

Strong-field ionization of xenon dimers: The effect of two-equivalent-center interference and of driving ionic transitions

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Strong-field ionization (SFI) of the homonuclear noble gas dimer Xe_2 is investigated and compared with SFI of the Xe atom and of the ArXe heteronuclear dimer by using ultrashort Ti:sapphire laser pulses and photoelectron momentum spectroscopy. The large separation of the two nuclei of the dimer allows the study of two-equivalent-center interference effects on the photoelectron momentum distribution. Comparing the experimental results with a new model calculation, which is based on the strong-field approximation, actually reveals the influence of interference. Moreover, the comparison indicates that the presence of closely spaced gerade and ungerade electronic state pairs of the Xe_2^+ ion at the Xe_2 ionization threshold, which are strongly dipole coupled, affects the photoelectron momentum distribution.

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I. INTRODUCTION

The effect of two equivalent emission centers on strong-field ionization (SFI) of molecules has attracted attention since the first hints of its possible influence were detected in the total ionization rate of homonuclear diatomic molecules and in the photoelectron momentum distribution. Molecules such as N_2 , O_2 , S_2 , and F_2 with different electronic ground-state symmetry have been investigated [1–4]. Experimentally, molecular SFI has usually been compared with SFI of a corresponding atom, which has a practically identical ionization potential. This kind of comparison makes sense, since for atomic SFI the total ionization rate and the overall kinetic-energy distribution of directly emitted photoelectrons, which did not rescatter on the ion core, has been found to be determined mainly by the ionization potential alone [5–9]. Differences of SFI rates and photoelectron kinetic-energy distributions for a corresponding molecule would thus directly indicate a molecular structure effect. Theoretical investigations actually showed an influence of the symmetry of the orbital of a homonuclear molecule, from which the electron is removed, on SFI [10–12]. Specifically for the O_2 molecule, a suppression found in the yield of low-kinetic-energy photoelectrons, compared with the companion atom Xe, has successfully been accounted for by considering the symmetry of the O_2 highest occupied molecular orbital (HOMO) from where the electron is removed [4]. This orbital gives rise to a modulation of the momentum distribution of directly emitted electrons of the form $\sin^2(\mathbf{R} \cdot \mathbf{p}/2)$ where $R = |\mathbf{R}|$ is the internuclear separation and $\mathbf{p}$ is the momentum of the photoelectron. This factor just suppresses the yield of photoelectrons with small momentum; that is, of those electrons which are emitted directly without rescattering. For N_2 , compared with the companion Ar atom, the situation is different. Removing an electron from the N_2 HOMO actually gives rise to a modulation of the photoelectron momentum distribution by a factor $\cos^2(\mathbf{R} \cdot \mathbf{p}/2)$ [4,12]. For the tightly bound N_2 molecule ($R = 2.1$ a.u.), this function does not change too much over the kinetic-energy range where directly emitted photoelectrons dominate the kinetic-energy distribu-

tion. Thus one would not expect a significant suppression of the total photoelectron yield and a marked difference in the kinetic-energy distribution to appear in comparison with the companion Ar atom. This result was actually found experimentally [3,4].

The experiments on tightly bound molecules are not able to completely reveal the influence of two-equivalent-center interference on the photoelectron momentum distribution. The main obstacle is the hardly possible observation of at least one half of the period of the cosine or sine functions modulating the momentum distribution within the momentum range where overwhelmingly directly emitted photoelectrons are found. This range is practically limited from above by the kinetic energy $E_{\text{kin}} = 2U_p$ (or for the momentum $|\mathbf{p}| < 2\sqrt{U_p}$, atomic units assumed) where classically directly emitted photoelectrons are found. The situation can be changed by investigating homonuclear diatomics with an intrinsic large internuclear separation, such as, for example, noble gas dimers (see, for example, Refs. [13–15]).

Similar to noble gas atoms, whose strong-field ionization has successfully been modeled by using the strong-field approximation (SFA), molecules usually also have an electronic ground state well separated from electronically excited states. One thus may expect the atomic SFA to be also applicable to molecules. However, different from noble gas ions, molecular ions usually possess many closely spaced electronic states next to the molecular ionization threshold. Their energy-level spacings are usually of the same order of magnitude as the photon energy typically used for SFI. Moreover, these states are normally strongly coupled by large transition dipole moments. In a high-intensity laser pulse, this means that SFI will end up in vastly perturbed ionic states while the laser pulse is applied. This has already been observed in and theoretically modeled for high-order harmonic generation in molecular samples [16–20].

