How to measure the internuclear vector from photoelectron angular distributions*

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This paper uses a nonperturbative scattering theory to study photoelectron angular distributions of homonuclear diatomic molecules irradiated by circularly polarized laser fields. This study shows that the nonisotropic feature of photoelectron angular distributions is not due to the polarization of the laser field but the internuclear vector of the molecules. It suggests a method to measure the molecular orientation and the internuclear distance of molecules through the measurement of photoelectron angular distributions.

Keywords: photoelectron angular distributions, internuclear distance, photoionization

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Physics measurements of microscopic structures of matters developed in the 20th century are mainly based on the observations of all kinds of light spectra or photon spectra. By observing and studying these light spectra one can obtain detailed knowledge of atoms, molecules, and matters. The experimental and theoretical studies of these spectra result in many light spectroscopies such as x-ray spectroscopy and laser spectroscopy. During the last two decades of the last century, a new and completely different type of spectra, say the electron spectra, occurred and showed importance in researches after the discovery of above-threshold-ionization (ATI).[1] Here, the word of "electron spectra" means electron four-momentum spectra, or electron energy-momentum spectra, with electron polarization. Electron spectra should include electron kinetic energy spectra which determine also the magnitude of electron momenta, electron angular distributions which give the direction of electron momenta, and electron spin, i.e. the electron polarization. Using electron spectra to measure microscopic structure of matters has some unique advantages in comparison with using light spectra, because the former may directly show electron structures of matters. For example, the Freeman resonances in ATI electron energy spectra directly manifest the unoccupied electron Rydberg states shifted in strong laser fields.[2] Earlier theoretical studies show that the photoelectron spectra can be used as a tool for probing dynamics of ultrafast molecules.[3−5] There is still a quite long distance between the current studies of electron spectra and a fully developed electron spectroscopy which should apply to the measurements of microscopic structures of matters just as light spectroscopies do. In this paper we propose a scheme to detect the internuclear distance and the orientation of molecules by analysing photoelectron angular distributions (PADs) from the ATI of molecules, which is a step to shorten the distance between the electron spectra and the electron spectroscopy.

Due to the multi-core nature of molecules, the laser-molecule interaction depends critically on internuclear distances and molecular orientation.[6−12] Aligning and testing the alignment of the molecular axis are one of the most basic problems in related molecular studies.[13,14] Nowadays, the molecular orientation is detected by fragments of aligned molecules exposed to intense laser fields. Following photoionization in intense laser fields, the rudimental ions will explode along the internuclear axis due to the Coulomb repulsion. Thus the trajectories of fragment ions signify the molecular orientation. To reduce the distur-

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bance from the polarization direction of driving laser fields to fragment ions, the circularly polarized laser light is preferred. In this paper we will show that the PADs produced in circularly polarized laser light possess more distinct signatures of both internuclear distance and molecular orientation.

Among all molecule models, the widely studied homonuclear diatomic molecule model is the simplest one with fundamental importance.[6,15−18] One advantage of using homonuclear diatomic molecule model in theoretical studies is that the electronic wave packet is symmetric around the geometric centre. According to the linear combination rule in molecular orbital theories,[19] the molecular state is a quantum superposition of atomic orbital. When the internuclear distance is not very small, this treatment provides a simple but effective technique for calculating molecular orbitals. So we take the initial state of a homonuclear diatomic molecule as

$$\Phi(\boldsymbol{R},\boldsymbol{r}) = \frac{\Phi_{\rm i}(\boldsymbol{r}+\boldsymbol{R}/2) \pm \Phi_{\rm i}(\boldsymbol{r}-\boldsymbol{R}/2)}{\sqrt{2[1\pm S(R)]}}, \qquad (1)$$

where $\Phi_{\rm i}(\boldsymbol{r})$ is the initial wavefunction of the outermost shell of the atoms composing the target molecule with the signs '−' and '+' denoting, respectively, the antibonding and bonding valence shells of electrons; while the atomic-orbital overlap integral $S(R)$ is defined as

