Photoelectron energy peaks shift against the radiation pressure in strong-field ionization

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The photoelectric effect describes the ejection of an electron upon absorption of one or several photons. The kinetic energy of this electron is determined by the photon energy reduced by the binding energy of the electron and, if strong laser fields are involved, by the ponderomotive potential in addition. It has therefore been widely taken for granted that for atoms and molecules, the photoelectron energy does not depend on the electron’s emission direction, but theoretical studies have questioned this since 1990. Here, we provide experimental evidence that the energies of photoelectrons emitted against the light propagation direction are shifted toward higher values, while those electrons that are emitted along the light propagation direction are shifted to lower values. We attribute the energy shift to a nondipole contribution to the ponderomotive potential that is due to the interaction of the moving electrons with the incident photons.

INTRODUCTION

In 1905, the concept of light quanta (termed as photons nowadays) was first proposed by Einstein to explain the photoelectric effect, where a bound electron can only be released to the continuum by absorbing a single photon of an energy that is larger than the ionization potential (1). The final kinetic energy of the liberated electron is \(E_e = \hbar \omega - I_p\), where \(\omega\) is the light’s frequency, and \(I_p\) is the ionization potential of the target. Later, in 1931, Göppert-Mayer (2) showed that bound electrons can absorb multiple photons simultaneously such that the electron energy is given by \(E_e = n \hbar \omega - I_p\), where \(n\) is an integer that is large enough such that the bound electrons can overcome \(I_p\). In 1979, with the advent of pulsed laser techniques, Agostini et al. (3) found that even free-free transition can happen if the laser intensity is high enough, or—more generally speaking—a bound electron can absorb more photons than needed to overcome \(I_p\). As a result, a series of discrete peaks in the photoelectron’s energy domain occur, which are equally spaced by the photon energy of the driving laser field. The phenomenon has been termed above-threshold ionization (ATI) (4–7) and is shown schematically in Fig. 1.

In case of strong-field ionization, the electric field strength of the driving laser pulse is comparable to the atomic or molecular Coulomb field. Thus, the field-free ionization potential of the atom or molecule is Stark-shifted (8), leading to an effective potential \(I_p + U_p\) with the ponderomotive energy \(U_p\) that is given in atomic units by (4)

\[
U_p = \frac{F^2}{4 \omega^2}
\]

Figure 1 illustrates the effect of this nondipole correction on the photoelectron spectrum and highlights that, for certain emission angles, the ATI peaks are not equally spaced anymore as depicted in Fig. 1B and that this nondipole effect is insensitive to the internal structure of the atom or molecule that is ionized. Thus, the difference \(\overline{E_{\text{ATI},n}}(p_x) - E_{\text{ATI},n}\) increases with the electron momentum in the light propagation direction \(p_x\). The nondipole shift points for all ATI peaks into the direction that is opposite to the radiation pressure. However, the envelope (green line in Fig. 1B) is shifted in the direction that points along the radiation pressure. Note that previously, a seemingly similar backward shift of the envelope for very low electron energies has been observed by Ludwig et al. (14). The shift that we observe is present for all ATI peaks and even vanishes for very low energy electrons and is thus very different from the one...
The expression that is found using the simple Doppler-like effect agrees qualitatively with Eq. 4, but both expressions differ by a factor of 2 in front of \( p_x \). The reason for this quantitative difference warrants further research, but recent theoretical findings by Brennecke and Lein (13) using circularly polarized light indicate that the nondipole strong field approximation (SFA) model is correct. However, we believe that the very intuitive approach of the Doppler-like model and its capability to make the correct qualitative prediction make it worth to be mentioned.