Besides affecting high-harmonic generation, driving of ionic transitions in molecular ions during SFI will certainly also influence the photoelectron momentum distribution, and, for homonuclear molecules, the two-equivalent-center interfer-

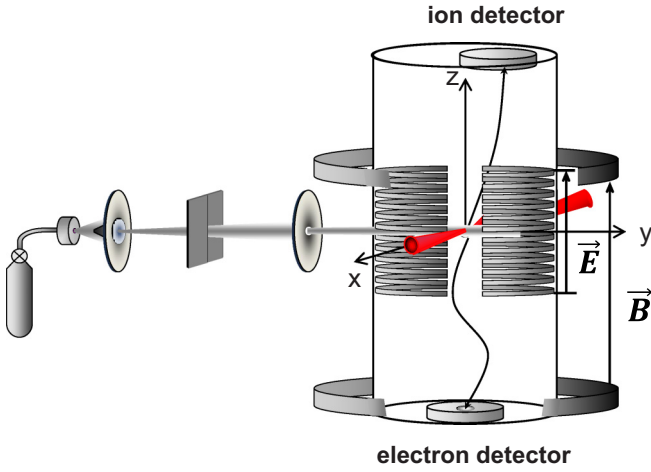


FIG. 1. Scheme of the reaction microscope setup.

ence expected to be found for directly emitted photoelectrons. Here we investigate this effect for SFI of Xe_2 dimers, which have an internuclear separation ($R = 8.35$ a.u. [13]), where it is possible to retrieve two-equivalent-emission-center interference together with the possible effect of strongly driving transitions in the Xe_2^+ ion during SFI of Xe_2 . The Xe_2^+ ion has altogether six closely spaced electronic states at the ionization threshold which are connected by large transition dipole matrix elements [21,22]. Based on the results for high-harmonic generation, the heavy perturbation of this state manifold during SFI is expected to leave an imprint on SFI. We analyze the experimental results for directly emitted photoelectrons using the SFA for a basic homonuclear model molecule which simulates main features of the Xe_2 SFI. Hartree atomic units, i.e., $\hbar = e = m_e = 1$, accompanied by the Gaussian system of units for the electromagnetic field, are used throughout the paper unless otherwise specified.

II. EXPERIMENTAL SETUP

A schematic view of the experimental setup is shown in Fig. 1. A reaction microscope was used for the investigation whose detailed principle of operation can be found in Ref. [23]. The reaction microscope allows the correlated determination of the momenta of all charged particles, electrons, and ions, formed in the interaction of, in our case, laser pulses with noble gas atoms and dimers.

In the experiment Xe_2 and ArXe dimers were formed in a supersonic expansion of either pure Xe gas or of a mixture of Xe with Ar (≈ 15 vol% Xe in Ar) at a stagnation pressure of 0.65 and 3 bar, respectively. The nozzle with an opening diameter of $20 \mu\text{m}$ was kept at room temperature. The supersonic beam then consisted of either a mixture of mainly Xe atoms and a small contribution of Xe_2 dimers (less than 2%) or of mainly Ar and Xe atoms with small amounts of Ar_2 , Xe_2 , and ArXe dimers (less than 2%). The expansion conditions were set to avoid excessive formation of bigger clusters. After passing through a skimmer and two differentially pumped vacuum stages, the beam was finally collimated by a slit with dimensions $25 \mu\text{m} \times 3 \text{ mm}$ positioned approximate 0.9 m downstream of the nozzle. The focused laser beam crossed

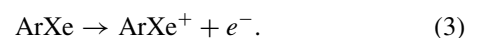
the supersonic beam approximately 0.15 m behind this slit. In this way, the width of the supersonic beam along the direction of propagation of the laser beam was limited to about $30 \mu\text{m}$.