$$\begin{aligned} S(R) &= \int {\rm d}\boldsymbol{r}\Phi_{\rm i}(\boldsymbol{r}+\boldsymbol{R}/2)\Phi_{\rm i}^{*}(\boldsymbol{r}-\boldsymbol{R}/2) \\ &= \left[1+\frac{Z^{*}R}{a_0}+\frac{1}{3}\left(\frac{Z^{*}R}{a_0}\right)^{2}\right]\exp\left(-\frac{Z^{*}R}{a_0}\right), \end{aligned} \qquad (2)$$

where a_0 is the Bohr radius, $R \equiv |\boldsymbol{R}|$ is the internuclear distance, and Z^{*} the effective nuclear charge. The Fourier transform of $\Phi(\boldsymbol{R},\boldsymbol{r})$, i.e., the corresponding wave function in momentum space, is obtained as

$$\begin{aligned} \Phi(\boldsymbol{P},\boldsymbol{R}) &= \frac{1}{\sqrt{(2\pi)^3}}\int {\rm d}\boldsymbol{r}\exp(-{\rm i}\,\boldsymbol{P}\cdot\boldsymbol{r})\Phi(\boldsymbol{R},\boldsymbol{r}) \\ &= \frac{2\Phi_{\rm i}(\boldsymbol{P})}{\sqrt{2[1\pm S(R)]}}M(\boldsymbol{P},\boldsymbol{R}), \end{aligned} \qquad (3)$$

where $\Phi_{\rm i}(\boldsymbol{P})$ is the Fourier transform of the initial wavefunction $\Phi_{\rm i}(\boldsymbol{r})$, and is independent of the internuclear vector; while the factor $M(\boldsymbol{P},\ \boldsymbol{R})$ is given by

$$\begin{aligned} &M(\boldsymbol{P},\boldsymbol{R}) = \cos(\boldsymbol{P}\cdot\boldsymbol{R}/2) \quad \text{for bonding shell,} \\ &M(\boldsymbol{P},\boldsymbol{R}) = \sin(\boldsymbol{P}\cdot\boldsymbol{R}/2) \quad \text{for antibonding shell,} \end{aligned} \qquad (4)$$

which arises from the multi-core nature of molecules and is often called the interference factor. Through the sine and cosine functions, this factor determines the interference pattern of the electrons from different atomic cores. Because the interference pattern depends only on inner product of the photoelectron momentum $\boldsymbol{P}$ and the molecular vector $\boldsymbol{R}$, the interference pattern may reveal the complete information of the internuclear vector, i.e., the internuclear distance and the molecular orientation.

Our previous study of PADs was successful in understanding the dynamics of atoms in strong fields.[20,21] In contrast to photoionization of atoms which depends mainly on the binding energy and the laser-field parameters,[22,23] photoionization of molecules may depend on more parameters such as the internuclear distance and molecular orientation.[6,24−27] In the current paper, we use our previous method with some new development to study PADs of molecules which may probe directly into the dynamics in the molecules.

We choose the PADs from molecules in the circularly polarized laser fields as samples in analysis for their simplicity, because the PADs from molecules in a linearly polarized field possess a more complicated structure than those in a circularly polarized field. With the modulation by the interference factor, the PADs show minima and maxima with varying positions in the space but are invariant to the molecular axis. Thus, one may recognize the molecular axis by the PADs of molecules exposed in circularly polarized intense laser fields.

The calculation of PADs in the current paper is based on a nonperturbative scattering theory for ATI developed by Guo, Aberg and Crasemann (GAC),[28] which has had notable success in explaining the intense laser-atoms interactions, such as the half Kapitza–Dirac effect performed by Bucksbaum *et al.*[29,30] the jet-like structure in PADs observed by Nandor *et al.*[20,31] and the anomaly in PADs observed by Reichle *et al.*[32−34]

The photoionization of a homonuclear diatomic molecule can be described by the following process. Under the interaction with a driving laser field, a molecular electron initially bounded by two identical cores may absorb multiphoton to be excited into a Volkov state; then, the electron in the Volkov state may leave the laser field to become an ATI electron. In each step of the transition, the total energy and momentum of the whole interacting system are conserved. In the leaving process, a spontaneous emission occurs to balance the energy–momentum