The origin of ATI peaks in the wave picture

Above, we have used the photon picture and the Stark shift to explain the \( p_x \)-dependent shift of the ATI peaks. Alternatively, one can derive Eq. 2 in the wave picture: To this end, we consider an electron bound with \(-I_p\). After a part of the electronic wave function has been liberated (and while the laser is still on), this continuum wave packet has an average energy of \( E_{\text{elec}} + U_{\text{eff,wave}}^{\text{nth}}\), where \( E_{\text{elec}} \) is the electron’s asymptotic energy (at a time when the laser pulse is off), and \( U_{\text{eff,wave}}^{\text{nth}}\) is the average kinetic energy of the electron due to its quiver motion in the time-dependent electromagnetic field of the laser pulse.

Let us consider two wave packets, which are \( \Psi_1 \) and \( \Psi_2\). \( \Psi_1 \) is released at time \( t_1\), and \( \Psi_2 \) is released at time \( t_2 = t_1 + T_{ph} \), where \( T_{ph} \)
is the duration of one cycle of the laser field. We assume that both wave packets are identical parts of the same bound state until \( t_1 \) and thus \( \Psi_1(t_1) = \Psi_2(t_1) \). If we neglect the Coulombic potential, then the time evolution (22) from \( t_1 \) to \( t_2 \) can be expressed via \( \Psi_1(t_2) = \Psi_1(t_1) \cdot \exp(i T_{\text{ph}}(E_{\text{elec}} + U_{p,\text{eff,wave}})/\hbar) \). The wave packet \( \Psi_2 \) is bound until \( t_2 \). Therefore, its time evolution is given via \( \Psi_2(t_2) = \Psi_2(t_1) \cdot \exp (T_{\text{ph}}( - I_p )/\hbar) \). After the time \( t_2 \), the relative phase of the two wave packets does not change anymore. Thus, asymptotically, the relative phase of \( \Psi_1 \) and \( \Psi_2 \) is given by \( \phi(E_{\text{elec}}) = T_{\text{ph}}(E_{\text{elec}} + U_{p,\text{eff,wave}})/\hbar - T_{\text{ph}}(- I_p )/\hbar = T_{\text{ph}}(E_{\text{elec}} + U_{p,\text{eff,wave}} + I_p )/\hbar \). This leads to the condition for constructive interference, which is \( 2\pi = T_{\text{ph}}(E_{\text{elec}} + U_{p,\text{eff,wave}} + I_p )/\hbar \). This expression can be transformed to \( E_{\text{elec}} = \omega h - I_p - U_{p,\text{eff,wave}} \), which equals Eq. 2 for \( U_{p,\text{eff,wave}} = U_{p,\text{eff}} \). As expected, the interference of wave packets that are released periodically in time leads to energy quantization. This well-known result illustrates the equivalence of the photon picture and wave picture (23, 24).

Unfortunately, it is evident from Eqs. 3 and 4 that the order of magnitude for the expected energy shifts is extremely small for typical experimental conditions in the strong-field regime. For example, a linearly polarized laser pulse with a central wavelength of 800 nm and a peak intensity of \( 1.0 \times 10^{14} \) W/cm\(^2\) has a ponderomotive potential of 6.0 eV. For an initial momentum component of \( p_x = 0.2 \) atomic units (a.u.), the expected change in ATI peak energy is only \( U_p p_x / c \approx 9 \) meV.

### Experiment with counterpropagating laser beams

The key to successfully resolve such a small energy shift is to minimize systematic errors by using an experimental setup that allows for the ionization of individual atoms or molecules from a gas jet in an experimental geometry where the light propagation direction can be inverted while everything else remains unchanged, as schematically shown in Fig. 2 (26, 27). Briefly, two counterpropagating laser beams are focused onto the same spot in a gas jet to trigger the ionization process. The energy spectra are recorded by a specialized cold target recoil ion momentum spectroscopy (COLTRIMS) setup with extremely high momentum resolution in light propagation direction. With this setup, it is possible to record energy spectra under the exact same experimental conditions except for the inversion of the light propagation direction by using two different laser pathways (see Materials and Methods for details).

