omega,\theta,\phi)}, \quad (2)$$

each term in Eq. (2) can be calculated by using strong-field approximation (SFA) formulation for HHG.[9,47] For different harmonic orders, $W(\omega)$ already contains the contribution of the electron trajectories ionized at different times. In the QRS, accurate $d^{||,\perp}(\omega,\theta,\phi)$ is obtained from quantum chemistry code for simple linear molecules.[48,49]

For impulsively aligned molecules by using a weak and loosely focused pump laser beam, the induced dipoles due to probe laser pulse $D^{||,\perp}(\omega,\theta,\phi)$ are coherently added according to the molecular alignment distribution.[44,50] Assuming that the pump and probe laser pulses propagate collinearly and we denote the angle between their polarization directions as α, then the parallel or perpendicular component for the averaged induced dipole of aligned molecules is given by[44,50]

$$\bar{D}^{||,\perp}(\omega,\alpha) = \int_0^{\pi}\int_0^{2\pi} D^{||,\perp}(\omega,\theta,\phi) \cdot \rho(\alpha,\theta,\phi)\sin\theta d\theta d\phi, \quad (3)$$

where $\rho(\alpha,\theta,\phi)$ is the angular distribution of the molecules with respect to the polarization direction of the probe pulse.[44,50,51]

Since $W(\omega)$ depends on the laser properties only and does not depend on the alignment angle θ and ϕ, $D^{||,\perp}(\omega,\theta,\phi)$ can be written in an alternative formulation as follows:

$$\bar{D}^{||,\perp}(\omega,\alpha) = W(\omega)\bar{d}^{||,\perp}(\omega,\alpha), \quad (4)$$

where

$$\bar{d}^{||,\perp}(\omega,\alpha) = \int_0^{\pi}\int_0^{2\pi} N(\theta)^{\frac{1}{2}} d^{||,\perp}(\omega,\theta,\phi) \cdot \rho(\alpha,\theta,\phi)\sin\theta d\theta d\phi \quad (5)$$

is the "averaged" transition dipole.

Only a single molecular orbital is considered to obtain the induced dipole in the above procedure. When inner orbitals contribute to the HHG process, following the procedure in Ref. [52], the induced dipole generated by each molecular orbital is coherently summed

as

$$\bar{D}^{||,\perp}_{\rm tot}(\omega,\alpha)=\sum_{j,n}\bar{D}^{||,\perp}_{j,n}(\omega,\alpha)e^{i\varphi_j}, \tag{6}$$

where index j refers to the molecular orbital, and n is an index accounting for degeneracy in each molecular orbital. In Eq. (6), φ_j is ionization phase, which is acquired during the ionization process and modifies the interference effect between different orbitals. This phase can also be used to record the "core dynamics"[53] and it affects the polarization of the harmonics.[54] In general, $\varphi_j=0$ in the static tunnelling limit, while the non-adiabatic dynamics of electron rearrangement in the strong-field ionization would lead to a nonzero φ_j.[4,53]

To simulate high-harmonic spectra which can be directly compared with experimental data, one needs to consider the macroscopic response of HHG from a gas medium. Thus the averaged induced dipoles obtained under different laser intensities are fed into the macroscopic propagation equations. The details can be found in Refs. [55–58].

Next, we use the QRS model to retrieve the angle-dependent ionization rate of the molecule. To retrieve the angle-dependent ionization from measured high-harmonic yields of aligned molecules, we assume that the alignment distribution and photo-recombination cross sections of fixed-in-space molecules are known from the theory. The retrieval method is based on the single-molecule QRS model with including only the HOMO contribution.