conservation.[35] The dynamic process of photoionization for molecules is the same as that for atoms, while the difference lies in the initial states of the bound electrons. For atoms, the electron is bound by a nucleus and for molecules the electron is bound by multiple nuclei. The molecules can be regarded as stationary during the photon–electron interaction, due to the shorter response time. Thus, the molecular inner structures determine the initial state of molecular electrons, and its influence on photoionization is reflected by the initial distribution of bound electrons. In this paper, we choose H_2^+ as our target molecule and H_2^+ molecule is in bonding shell (σ_g). The differential ionization-rate formula for a photoelectron with a given kinetic-energy (for more details, see Ref. [36]) is ($\hbar = c = 1$),

$$\left.\frac{\mathrm{d}^2W}{\mathrm{d}\Omega_{\boldsymbol{P}_\mathrm{f}}}\right|_j = \frac{2e^2\omega^{9/2}}{(2m_\mathrm{e})^{1/2}}(j - E_\mathrm{b}(R)/\omega - u_\mathrm{p})^{1/2}(j-u_\mathrm{p})^2[1+S(R)]^{-1}\sum_q(u_\mathrm{p}-j+q) \times \int \mathrm{d}^2\Omega_{k'}|\chi_q(\boldsymbol{P}_\mathrm{f},\boldsymbol{k}')|^2|\Phi_\mathrm{i}(\boldsymbol{P}')|^2_\mathrm{av}|M(\boldsymbol{P}_\mathrm{f},\boldsymbol{R})|^2, \tag{5}$$

where $\boldsymbol{P}_\mathrm{f}$ is the final momentum of the photoelectron, which is an experimentally observable quantity; $\mathrm{d}\Omega_{\boldsymbol{P}_\mathrm{f}} = \sin\theta_\mathrm{f}\mathrm{d}\theta_\mathrm{f}\mathrm{d}\varphi_\mathrm{f}$ is the differential solid angle in momentum space, where θ_f and φ_f are the scattering angle and azimuthal angle respectively; j is the net absorbed-photon number for ionization of the electron and is related to the final kinetic energy of photoelectrons by

$$\frac{P_\mathrm{f}^2}{2m_\mathrm{e}} = j\omega - E_\mathrm{b}(R) - u_\mathrm{p}\omega. \tag{6}$$

Here $E_\mathrm{b}(R)$ is the binding energy with the dependence on the internuclear distance,[37] and $u_\mathrm{p}\omega$ is the ponderomotive energy. The quantity $|\chi_q(\boldsymbol{P}_\mathrm{f},\boldsymbol{k}')|^2$ describes the photonic transition amplitude for the electron interacting with light, which is the same as the one for atoms (see Ref. [20] for details). The subscript av of $|\Phi(\boldsymbol{P}')|^2_\mathrm{av}$ means the average over the initial-state magnetic quantum numbers, $\boldsymbol{P}' = \boldsymbol{P}_\mathrm{f} - q\boldsymbol{k} + \boldsymbol{k}'$ where $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the wave vectors of the driving laser field and the spontaneous emission respectively. The PADs are calculated using Eq. (5) by setting $\theta_\mathrm{f} = 90^\circ$ and changing φ_f from 0° to 360°.

The ionization-rate formula for molecules given by Eq. (5) differs from that for atoms mainly in the dependence on the internuclear vector $\boldsymbol{R}$ in two different aspects.[20] The first one is an indirect dependence on internuclear distance R through the binding energy $E_b(R)$.[37] The second one is a direct dependence on both the internuclear distance and the molecular orientation through the interference factor. For circular polarization, the PADs are uniquely determined by the interference factor given by Eq. (4), because neither the binding energy change nor other factors in Eq. (5) will affect PADs. In the long-wavelength approximation, one can neglect the photonic momentum which is very small in comparison with the electronic momentum. So the factor $|\Phi_\mathrm{i}(\boldsymbol{P}')|^2_\mathrm{av} = 4\pi|\Phi_\mathrm{i}(\boldsymbol{P}')|^2$ derived from the atomic initial state relies only on its radial part thus it has nothing to do with the PADs.[20] The other factor $|\chi_q(\boldsymbol{P}_\mathrm{f},\boldsymbol{k}')|^2$ is independent of the azimuth for the circular polarization case, it has also no effects on PADs.