Assuming a residual thermal velocity distribution along the axis of the supersonic beam, an axial translational temperature $T_{\parallel}$ (see Ref. [24]) can be determined from the measured velocity distribution of Xe^+ ions along the beam axis after SFI of xenon atoms. It amounts to $T_{\parallel} = 8 \text{ K}$ for the pure Xe expansion and $T_{\parallel} = 5.5 \text{ K}$ for the mixed gas expansion. On the basis of this residual translational temperature, it is possible to estimate which vibrational states of the Xe_2 or ArXe dimers in the beam are significantly populated. To do this, we assume that the translational temperature is equal to the internal vibrational temperature. For the Xe_2 dimer, one can estimate the population probability of the first vibrationally excited state ($v = 1$) to be about 3×10^{-2} ($T = 8 \text{ K}$, pure Xe gas expansion), while for the ArXe dimer this probability is approximately equal to 1×10^{-3} ($T = 5.5 \text{ K}$, mixed gas expansion). The vibrational constants of Xe_2 and ArXe in the electronic ground state used here were taken from Refs. [13,25], respectively. Thus, in the supersonic beam, practically only the vibrational ground state of the dimers was populated.

A Ti:sapphire laser system (center wavelength of 780 nm) delivering ultrashort laser pulses with a full width at half maximum of 40 fs at a repetition rate of 3 kHz was used to ionize the noble gas dimers and monomers. The energy of the pulses was adjusted in a range between $\approx 30 \mu\text{J}$ and $\approx 60 \mu\text{J}$. The laser beam was focused at the supersonic beam by using an on-axis spherical mirror with a focal length of 150 mm. The width of the supersonic beam along the laser-beam propagation axis (see above) was thus short compared with the confocal parameter of the laser beam. With this focusing geometry the light intensities reached in the focal spot ranged from 5×10^{13} to $1.1 \times 10^{14} \text{ W/cm}^2$.

A weak homogeneous electric field (4.8 V/cm) was applied across the interaction region, parallel to the axis of the momentum spectrometer, to extract photoelectrons and ions (Fig. 1). After acceleration and subsequent field-free drift, these particles were detected by position-sensitive multichannel plate detectors with an active area diameter of 80 mm. In this way, a 4π solid angle of detection was reached for the ions of interest here (i.e., Xe^+ , Xe_2^+ , and ArXe^+). A homogeneous magnetic field (field strength 1.9 Gauss) parallel to the electric field was applied to guide all photoelectrons with a momentum component less than ≈ 0.35 a.u. in the plane of the detector (perpendicular to the spectrometer axis) to the electron detector. It forces the electrons onto cyclotron orbits in the plane perpendicular to the magnetic field. For each particle, the time of flight was determined along with the position where it hit the detector. From these data, the full momentum vector of each individual detected particle can be reconstructed.

We recorded the individual photoelectron momentum distributions for the ionization processes:



To be able to identify whether a photoelectron hitting the detector originates from the ionization of a Xe atom, of a Xe₂ dimer, or of ArXe, each electron was detected together with the corresponding photoion. For an unambiguous correspondence, we restricted the rate of detecting ions to $\approx 20\%$ of the repetition rate of the laser pulses. To further reduce the possibility of false ion-electron coincidences in the photoelectron momentum distributions, we used momentum conservation for the z component p_z of the ion and electron momenta, i.e., the momentum component along the axis of the spectrometer which is accessed by the time of flight of the ion and electron, respectively (see Fig. 1). Since p_z is a momentum component perpendicular to the direction of propagation of the supersonic beam, the sum of these momentum components for an electron and the corresponding photoion from any one of the ionization processes (1)–(3) is practically zero [$p_z(\text{ion}) + p_z(e^-) = 0$]. Applying momentum conservation also reduces the contribution of photoelectrons to the photoelectron momentum distributions for the ionization processes (1)–(3) which originate from ionization of larger clusters to a negligible level. It was not possible to avoid the presence of larger clusters in the beam completely. Different from the ionization processes (1), (2), and (3), Xe⁺, Xe₂⁺, and ArXe⁺ ions emerging from dissociative ionization of these bigger clusters gain momentum from dissociation. Thus, for these ions the sum momentum $p_z(\text{ion}) + p_z(e^-)$ is not close to zero.

