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Molecular orbital imaging for partially aligned molecules

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ABSTRACT

We investigate molecular orbital reconstruction using high-order harmonic emissions from partially aligned molecular ensembles. By carrying out the reconstruction procedure using the harmonic sampling with or without the spectral minimum, the roles of the harmonic phase and amplitude modulation due to the partial alignment can be separately studied. It is found that with the prior knowledge of the orbital symmetry, the reconstructed result is very sensitive to the modulation of the harmonic phase for the π_g orbital, while in the case of σ_g orbital, the reconstructed result is mainly determined by the harmonic amplitude. These results can provide an important reference for the future experiment of molecular orbital imaging.

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1. Introduction

Imaging structures and dynamics at different temporal and spatial scales is a major direction of modern science that encompasses physics, chemistry and biology [1–7]. Among the existing imaging technique, high-order harmonic spectroscopy (HHS) has been shown as an effective approach to resolving molecular structures and dynamics with unprecedented spatial and temporal resolutions [8–11]. Along with its another important application in producing coherent attosecond laser pulses in the soft x-ray range, high-order harmonic generation (HHG) has attracted a lot of interest in the past two decades [12–20]. The HHG occurs during the interaction of a strong laser field with a gas target and can be understood by a three-step model [21,22]. According to this model, an electron wavepacket (EWP) is first produced by laser ionization, then it is accelerated and driven back to the core by the laser field, and finally recombines with the parent ion to emit high-order harmonic photons. As the recolliding EWP has a duration of a few hundred attoseconds at recollision time, it gives rise to the attosecond temporal resolution of HHS. Meanwhile, the ultrashort de Broglie wavelength of the recolliding EWP allows for sub-Ångström spatial resolution.

An important method based on HHG to resolve molecular structure and dynamics with sub-Ångström and attosecond resolutions is the molecular orbital tomography (MOT), which was first proposed by J. Itatani et al. [23]. With this MOT scheme, a two-dimensional projection of the molecular orbital on the plane

orthogonal to the pulse-propagation direction can be reconstructed [24–26]. In detail, by calibrating the harmonic signals from molecule aligned at various angles using that of a reference system with the same ionization energy, the recombination dipole matrix element of the molecular orbital is extracted. Then, by performing the inverse Fourier transform of the recombination dipole matrix elements, the target molecular orbital can be reconstructed. Note that in order to accurately extract the recombination dipole matrix element, the high-order harmonics from perfectly aligned molecules are needed. In experiments, however, the harmonic signals are generated from partially aligned molecular ensemble [27,28]. The measured harmonic signals are coherent superposition of the harmonic emissions at various alignment angles weighted by the angular distribution [11,24]. In most of previous works, these harmonic signals are treated as the harmonics generated from molecules purely aligned at the dominate angle in the MOT procedure to extract the dipole matrix element. Recently, it has been shown that the harmonic spectra, especially the spectral minimum position that contains important information on the molecular structure and dynamics, can be significantly modulated by the degree of alignment [29,30]. Hence, when the degree of alignment is changed the extracted dipole matrix element will be different. This may lead to a different reconstruction result. As the degree of alignment is sensitive to the experimental conditions, the degree of alignment achieved in different experiments is generally not the same. Hence, in order to better understand and compare the results obtained in different experiments, it is necessary to investigate how the degree of alignment affect the result of the orbital reconstruction.

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In this paper, molecular orbital tomography based on high-order harmonic generation from partially aligned molecular ensembles is investigated for molecules with different orbital symmetries and various degrees of alignment. By carrying out the reconstruction procedure using the harmonic sampling with or without the spectral minimum, the roles of the harmonic phase and amplitude modulation due to the partial alignment can be separately studied. It is found that with the prior knowledge of the orbital symmetry, the reconstructed result is very sensitive to the modulation of the harmonic phase for the π_g orbital, while in the case of σ_g orbital, the reconstructed result is mainly determined by the alignment-dependent harmonic amplitude.