In the following we use our calculated PADs from H_2^+ as samples to show how to measure the internuclear vector $\boldsymbol{R}$ of molecules. Firstly, we show the correspondence between the calculated PADs and the internuclear vector. Several PADs are depicted in Figs. 1 and 2 for different $\boldsymbol{R}$'s. For H_2^+, the interference factor is a cosine function. From these figures we find: 1) the PADs are no longer isotropic but four-fold symmetric about the internuclear vector and its vertical; 2) the PADs show maxima and minima in positions varying with the molecular orientation, two maxima always appear in the direction perpendicular to the molecular axis, irrespective of the values of $\boldsymbol{P}_\mathrm{f}$ and $\boldsymbol{R}$; 3) the PADs vary with $\boldsymbol{P}_\mathrm{f}$ and $\boldsymbol{R}$. The PADs of low-energy electrons at smaller R are in wider shape and become thinner and thinner as R increases, the PADs of higher-energy electrons highly peak out along the axis perpendicular to the internuclear vector; 4) jet-like structures appear in the PADs of higher-energy photoelectrons and indicate the value of $P_\mathrm{f}R$ beyond π. The two main lobes, as the main structure of PADs featuring the two maxima, are perpendicular to $\boldsymbol{R}$; while the jets, as side structure of PADs, stick out from the waist between the two main lobes. These features are all made by the modulation of the cosine function. The direct correspondence between the molecular axis and the PADs suggests an applicable

method to determine the molecular orientation with PADs. A distinct advantage of using circularly polarized laser light is that the PADs are independent of the laser intensity and the carrier frequency with a given kinetic energy photoelectron.

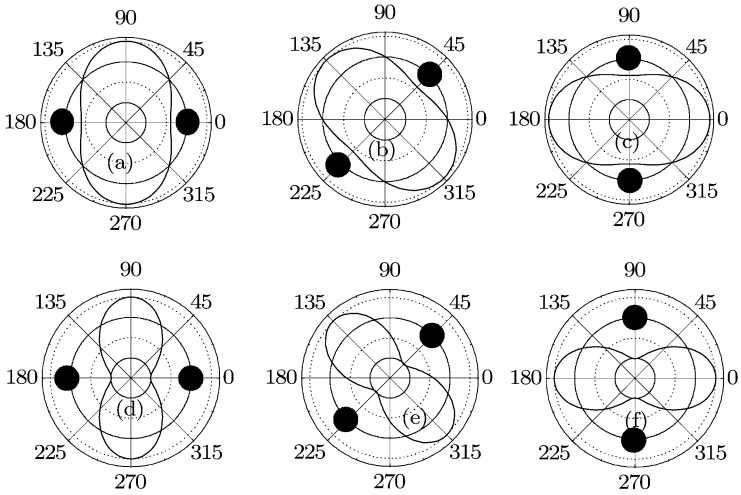


Fig. 1. Polar plots of the PADs for H_2^+ molecules irradiated by a circularly polarized laser field. Panels (a)–(c) are for photoelectrons with kinetic energy 7.4 eV and (d)–(f) for 15.2 eV. Other parameters are: the internuclear distance $R = 2.0$ a.u. with $E_b = 30.0$ eV, the effective charge $Z^* = 1.228$, laser intensity 10^{14} W/cm^2 and wavelength 800 nm. The two bullets stand for the two nuclei. The PADs in (a–c), as well as those in (d–f), are identical with respect to the molecular orientation axis, which discloses the one-by-one correspondence between the PAD and the molecular orientations for fixed photoelectron energy.

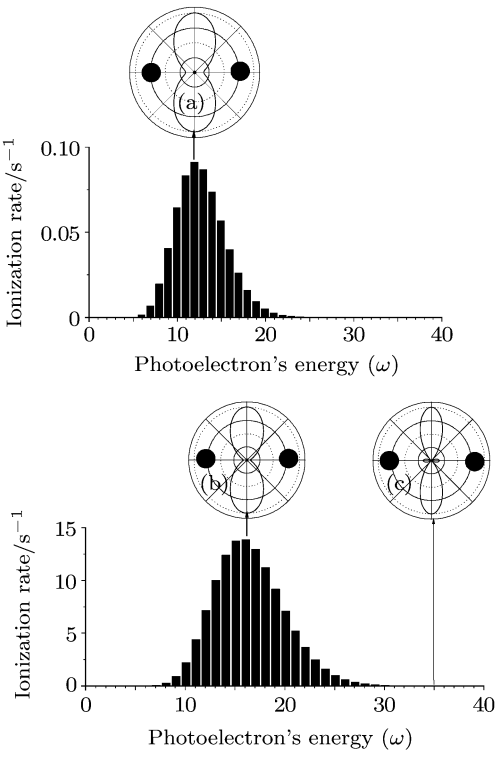


Fig. 2. The energy-resolved spectra of H_2^+ molecules irradiated by the laser fields of intensity 2×10^{14} W/cm^2 (top panel) and 3×10^{14} W/cm^2 (bottom panel). The insets are the PADs with electrons' energy indicated by arrows. Other conditions are the same as that in Fig. 1.