For symmetric linear molecules, the angle-dependent ionization probability $N(\theta)$ is an even function, that is,

$$N(\theta)=N(\pi-\theta). \tag{7}$$

Taking the even power of $\cos\theta$ as the basis of expansion of the generalized Fourier expansion as in Ref. [54], we can expand $N^{1/2}(\theta)$ as

$$N^{1/2}(\theta)=\sum_{J=0}^{\infty}a_J(\cos\theta)^{2J}, \tag{8}$$

where a_J is the expansion coefficients. Truncating the infinite series expansion at $J_{\max}$, we have

$$N^{1/2}(\theta)=\sum_{J=0}^{J=J_{\max}}a_J(\cos\theta)^{2J}. \tag{9}$$

Substituting Eqs. (9) and (1) into Eq. (3) yields

$$\bar{D}^{||,\perp}(\omega,\alpha)=\sum_{J=0}^{J=J_{\max}}a_JQ^{||,\perp}_J(\omega,\alpha), \tag{10}$$

with

$$Q^{||,\perp}_J(\omega,\alpha)=W(\omega)\int_0^{\pi}\int_0^{2\pi}d^{||,\perp}(\omega,\theta,\phi)\cdot\rho(\alpha,\theta,\phi)(\cos\theta)^{2J}\sin\theta d\theta d\phi. \tag{11}$$

Then the intensity of the harmonic field can be written as

$$\begin{aligned}&|\bar{D}^{||,\perp}(\omega,\alpha)|^2\\&=\sum_{J,k=0}^{J=J_{\max},k=J_{\max}}a_Ja_kQ^{||,\perp}_J(\omega,\alpha)[Q^{||,\perp}_k(\omega,\alpha)]^*\\&=\sum_{J}^{J_{\max}}\frac{1}{2}a_J^2T_{JJ}(\omega,\alpha)\\&\quad+\sum_{J=0,k>J}^{J=J_{\max},k=J_{\max}}a_Ja_kT_{Jk}(\omega,\alpha),\end{aligned} \tag{12}$$

with

$$T_{Jk}(\omega,\alpha)=Q^{||,\perp}_J(\omega,\alpha)[Q^{||,\perp}_k(\omega,\alpha)]^*+c.c. \tag{13}$$

Introducing

$$A=\begin{pmatrix}a_0^2\\\vdots\\a_{J_{\max}}^2\\a_0a_1\\\vdots\\a_{J_{\max}-1}a_{J_{\max}}\end{pmatrix},$$

$$y(\omega,\alpha)=\begin{pmatrix}T_{00}(\omega,\alpha)/2\\\vdots\\T_{J_{\max}J_{\max}}(\omega,\alpha)/2\\T_{01}(\omega,\alpha)\\\vdots\\T_{J_{\max}-1J_{\max}}(\omega,\alpha)\end{pmatrix}, \tag{14}$$

we can rewrite Eq. (12) as

$$|\bar{D}^{||,\perp}(\omega,\alpha)|^2=y^{\rm T}(\omega,\alpha)A, \tag{15}$$

where T stands for transpose. Equation (15) shows that the intensity of the harmonics field is a linear combination of the quadratic products $a_Ja_k(0\leqslant J,k\leqslant J_{\max})$, and the coefficients before each quadratic product can be obtained by Eqs. (11) and (13). For a given $J_{\max}$, there are a total number of $J_{\max}(J_{\max}+1)/2$ quadratic products a_Ja_k that need to be determined. Therefore, it is necessary to choose more than $J_{\max}(J_{\max}+1)/2$ pump-probe angles α in measurement to get sufficient data to obtain all the quadratic products a_Ja_k. Using $M(M>J_{\max}(J_{\max}+1)/2)$ pump-probe angles α and introduce

$$H=\begin{pmatrix}|\bar{D}^{||,\perp}(\omega,\alpha_1)|^2\\\vdots\\|\bar{D}^{||,\perp}(\omega,\alpha_M)|^2\end{pmatrix},\ Y=\begin{pmatrix}y^{\rm T}(\omega,\alpha_1)\\\vdots\\y^{\rm T}(\omega,\alpha_M)\end{pmatrix}, \tag{16}$$

we obtain a matrix equation

$$H=YA. \tag{17}$$

Then we can achieve the quadratic products $a_J a_k$ by fitting Eq. (17). After getting all the quadratic products $a_J a_k$, the angle-dependent ionization $N(\theta)$ can be obtained by squaring of Eq. (9),

$$N(\theta) = \sum_{J,k=0}^{J=J_{\max},k=J_{\max}} a_J a_k (\cos\theta)^{2(J+k)} = C^{\mathrm{T}}(\theta) A, \tag{18}$$

where

$$C(\theta) = \begin{pmatrix} 1 \\ \vdots \\ (\cos\theta)^{4J_{\max}} \\ (\cos\theta)^{2} \\ \vdots \\ (\cos\theta)^{4J_{\max}-2} \end{pmatrix}. \tag{19}$$

In practice, the retrieval of the angle-dependent ionization can be carried out by only using the parallel or the perpendicular component of the harmonic field or by using both components together. From theoretical point of view, the retrieved results are not significantly different no matter which component of the harmonic field is used. From experimental point of view, one prefers to use the parallel component since it is much stronger than perpendicular one.[54,59] In the following, we only show the retrieved angle-dependent ionization by using the parallel component of the high-harmonic field.