### RESULTS

Figure 3A displays the measured electron energy spectrum for one of the two laser pathways after restricting the data to a subset of electron emission angles of 9° to 11° with respect to the y-z plane that is perpendicular to the light propagation direction. Here, the z axis is the laser’s polarization axis, and the x axis is the light propagation direction, as schematically shown in Fig. 2 (see Materials and Methods for more details). This corresponds to values of \( \beta \) from 79° to 81°.
Experiment

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the order of tens of millielectron volts, agrees with the expectation. In addition, the magnitude of the difference, which is on the order of only 18 meV for the two energy spectra collected from the two counterpropagating laser pathways as reference. The expectations from nondipole SFA are shown fitting Gaussians to the data and taking the average of the two counterpropagation directions.

Fig. 4. Measured nondipole electron energy shift. (A to E) Shift of the peak position of the ATI peaks as a function of the momentum in light propagation direction $p_x$ for the first five ATI peaks (see Fig. 3A). The data points are determined by fitting Gaussians to the data and taking the average of the two counterpropagating laser pathways as reference. The expectations from nondipole SFA are shown in black dashed lines. The error bars show fitting errors.

For a full quantitative analysis, we plot the extracted nondipole energy shift for the first five ATI peaks as a function of photoelectron momentum along the light propagation direction $p_x$ in Fig. 4. The position of each ATI peak is obtained by Gaussian fits. The systematic error is minimized by taking the average of the two peak energy values, which are obtained from the two incident beams propagating in opposite directions, as reference. Figure 4 shows the case where the light propagation direction points to the positive $p_x$ direction. The decrease in the ATI peak energy as a function of $p_x$ is clearly visible. Thus, our experimental results confirm the prediction that the ATI peak energies for electron emission directions that are parallel to the light propagation direction are lower than for electrons that are emitted antiparallel to the light propagation direction. The shift is thus indeed opposite to what one might have naively expected from the direction of the radiation pressure.

**DISCUSSION**

Figure 5 summarizes the experimental results by depicting the slopes of the linear fits from Fig. 4 for each energy peak separately (see open circles in Fig. 5). To compare our experimental findings, we show the results together with the prediction from the nondipole SFA (Eq. 4) (10–12). For the SFA model, we use a ponderomotive potential that corresponds to the laser intensity used in the experiment (taking the uncertainty of the intensity calibration into account). It is unexpected that our measurement shows a substantially higher $p_x$ dependence compared to the result from the nondipole SFA.

To further cross-check our experimental findings, we make use of the symmetry of linearly polarized light. For Fig. 4, we only analyzed half of the electron momentum distribution that has negative values for $p_x$ (momentum in the polarization direction). The filled circles in Fig. 5 are obtained in full analogy to the open circles, but...
for these data points, the other half of the electron momentum distribution is used, which has positive p_z.

As expected, the filled and open circles show consistent results and indicate that the systematic errors are comparable to the statistical errors. Possible reasons for the experimentally observed enhancement of the energy shift compared to the nondipole SFA model are recollision dynamics (14, 28) and Coulomb interaction during and after tunneling (29), which are not included in the nondipole SFA model but could be relevant (especially for linearly polarized light). Furthermore, the nondipole SFA model was developed for atoms. In our experiment, we study H_2 that is expected to show very similar tunneling dynamics in comparison with atoms (30). However, recollision dynamics are sensitive to the excited states of the ion (31), which might be a reason for the experimentally observed enhancement of the energy shift compared to the nondipole SFA. As outlined above, ATI peaks can be explained by intercycle interference (24). Consequently, different types of interference could contribute to the observed energy shift. For instance, it is conceivable that the interplay of Coulomb interaction with subcycle interference (32) or holography (33–35) is affected by nondipole corrections, which could modulate (36) the ATI peak positions. This is in line with the findings of Brennecke and Lein (37) who showed that a rigorous treatment of nondipole effects is necessary to model interference using semiclassical models. Moreover, the liberated electron stems from a σ orbital. Thus, the initial electronic state cannot have angular momentum. Furthermore, the symmetry of linearly polarized light implies that a potential fingerprint of a nonvanishing magnetic quantum number would not manifest as rotation as in (38). Future theoretical studies might also investigate the role of properties of the initial electronic state (as, e.g., the electron’s magnetic quantum number) on the ATI peak positions.