2. Theoretical model

In our simulation, the complex amplitude of the harmonic signal at the delay τ with respect to the alignment pulse is calculated by

$$\tilde{S}(\omega_n, \alpha) = \int_{\varphi'=0}^{2\pi} \int_{\theta'=0}^{\pi} \rho(\theta(\theta', \varphi', \alpha); \tau) \tilde{\mathbf{E}}(\omega_n, \theta', \varphi') \times \sin \theta' d\theta' d\varphi'. \quad (1)$$

Here, ω_n and α are the harmonic frequency and the angle between the alignment and probe pulse polarization, respectively. Linearly polarized alignment and probe pulses are used in our study. Both of them are set to propagate along the x axis of the laboratory frame, the polarization of the probe laser field is along the z axis of the laboratory frame. θ' and φ' are the polar and azimuthal angles in the frame of probe pulse, respectively. $\rho(\theta; \tau)$ is the time-dependent angular distribution in the frame of alignment pulse. It can be transformed to the frame of probe pulse using the relation $\cos \theta = \cos \alpha \cos \theta' + \sin \alpha \sin \theta' \cos \varphi'$. For clarity, a schematic illustration of our coordinate system is given in Fig. 1. As shown in this figure, the probe laser frame coincides with the laboratory frame and is fixed. The x axis of the probe and the alignment pulse frames are defined as the propagation direction of the two pulses. They coincide with each other. The z axis of the probe and the alignment pulse frames are defined by the polarization direction of their electric field, respectively. The alignment pulse frame is rotated about the x axis of the probe frame at an angle α .

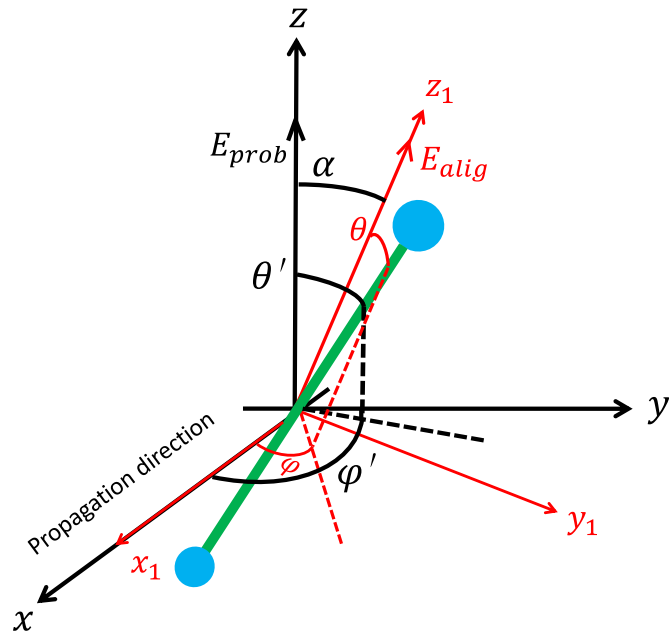


Fig. 1. A schematic illustration of our coordinate system.

By solving the time-dependent Schrödinger equation (TDSE) based on the rigid-rotor model [31,32], $\rho(\theta; \tau)$ can be calculated by

$$\rho(\theta; \tau) = \sum_{J_i} g(J_i) \sum_{M_i=-J_i}^{J_i} \int |\Psi^{J_i M_i}(\theta, \varphi; \tau)|^2 d\varphi, \quad (2)$$