Results and Discussion. Before using our method to retrieve the angle-dependent ionization probability, we first use the single-molecule HHG as a function of pump-probe angle calculated by the QRS model as input data to test the retrieval method. The HHG data is obtained with pump-probe scheme. We use a 120-fs pump laser pulse with an intensity of $3.0 \times 10^{13}\,\mathrm{W/cm^2}$, and a 30-fs probe laser pulse with an intensity of $2 \times 10^{14}\,\mathrm{W/cm^2}$. The rotational temperature of the gas is 100 K. Both pump and probe lasers are with the wavelength of 800 nm and the time delay between these two pulses is selected at the half revival (about 4.12 ps) when the alignment degree reaches its maximum 0.5. The retrieved angle-dependent ionization (normalized) is shown in Fig. 1 by varying $J_{\max}$ from 1 to 3. The ionization probability calculated from MO-ADK[60,61] at probe intensity of $2.0 \times 10^{14}\,\mathrm{W/cm^2}$ is also plotted for comparison, which is considered as the "real" one. For two selected harmonics, harmonic 17 (H17) and H21, the perfect agreement between retrieved ionization and the real one is reached when $J_{\max} = 3$. Therefore, we use $J_{\max} = 3$ for retrieval in the following.

Next, we use the experimentally measured high harmonics to retrieve the angle-dependent ionization probability. As we know, the experimentally measured high harmonics are produced by a focused laser beam and are suffered from propagation in a macroscopic gas medium. Thus, there are two issues to be checked in our retrieval method. Firstly, since the macroscopic high harmonics are resulted from the interference of many different laser intensities, can the angle-dependent ionization be obtained at an equivalent single laser intensity? Secondly, is the retrieval method based on the single-molecule response theory still applicable by including propagation effects in the input HHG?

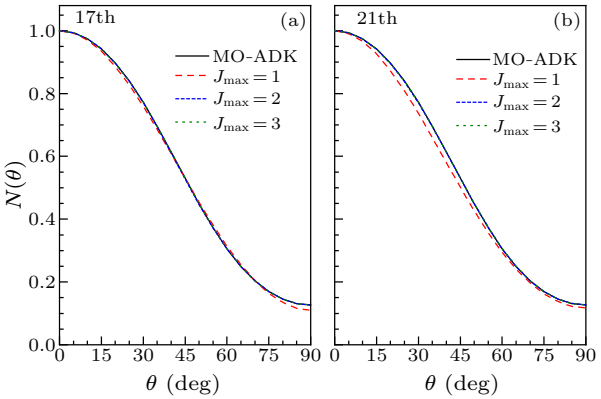

Fig. 1. Comparison of the real (given by MO ADK) and retrieved angle-dependent ionization probability (normalized) by setting $J_{\max} = 1$, 2 and 3. The single-molecule HHG simulated by only including the HOMO are used as the input data. H17 (a) and H21 (b) are used in the retrieval procedure. Peak intensity of probe laser is $2.0 \times 10^{14}\,\mathrm{W/cm^2}$, maximum alignment degree is $\langle\cos^2\theta\rangle = 0.5$.