III. THEORETICAL BACKGROUND

The impact of two-emission-center interference on SFI of a homonuclear dimer and of driving transitions among ionic bound states during SFI on the photoelectron momentum distribution is modeled by using the strong-field approximation (SFA) [5–7,9]. We consider here only directly emitted photoelectrons without taking rescattering on the ion core into account. For the model calculation, we reduce the dimer ion to a two-level system consisting of an electronic eigenstate pair $\{\phi_+^I, \phi_-^I\}$ coupled by the electric field of the applied laser pulse. This idealizes the actual situation where, due to spin-orbit splitting and the presence of $\Pi_{g,u}$ and $\Sigma_{g,u}$ states, altogether six closely spaced ionic states are present. They are strongly coupled by the applied laser pulse due to the presence of large transition dipole matrix elements [21,22]. However, the simple model will give insight into the effect of two equivalent emission centers and of the accompanying driving of ionic transitions during the application of the laser pulse on the photoelectron momentum distribution. In the model calculation we approximate the actual transition dipole moment $\mathbf{d}$ which couples the gerade and ungerade ionic state pairs ($\Sigma_g - \Sigma_u$, $\Pi_g - \Pi_u$) by $-\mathbf{R}/2$ ($R = |\mathbf{R}|$ is the

internuclear separation), pointing along the internuclear axis. In a real experimental situation, a $\Sigma - \Pi$ dipole coupling is also present; however, the strength is approximately two orders of magnitude lower than the $\Sigma_g - \Sigma_u$ and $\Pi_g - \Pi_u$ couplings at the equilibrium internuclear separation of the Xe₂⁺ dimer [22]. Thus, a restriction to a single gerade-ungerade state pair for the model appears justified. Moreover, we assume the vibration and the rotation of the model dimer ion to be frozen while the laser pulse is applied. This is reasonable since for Xe₂⁺ the duration of the laser pulse applied in the experiment is short enough [26,27]. Therefore, we can restrict ourselves to calculating the SFA matrix element at a fixed internuclear separation which corresponds to the equilibrium internuclear separation of Xe₂.

The equilibrium internuclear separation R of the Xe₂ dimer is large ($R = 8.35$ a.u. [13]), therefore the Dyson orbitals appearing in the general SFA transition matrix element (A7), derived in the appendix, are approximated by linear combinations of atomic orbitals $\phi^A(\mathbf{x})$; namely $\phi_{+,-}^D(\mathbf{x}) = [\phi^A(\mathbf{x} - \mathbf{R}/2) \pm \phi^A(\mathbf{x} + \mathbf{R}/2)]/\sqrt{2}$. Here the overlap of the two atomic orbitals is assumed to be negligible. For the atomic orbital, we choose a simple hydrogenic orbital $\phi_{n,l,m}$ with principle quantum number $n = 5$, angular momentum $l = 1$, magnetic quantum number $m = 0$ with respect to the internuclear axis of the dimer as quantization axis and a nuclear charge ($Z = 4.72$ a.u.) which adapts the ionization potential of the orbital to that of the Xe atom ($I_p = 12.13$ eV). We thus restrict ourselves to a σ -orbital pair. This results in

$$\tilde{\phi}_{+,-}^D(\mathbf{p}) = \sqrt{2}\tilde{\phi}_{n,l,m}(\mathbf{p}) \begin{cases} \cos\left(\frac{\mathbf{R}\cdot\mathbf{p}}{2}\right) & + (\text{ungerade}) \\ -i \sin\left(\frac{\mathbf{R}\cdot\mathbf{p}}{2}\right) & - (\text{gerade}), \end{cases} \quad (4)$$

for the Fourier transform of the dimer Dyson orbital pair with $\tilde{\phi}_{n,l,m}(\mathbf{p})$ being the Fourier transform of the atomic orbital. In our specific case, the inversion symmetry of the two orbitals is determined by the ungerade symmetry of the atomic orbital with angular momentum $l = 1$.

With the approximation to the ionic transition dipole moment introduced above, the time-dependent Schrödinger equation for the two involved molecular ionic states, which we identify by ϕ_+^I and ϕ_-^I according to the two corresponding Dyson orbitals (4), reads

$$i \frac{d}{dt} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} = \begin{pmatrix} \epsilon_- & -\frac{\mathbf{R}\cdot\mathbf{E}(t)}{2} \\ -\frac{\mathbf{R}\cdot\mathbf{E}(t)}{2} & \epsilon_+ \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix}, \quad (5)$$

with $\mathbf{E}(t)$ being the electric-field strength of the laser pulse and ϵ_+ and ϵ_- being the energy levels of the ionic states ϕ_+^I and ϕ_-^I , respectively. The time-dependent ionic wave function then reads