where $\Psi^{J_i M_i}(\theta, \varphi; \tau)$ is the rotational wavepacket corresponding to the initial state $|J_i, M_i\rangle$. $g(J_i) = Q(J_i) / (\sum_{J=0}^{J_{\max}} (2J+1)Q(J))$ with $Q(J_i) = \exp[-B J_i(J_i+1)/(k_B T)]$ being the Boltzmann distribution function of the initial field-free state $|J_i, M_i\rangle$ at temperature T . $\tilde{\mathbf{E}}(\omega_n, \theta', \varphi')$ is the complex amplitude of the high-order harmonics generated from the molecule aligned at θ' with respect to the polarization of the probe laser pulse. It is calculated by using the strong-field approximation (SFA) model for molecules within the single-active-electron (SAE) approximation [21]. Generally, $\tilde{\mathbf{E}}(\omega_n, \theta', \varphi')$ has two components, \tilde{E}_z and \tilde{E}_y , which are parallel and perpendicular to the probe pulse polarization, respectively [33]. As a result, the observed harmonic signal $\mathbf{S}(\omega_n, \alpha)$ also has two components $S_z(\omega_n, \alpha)$ and $S_y(\omega_n, \alpha)$. In experiment, these two components can be separately collected by a silver-coated mirror acting as a polarizer [34] or an XUV reflective polarizer consisting of three fused-silica blanks [35,36]. In our simulation, the complex amplitude of the z component $\tilde{S}_z(\omega_n, \alpha)$ is used to reconstruct the molecular orbital [37]. The corresponding \tilde{E}_z is calculated based on the velocity form of the transition dipole, which is better suited to quantify the recombination step in molecular HHG [38]. Since small linear molecules are considered in our work, $\tilde{E}_z(\omega_n, \theta')$ is φ' -independent [33]. More details about our calculation of $\tilde{E}_z(\omega_n, \theta')$ and $\rho(\theta; \tau)$ can be found in our previous works [39,40].

By fixing the delay time τ at the first half revival and rotating the polarization of the alignment pulse with respect to that of the probe pulse, the harmonic signals for a set of angles α can be obtained. Using these harmonic signals, the molecular orbital can be reconstructed by following the MOT procedure. In our simulation, the reconstruction of molecular orbital is performed in the velocity form. Hence, the dipole velocity is extracted from the harmonic signals by using [37]

$$\mathbf{d}^V(\mathbf{k}, \alpha) = \frac{1}{\eta(\alpha)} \frac{\tilde{S}_z(\omega_n, \alpha)}{\tilde{S}_z^{\text{ref}}(\omega_n)} \mathbf{d}_{\text{ref}}^V(\mathbf{k}), \quad (3)$$

where $\tilde{S}_z^{\text{ref}}(\omega_n)$ and $\mathbf{d}_{\text{ref}}^V(\mathbf{k})$ are the complex amplitude of the harmonics and the dipole velocity of the reference atom, respectively. $\mathbf{d}_{\text{ref}}^V(\mathbf{k})$ is calculated by $\mathbf{d}_{\text{ref}}^V(\mathbf{k}) = i\omega_n \mathbf{d}_{\text{ref}}^L(\mathbf{k})$ where $\mathbf{d}_{\text{ref}}^L(\mathbf{k}) = i \left(\frac{2^{7/2} (2I_p)^{5/4}}{\pi} \right) \frac{\mathbf{k}}{(\mathbf{k}^2 + 2I_p)^3}$ and I_p equals to the ionization energy of the corresponding target molecular orbital. \mathbf{k} represents the electron wavevector at the recollision instant. It is related to the harmonic energy by $\omega_n = \mathbf{k}^2/2$. $\eta(\alpha)$ is the k -independent scaling factor. After obtaining the dipole velocity, the molecular orbital is reconstructed by

$$\tilde{\Psi}^D(y, z) = \mathcal{F}_{k \rightarrow r} \left[\frac{d_z^V(k_y, k_z)}{k_z} \right]. \quad (4)$$

By performing the same procedure for various degrees of alignment, the effect of molecular alignment on the molecular orbital tomography is investigated.

3. Results and discussions

We use CO_2 and N_2 molecules as the examples to study the molecular orbital reconstruction with high-order harmonic emission from partially aligned molecules. The highest occupied

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