Figures 2(a) and 2(b) show the single-molecule and macroscopic HHG spectra at different pump-probe angles respectively. Degree of molecular alignment is 0.5. The former is obtained at probe intensity of $1.8 \times 10^{14}\,\mathrm{W/cm^2}$, while the latter is calculated by setting the macroscopic parameters as follows: beam waist of driving laser is 35 μm, gas length is 0.5 mm, which is put at 2.75 mm after laser focus, laser peak intensity at the center of gas medium is $2.0 \times 10^{14}\,\mathrm{W/cm^2}$. In comparison of these spectra, one can see that clear peaks of odd harmonics are present in the macroscopic HHG spectra. In Figs. 2(c) and 2(d), single-molecule HHG spectra are plotted together with macroscopic ones for two selected harmonics, H17 and H21. After normalization, the change of harmonic yields as a function of pump-probe angles is almost the same for them. In the retrieval method, our target is the HHG yield versus pump-probe angles. Therefore, the angle-dependent ionization of molecules can be retrieved from macroscopic HHG spectra at an "equivalent" laser intensity of $1.8 \times 10^{14}\,\mathrm{W/cm^2}$. Therefore, finding the equivalent laser intensity is the first step in the retrieval. For different peak intensities at the center of gas medium, the equivalent single-molecule probe intensity can be obtained by searching the single-molecule HHG that changes as the same as the macroscopic HHG with the pump-probe angle. We find that when the probe intensity at the center of gas medium is small, such

as $1.6 \times 10^{14}\,\mathrm{W/cm^2}$, the equivalent intensity is almost the same as the probe intensity; when the probe intensity at the center of gas medium increases to $2.0 \times 10^{14}\,\mathrm{W/cm^2}$, the equivalent intensity is about 90% of the probe intensity.

Figures 3(a) and 3(b) show the retrieved angular dependence of molecular ionization by using macroscopic HHG spectra generated at a relatively low degree of alignment, 0.5. For comparison, the ionization calculated by MO-ADK at equivalent intensity of $1.8 \times 10^{14}\,\mathrm{W/cm^2}$ is also given. The agreement between them indicates that even though the propagation effects are included in the input data, the equivalent angle-dependent ionization can still be retrieved. We further test our retrieval method by using input HHG data obtained at a relatively high degree of alignment, 0.85. The retrieved angle-dependent ionization by using two different harmonic orders are shown in Figs. 3(c) and 3(d), respectively. From the retrieved results of Figs. 3(a), 3(b) and Figs. 3(c), 3(d), it can be seen that different alignment degrees have slightly different effects on the retrieval procedures. A higher alignment degree means a narrower alignment distribution, which may cause larger errors in the integral calculation of Eq. (11) and would lead to larger errors in the retrieved results as shown in Figs. 3(a) and 3(c) for order 17 near 45° or shown in Figs. 3(b) and Fig. 3(d) for order 21 near 90°. However, due to the difference of the photo-recombination (PR) transition dipole, the error caused by the difference of the alignment degree behaves slightly differently in the retrieval procedures of the harmonic orders 17 and 21. In general, the angle-dependent ionization given by our retrieved method is in good agreement with the result given by MO-ADK.