$$\psi^I(t) = a_1(t)\phi_-^I + a_2(t)\phi_+^I. \quad (6)$$

Considering these ingredients, the general SFA transition matrix element (A7) can be reduced to

$$M_{(+,-),i}^{(1)}(\mathbf{p}) \cong -\sqrt{2} \cos\left(\frac{\mathbf{R}\cdot\mathbf{p}}{2}\right) \int_{T_i}^{T_f} dt \exp[i\tilde{\chi}] \left\{ c_2^*(t) \frac{\partial}{\partial t} \left[\tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right] + i c_1^*(t) \frac{\mathbf{R}\cdot\mathbf{E}(t)}{2} \tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right\} \\ + \sqrt{2} \sin\left(\frac{\mathbf{R}\cdot\mathbf{p}}{2}\right) \int_{T_i}^{T_f} dt \exp[i\tilde{\chi}] \left\{ i c_1^*(t) \frac{\partial}{\partial t} \left[\tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right] - c_2^*(t) \frac{\mathbf{R}\cdot\mathbf{E}(t)}{2} \tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right\}, \quad (7)$$

for the homonuclear model dimer where the phase $\bar{\chi}$ is defined by $\bar{\chi}(t, \mathbf{p}, T_f, T_i) = \chi(t, \mathbf{p}, T_f, T_i) + (\epsilon_+ + \epsilon_-)(t - T_f)/2$. The amplitudes c_1 and c_2 are the solutions of the transformed ionic Schrödinger equation

$$i \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \frac{\epsilon}{2} \begin{pmatrix} -\cos[2f(t)] & -i \sin[2f(t)] \\ i \sin[2f(t)] & \cos[2f(t)] \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \quad f(t) = -\frac{\mathbf{R} \cdot \mathbf{A}(t)}{2c}, \quad \epsilon = \epsilon_+ - \epsilon_-, \quad (8)$$

with the amplitudes c_1 and c_2 related to a_1 and a_2 in Eq. (5) via

$$\begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} = e^{-i(\epsilon_+ + \epsilon_-)(t - T_f)/2} \begin{pmatrix} \cos[f(t)] & i \sin[f(t)] \\ i \sin[f(t)] & \cos[f(t)] \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}. \quad (9)$$

The momentum distribution of the ionized electron, represented by the SFA transition amplitude (7), thus depends on the state of the ion detected at the end of the laser pulse. In the calculation this final ionic state, provided it is one of the eigenstates ϕ_+^I or ϕ_-^I of the unperturbed Hamiltonian of the ion, is fixed by integrating the ionic Schrödinger equation (8) subject to the condition $c_1(T_f) = 1$, $c_2(T_f) = 0$ or $c_1(T_f) = 0$, $c_2(T_f) = 1$, respectively. The first initial condition means the ionic state ϕ_-^I , corresponding to the Dyson orbital $\tilde{\phi}_-^D(\mathbf{p})$, is the final state, while the second initial condition chooses the ionic state ϕ_+^I to be the final ionic state.

The SFA transition matrix element in Eq. (7) explicitly reveals the effect of the presence of two emission centers; namely, a two-center interference effect, on the momentum distribution of directly emitted photoelectrons. The $\cos(\mathbf{R} \cdot \mathbf{p}/2)$ and $\sin(\mathbf{R} \cdot \mathbf{p}/2)$ factors multiplying the integrals in Eq. (7) are responsible for this interference to appear. For example, if only the first integral on the right-hand side of Eq. (7) is significantly different from zero, the photoelectron momentum distribution $|M_{(+,-),i}^{(1)}(\mathbf{p})|^2$ would be modulated by $\cos^2(\mathbf{R} \cdot \mathbf{p}/2)$. This would give rise to zeros and a suppression of the photoelectron yield in the momentum distribution close to the zeros of $\cos^2(\mathbf{R} \cdot \mathbf{p}/2)$; namely, $\mathbf{R} \cdot \mathbf{p} = (2n + 1)\pi$ with $n = 0, \pm 1, \dots$. Moreover, Eq. (7) also shows that the actually observable interference will be affected by the driving of transitions in the ion while the laser pulse is applied through the presence of the $c_1(t)$ and $c_2(t)$ amplitudes appearing under the integrals.