By inspecting the spectra of photoelectron kinetic-energy, we find that the PADs with higher energy are more suitable in the measurement of the molecular orientation. Firstly, in the circular-polarization case, the higher-energy photoelectrons have the higher yields which make the measurement of PADs more effectively. Secondly, as mentioned previously, the peaking out feature of PADs for higher-energy photoelectrons is favorable in the measurement of the molecular orientation. And finally, due to relatively larger momenta, the PADs of higher-energy photoelectrons which are more sensitive to the molecular distance can be used to deduce the internuclear distance more accurately.

Once the molecular orientation is known, the evaluation of internuclear distance from the PADs becomes straightforward. In many cases the photoelectron rates are given in an arbitrary unit. The following suggested method should be favorable for using PADs given in an arbitrary unit. One can derive the internuclear distance by the partial ionization rates at two arbitrary directions:

$$\begin{cases} F\cos^2(P_f R/2\cos\theta_1) = A_1, \\ F\cos^2(P_f R/2\cos\theta_2) = A_2, \end{cases} \tag{7}$$

where F is an overall common factor, θ_1 and θ_2 are the angles between $\boldsymbol{P}_f$ and $\boldsymbol{R}$ where the partial ionization

rates A_1 and A_2 are detected, respectively. The values of θ_1 and θ_2 are directly measured in experiments while the value of $\boldsymbol{P}_\mathrm{f}$ is related to the photoelectrons' kinetic energy E_f by $P_\mathrm{f} = \sqrt{2m_\mathrm{e}E_\mathrm{f}}$. We suggest that one datum is taken in the top of the main lobe where $\theta_1 = \pi/2$ which can be set as the common factor F, and another datum is taken in the main lobes nearby the top to ensure the value of $P_\mathrm{f}R$ being less than π. Thus, one can derive the magnitude of $\boldsymbol{R}$ by the measured partial ionization rates. We find

$$R = \frac{2\arccos\sqrt{A_2/A_1}}{P_\mathrm{f}\cos\theta_2}. \tag{8}$$

The idea to probe the molecular dynamics by the PADs was suggested by Zuo *et al.*[3] and the linearly polarized laser pulses are used in their scheme. Compared to the linear polarization case, the use of circular polarization has additional advantages. Recent studies have revealed that the PADs for linear polarization depend not only on the parameters of laser field but also on the molecular orientation.[6,25,26] The PADs for linear polarization vary sensitively with the intensity and frequency of the laser field and the number of absorbed photons. Thus it is difficult to deduce the molecular orientation from PADs. Meanwhile, for linear polarization, the PADs of photoelectrons are strongly affected by the polarization of the laser field with respect to the molecular orientation. For circular polarization, the direction of the polarization of the laser field, when the molecular axis lies in the polarization plane, has no effect at all on the shape of PADs. Thus any change on PADs is due to a change of the internuclear factor. Using this property, one can deduce the information of internuclear factor from PADs.

In conclusion, the main characters of the PADs of diatomic molecules irradiated by intense laser light of circular polarization depend only on the momentum of photoelectrons and the internuclear vector. The one to one correspondence between the PADs and the internuclear vector can be utilized reversely to measure the molecular orientation and the internuclear distance of homonuclear diatomic molecules. This scheme is practical since the PADs are measured with high resolutions in recent years. Because the correspondence between the PADs and the internuclear vector is independent of the intensity and frequency of the incident laser light, the technique suggested by the scheme is not sensitive to the laser intensity fluctuation and frequency chirp. This scheme may also be used to molecules with symmetric-distributed structures, such as carbon dioxide, benzene and ethylene, and more complicated molecules with further development.

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