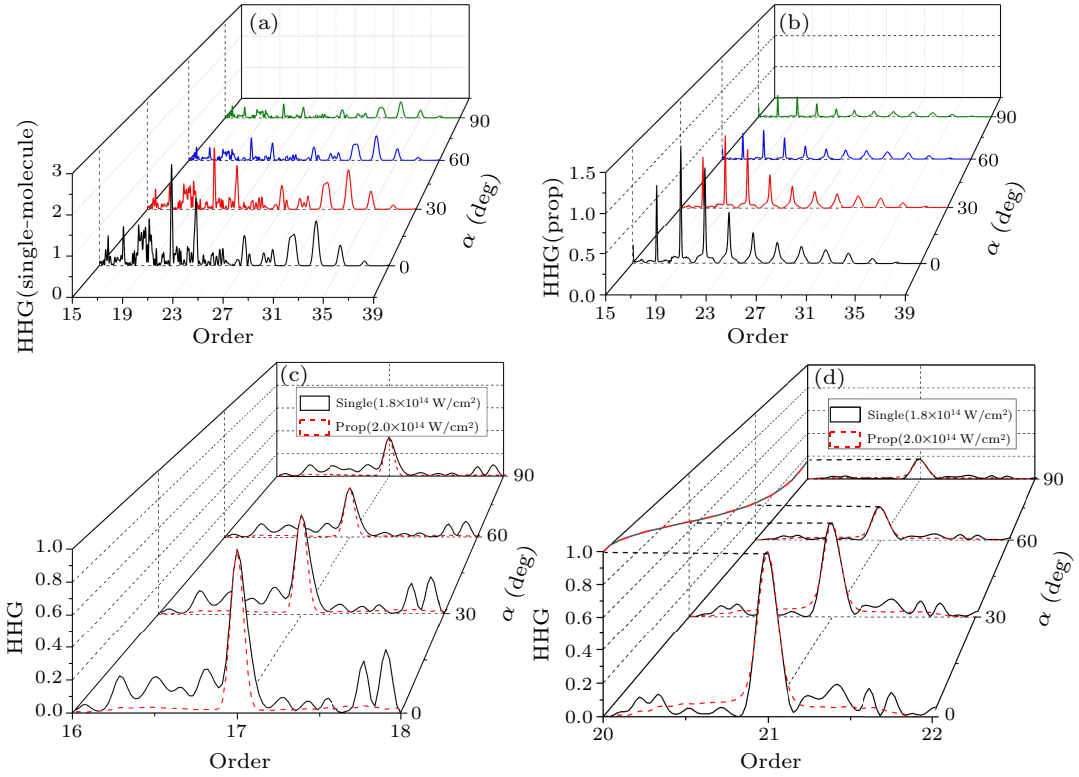

Fig. 2. (a) Single-molecule high-harmonic spectra with peak probe laser intensity of $1.8 \times 10^{14}\,\mathrm{W/cm^2}$ and (b) macroscopic high-harmonic spectra with laser intensity of $2.0 \times 10^{14}\,\mathrm{W/cm^2}$ at the center of gas medium. The spectra are generated by only including the HOMO at different pump-probe angles α. [(c), (d)] Comparison of normalized single-molecule (black solid lines) and macroscopic (red dashed lines) high-harmonic spectra near H17 (c) and H21 (d) at different pump-probe angles α. The high-harmonic spectra are normalized by the high-harmonic at $\alpha = 0°$ for the two harmonic orders. The curves on the left shows yields of H17 and H21 as a function of pump-probe angle α.

Since the alignment degree in the experiment cannot be measured precisely, we check how our retrieval method works if there are some uncertainties in the alignment degree. We use two alignment distributions with the maximum alignment degree $\langle\cos^2\theta\rangle = 0.55$ and $\langle\cos^2\theta\rangle = 0.46$ as the measured alignment degree in the retrieval procedure, which are about 10% higher or lower than the real alignment degree $\langle\cos^2\theta\rangle = 0.5$ used to generate HHG. Here the input data are macroscopic HHG simulated under the same macroscopic conditions as those in Fig. 2. The retrieved results are shown in Fig. 4. In this case, the retrieved results have a large deviation from the real angle-dependent ionization especially for larger alignment-angles. Figure 4 shows that, if the alignment degree used in the retrieval is greater than the real alignment degree, the

retrieved ionization probability will drop fast than the real ionization probability with increasing angle. On the contrary, if the alignment degree used in the retrieval is smaller than the real one, the retrieved ionization probability will drop slower than the real ionization probability with the increasing angle. Moreover, comparing the retrieved results by using H17 and H21, the uncertainty of alignment degree has a greater impact on the retrieval of ionization probability for H21.

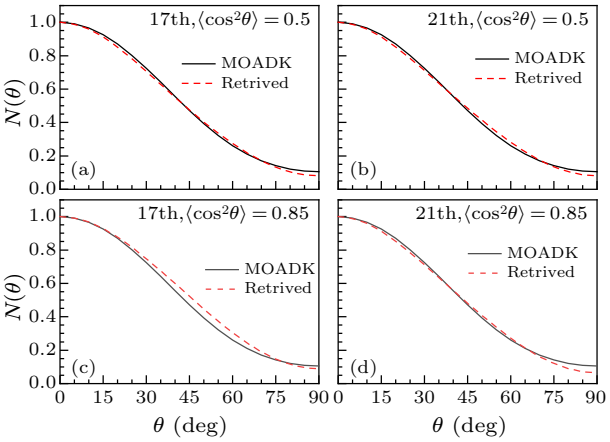

Fig. 3. The real (given by MO-ADK) and retrieved angle-dependent ionization, with maximum alignment degree $\langle\cos^2\theta\rangle = 0.5$ in [(a), (b)] and $\langle\cos^2\theta\rangle = 0.85$ in [(c), (d)]. Macroscopic HHG for order 17 [(a), (c)] and order 21 [(b), (d)] with peak probe intensity of 2.0×10^{14} W/cm^2 are used in the retrieval procedure and $J_{\max} = 3$ is used in the retrieval.