Assuming the values of the two integrals in Eq. (7) named $I_1(\mathbf{p})$ (multiplying the cosine function) and $I_2(\mathbf{p})$, the photoelectron momentum distribution can be explicitly represented by

$$|M_{(+,-),i}^{(1)}(\mathbf{p})|^2 \cong \{|I_1|^2 + |I_2|^2\} + \{|I_1|^2 - |I_2|^2\} \cos(\mathbf{R} \cdot \mathbf{p}) - 2\text{Re}(I_1 I_2^*) \sin(\mathbf{R} \cdot \mathbf{p}), \quad (10)$$

with $\text{Re}(I_1 I_2^*)$ being the real part of the product $I_1 I_2^*$. This expression shows that, independent of the dependence of the integrals on the electron momentum $\mathbf{p}$, a modulation of the distribution originating from two-center interference will appear in the photoelectron momentum distribution. The actual modulation depth and shape, however, will depend on the values of these integrals and on their dependence on $\mathbf{p}$.

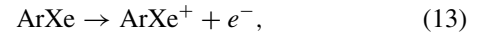
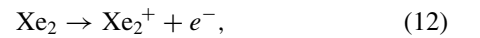
IV. RESULTS

A. Experiment

Experimentally we investigated the effects of interference and of driving ionic transitions while the laser pulse is applied

by using the homonuclear Xe_2 dimer. The vertical ionization potential of this dimer ($I_p = 11.845$ eV [28]) is close to that of the Xe monomer ($I_p = 12.13$ eV [29]). As a further reference the mixed atom dimer ArXe was investigated. It also has an ionization potential ($I_p = 11.985$ eV) very close to that of its Xe constituent [30]. Considering the light intensities used in our experiment, the ionization probability of the Ar constituent of this dimer is negligibly small. Thus, ionization of ArXe can be expected to proceed by ionization of its Xe constituent only, meaning that the positive charge is localized at the Xe constituent. Therefore this heteronuclear dimer should not show any interference effect. The first-excited states of the ArXe^+ dimer ion, which have a nonzero dipole coupling to the spin-orbit split ionic states at the ionization threshold, correspond to charge-transfer states where the positive charge is localized at the Ar site [31]. They are energetically separated by approximately 3 eV from the ionization threshold [31]. The internuclear separation where ionization takes place is the equilibrium separation of the dimers; that is, $R = 8.35$ a.u. for Xe_2 and $R = 7.73$ a.u. for ArXe [13,31]. While the laser pulse is applied, this separation may be assumed to be fixed, i.e., nuclear vibrational motion can be ignored.

From top to bottom Fig. 2 shows the photoelectron momentum distributions for the SFI processes:



measured at a light intensity of 8.0×10^{13} W/cm². The intensity has been determined from the measured cutoff kinetic energy for rescattered electrons which amounts to ten times the ponderomotive energy ($10U_p$) in the ionization process (11) [32]. The peak ponderomotive energy in the focused laser pulse thus is $U_p = 4.55$ eV. For all investigations reported here, the polarization of the light pulses was linear, and the z axis of any coordinate system used is assumed parallel to this direction. In Fig. 2, p_z thus is the momentum component along the polarization axis, and $p_r = (p_x^2 + p_y^2)^{1/2}$ is the absolute value of the momentum vector projected onto the plane perpendicular to the z axis. The distributions are rotationally symmetric about the polarization vector. As p_r tends to zero, the photoelectron yield always decreases to zero, because the phase-space volume element in a cylindrical coordinate system is proportional to $p_r dp_r$. This behavior is obviously present in Fig. 2.

The momentum distributions of the photoelectrons for SFI of the Xe monomer and ArXe heteronuclear dimer are very similar (top and bottom spectra). This result shows that SFI