In our previous work (27), another electric nondipole effect was reported for strong-field ionization driven by a circularly polarized laser pulse. In that work, it was found that the most probable photoelectron’s momentum component in the polarization plane varies as a function of momentum component in the light propagation direction. It is important to note that in (27), the envelope shifts (see Fig. 1B), and in our current work, we see a shift of the ATI peak positions. Furthermore, the shift in our current work leads to a decrease in energy as a function of p_x, and in (27), the shift leads to an increase in the energy of the peak of the envelope as a function of p_x. Thus, the shift in our current work points into the opposite direction compared to the shift in (27) and is related to an independent observable. As the observable in the current work, the ATI peak position is modified by nondipole effects that alter the phase of the electronic wave function in momentum space representation and thereby shift the ATI peak positions, which are an interference phenomenon. The shift in (27) is not related to inference and can be explained by classical acceleration. Nevertheless, both shifts are closely related to the ponderomotive potential as it has been shown theoretically in (13).

We show that ATI peaks occurring in strong-field ionization are only equally spaced in energy for electrons that are emitted perfectly at the right angle to the light propagation direction, qualitatively confirming a theoretic prediction from 1990 (9). For all other emission directions, the spatiotemporal evolution of the electric field results in ATI peaks that are not equally spaced in energy. Moreover, we have observed that the nondipole energy shift depends on the photoelectron momentum in light propagation direction (p_x). The ATI peak energies decrease (increase) compared to the expectations from the dipole approximation for electrons that are emitted in the forward (backward) hemisphere. The shifts of the ATI peaks as a function of the momentum in the light propagation direction (p_x) can be described as a p_x-dependent ac Stark shift (13). Our results show that the shifts of the ATI peak energies have a direction that is opposite to the direction of the shift that is due to the photon momentum (i.e., light pressure) (27). We expect that similar corrections should lead to a broadening of the photon’s energy spectra for high harmonic generation.

MATERIALS AND METHODS

Experimental design

The two counterpropagating laser beams were generated from a Ti: Sapphire laser system (Coherent Legend Elite). The output of the laser system (25 fs, 800 nm, 10 kHz) is split into two pathways using a dielectric beam splitter, termed as pathways A and B, respectively. The intensity and polarization of each laser pathway can be adjusted independently. Eventually, the two linearly polarized laser beams are focused into the vacuum chamber of a COLTRIMS reaction microscope (39) from two opposite sides using two independent lenses (f = 25 cm) onto the same spot inside a supersonic gas jet of H_2 molecules. For both laser pulses, the polarization axis is aligned along the z direction. Two motorized shutters placed in the two beam pathways are used to toggle between both pathways every 3 min to minimize systematic errors. The peak intensity in the laser focus is found to be 1.0 × 10^14 W/cm^2 with an uncertainty of ±20%. For laser intensity calibration, the ratio between double and single ionization yield of xenon atom is recorded and compared to values given in (40).

A static electric field of 29.8 V/cm was applied to guide the electrons and ions created from single ionization of H_2 molecules to two time- and position-sensitive detectors at opposite ends of the spectrometer (41). The acceleration lengths of the field region for electrons and ions are 15 and 58 cm, both of which are followed by a field-free drift region of 30 and 108 cm, respectively. The electron (ion) detector is composed of a three-layer (two-layer) stack of multichannel plates followed by a three-layer delay-line anode. The three-dimensional momenta of the electrons and ions were retrieved coincidently from the times of flight and positions of impact. The z direction is the time-of-flight direction of the COLTRIMS reaction microscope. The single-event momentum resolution of our COLTRIMS reaction microscope for the detection of a single electron is 0.003 a.u. in p_x and p_y directions and 0.03 a.u. in p_z direction.

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