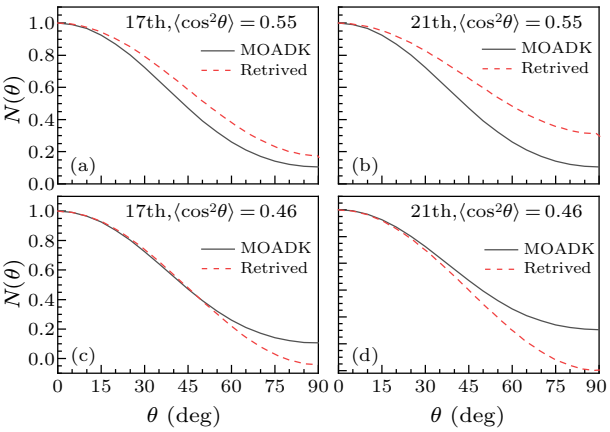

Fig. 4. The real (given by MO-ADK) and retrieved angle-dependent ionization, with maximum alignment degree $\langle\cos^2\theta\rangle = 0.55$ in [(a), (b)] and $\langle\cos^2\theta\rangle = 0.46$ in [(c), (d)] assumed in the retrieval procedure. The real alignment degree used to generate HHG is $\langle\cos^2\theta\rangle = 0.5$. Macroscopic HHG for order 17 [(a), (c)] and order 21 [(b), (d)] with peak probe intensity of 2.0×10^{14} W/cm^2 are used in the retrieval procedure, and $J_{\max} = 3$ is used in the retrieval.

Apart from the uncertainty of the alignment degree, another factor that affects the retrieved results comes from the contribution of inner molecular orbitals to HHG. In the molecular HHG process, both HOMO and inner orbitals could contribute, which depends on the intensity of probe laser. When the inner orbitals interfere with the outmost one, can one retrieve the angle-dependent ionization of HOMO? In Fig. 5, we show the macroscopic HHG as a function of pump-probe angle obtained from only HOMO and from the interference of HOMO and HOMO-1 with relative ionization phase $\varphi_{\rm HOMO-1} - \varphi_{\rm HOMO} = 1.2\pi$ for H17 and H21 by varying the intensity of probe laser. The other macroscopic conditions are kept as the same as those in Fig. 2. Since the relative ionization probability of HOMO-1 increases with the probe intensity, the discrepancy between total macroscopic HHGs with or without HOMO-1 becomes larger. For different harmonic orders, it is obvious that the HOMO-1 contribution behaves quite differently.

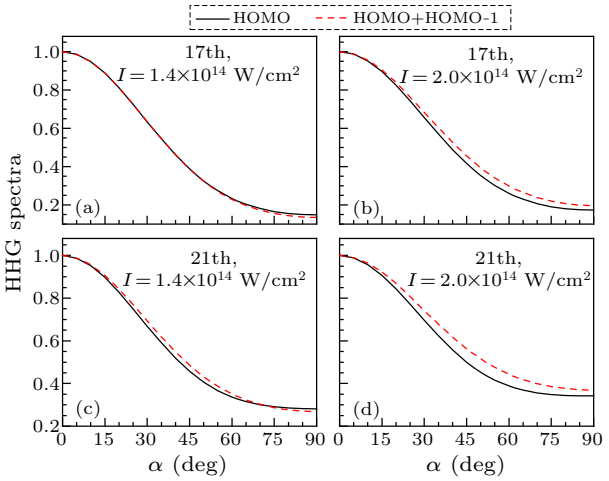

Fig. 5. Comparison of macroscopic HHG versus pump-probe angle for H17 [(a), (b)] and H21 [(c), (d)] generated by only including HOMO and by considering the interference of HOMO and HOMO-1. The laser intensity at the center of gas medium is 1.4×10^{14} W/cm^2 in [(a), (c)] and 2.0×10^{14} W/cm^2 in [(b), (d)].