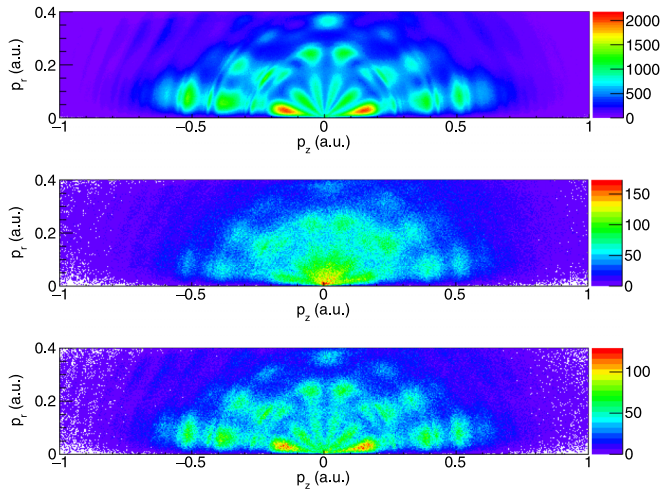


FIG. 2. From top to bottom: momentum distributions of photoelectrons detected together with Xe^+ , Xe_2^+ , and ArXe^+ ions at a light intensity of $8.0 \times 10^{13} \text{ W/cm}^2$. The polarization of the laser pulses was linear and directed along the z axis. The molecular axis of the dimers was not aligned with respect to the direction of polarization. The numbers on the color scale represent electron counts per momentum bin.

of ArXe indeed means the Xe constituent of this dimer is ionized. A similar behavior has been found for SFI of ArNe dimers [15]. On the other hand, the momentum distribution found for the Xe_2 dimer (center spectrum in Fig. 2) significantly differs from that of the Xe monomer. The most obvious difference is the pronounced narrow yield maximum at the momentum $p_r = p_z \cong 0$ which is absent in the Xe monomer and in the ArXe spectra. This behavior appears independent of the light intensities used in our experiment (5.0×10^{13} – $1.1 \times 10^{14} \text{ W/cm}^2$). The narrow maximum we find here at $p_r = p_z \cong 0$ has previously also been observed in SFI of Ne_2 , Ar_2 , and Kr_2 [15]. It was attributed to frustrated tunnel ionization of the dimers where the electron excited in the laser pulse first gets trapped in a Rydberg state of the molecule at the end of the pulse. Subsequently this Rydberg electron is shaken off by a charge oscillation in the dimer ion core [15]. A charge oscillation in the ion core is brought about by coherently populating gerade as well as ungerade eigenstates of the ion core in the laser pulse which are found closely spaced at the ionization threshold [21].

For a more quantitative comparison, we show in Fig. 3 the kinetic-energy distribution of the photoelectrons for SFI of Xe , Xe_2 , and ArXe measured at the light intensity of $8.0 \times 10^{13} \text{ W/cm}^2$. Included in the figure are all electrons emitted with a momentum $\mathbf{p}$ enclosing an angle θ with the positive z axis (polarization direction) in the range between 160° and 180° (see Fig. 2). Corresponding to the light intensity of $8.0 \times 10^{13} \text{ W/cm}^2$, the kinetic-energy range where directly emitted photoelectrons dominate the spectrum is limited to the interval $0 \leq E_{\text{kin}} \leq 2U_p = 9.1 \text{ eV}$. The inset in the figure shows an enlarged view of the kinetic-energy distribution for SFI of Xe_2 and ArXe on a linear scale to reveal the main differences. As already mentioned in connection with the two-dimensional momentum distributions in Fig. 2, the kinetic-energy distribution for SFI of ArXe closely resembles