Figure 6 shows the retrieved ionization versus alignment angle using the macroscopic HHG including both the contributions from HOMO and HOMO-1, while the retrieved method we used is still based on the QRS model for single-molecule HHG of HOMO. With the contribution of HOMO-1 to the macroscopic HHG, the retrieved results are deviated from those when only the contribution of HOMO is considered. Since HOMO and HOMO-1 have different symmetries, the ionization probability peaks at 0° for HOMO and peaks at 90° for HOMO-1 as shown by the insets in Figs. 6(a) and 6(b). This different angular dependence makes the deviation of the two retrieved ionization probabilities increase with the alignment angle, and reaches its maximum at 90°. As the probe intensity increases, the relative ionization probabilities between HOMO-1 and HOMO also increase as shown by the insets in Figs. 6(a) and 6(b), which makes the contribution of the HOMO-1 to the macroscopic HHG increase. Therefore, the deviation of the retrieved ionization probability also increases with the probe intensity as shown in Fig. 6. The deviation of the retrieved ionization probabilities due to HOMO-1 for H17 and

H21 are different. Compared to the H17, HOMO-1 has a greater effect on the retrieval of the ionization probability for H21.

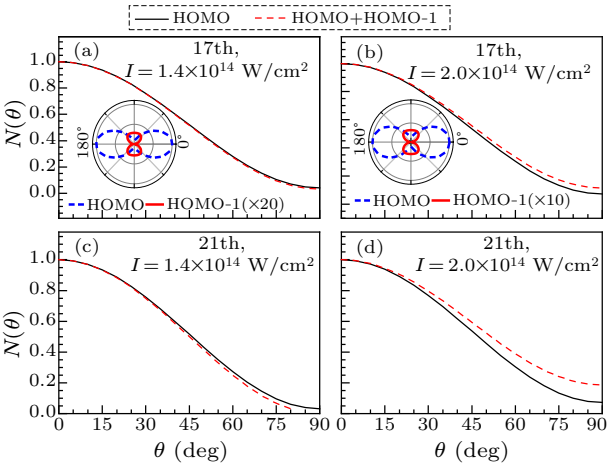

Fig. 6. Comparison of the retrieved angle-dependent ionization by using the macroscopic HHG generated by only HOMO or by the interference of HOMO and HOMO-1. The maximum alignment degree $\langle\cos^2\theta\rangle = 0.5$. Macroscopic harmonic yields at H17 [(a), (b)] and H21 [(c), (d)] shown in Fig. 5 are used as input data. The insets in [(a), (b)] show the angle-dependent ionization for HOMO (blue dashed) and HOMO-1 (red solid) with probe intensity 1.4×10^{14} W/cm^2 and 2.0×10^{14} W/cm^2.

In conclusion, we have proposed a method to retrieve the angle-dependent strong-field ionization of HOMO by using HHG under pump-probe scheme based on the single-molecule QRS model. We have chosen aligned N_2 molecules as an example. The retrieval method has been first tested by taking single-molecule HHG as input data, and it then has been checked by employing macroscopic HHG as input data. The angle-dependent ionization has been successfully retrieved at an equivalent single laser intensity. We have checked that the retrieval method works well for both high and low alignment degrees. The method has been further examined if there is a 10% deviation of alignment degree involved in the retrieval procedure. The deviation between the retrieved results and real ones indicates the precise alignment degree plays an import role in the retrieval method. We finally tested the retrieval method by including the contribution from inner molecular orbitals in the input macroscopic HHG. Our method performs quite well if intensity of probe laser is low because ionization and recombination would occur mostly for electrons in the HOMO. With the increase of probe laser intensity, electrons in the inner orbital, such as HOMO-1, would be ionized, and contribute to the harmonic emission, which makes the retrieved ionization probability deviating much from the retrieved one with only including the HOMO.

Our retrieval method provides with a new route to deal with angle-dependent ionization of molecules, which has been an intensively studied fundamental problem. The retrieval method should be modified to improve the accuracy of retrieved ionization in the future if the alignment distribution of molecules has some uncertainties. In the current study, only the angle-dependent ionization of HOMO is retrieved. It is also interesting to investigate whether the similar ionization for inner molecular orbitals can be retrieved by using HHG generated at high intensity of probe laser.

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