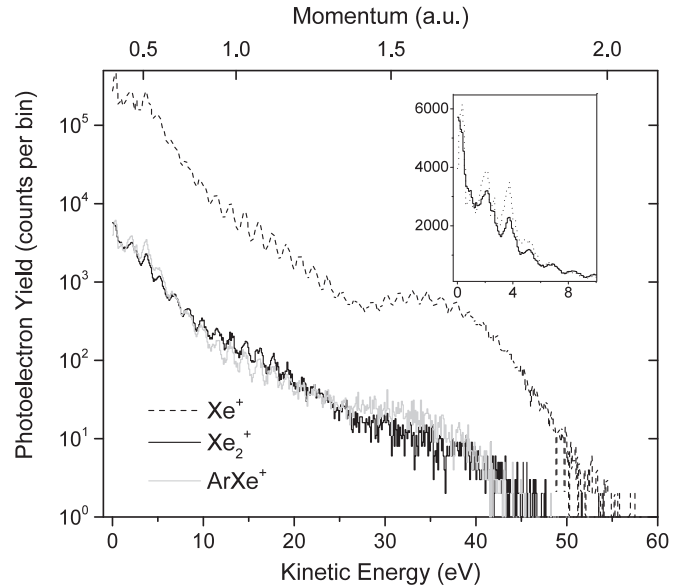


FIG. 3. Kinetic-energy distribution of photoelectrons detected together with Xe^+ (dashed line), Xe_2^+ (black line), and ArXe^+ (gray line) ions. Included are only those electrons emitted into the solid-angle range $160^\circ \leq \theta \leq 180^\circ$ and $0 \leq \varphi \leq 360^\circ$ (θ is the polar angle with respect to the p_z axis; see Fig. 2). The inset shows the Xe_2 (full line) and ArXe spectra (dotted line) in the energy range zero to 9 eV on a linear scale. In this range directly emitted photoelectrons prevail, which have not rescattered on the ion core.

that for Xe up to $2U_p$. The main differences among the Xe , ArXe , and Xe_2 kinetic-energy distributions for directly emitted photoelectrons are most obviously visible in the inset of Fig. 3. Specifically in the energy range between approximately 1.5 and 6 eV, the yield of photoelectrons in the Xe_2 spectrum is significantly suppressed compared with that in the ArXe spectrum. A similar suppression is thus also found with respect to the photoelectron yield in the Xe spectrum in this kinetic-energy range.

The suppression of the Xe_2 photoelectron yield compared with that for Xe in the kinetic-energy distributions shown in Fig. 3 can be quantified by calculating the ratio $r(E_{\text{kin}}) = Y_D(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$. Here $Y_D(E_{\text{kin}})$ is the photoelectron yield measured for the homonuclear and for the ArXe dimer, respectively, and $Y_{\text{Xe}}(E_{\text{kin}})$ is the yield measured for the Xe monomer. For the determination of this ratio, the yield of all photoelectrons emitted into the solid-angle range $160^\circ \leq \theta \leq 180^\circ$ and $0 \leq \varphi \leq 360^\circ$ (see Fig. 3) is taken into account. The ratios as a function of the photoelectron kinetic energy are shown in Fig. 4. We normalized them to unity at the minimum of each curve shown. At each light intensity, we marked the point where the kinetic-energy reaches $2U_p$, which is the classical upper limit of the kinetic energy where directly emitted photoelectrons are found. Beyond this kinetic energy, virtually only photoelectrons which have rescattered on the ion core contribute.

As can be seen in Fig. 4, the ratio for the Xe_2 dimer reaches a minimum at each light intensity which is well located within the kinetic-energy range $E_{\text{kin}} < 2U_p$ where directly emitted photoelectrons predominate. We may thus assume that just these electrons are responsible for the formation of this

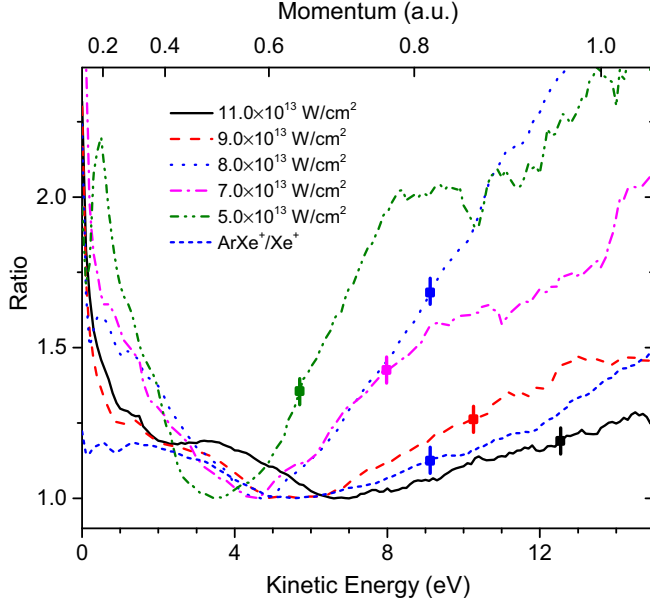


FIG. 4. Ratios $r(E_{\text{kin}})$ of the dimer to monomer photoelectron yields at laser pulse intensities in the range between 5.0×10^{13} and 11.0×10^{13} W/cm². The ratio for the ArXe dimer is only shown at an intensity of 8.0×10^{13} W/cm². The ratios are normalized to unity at the respective minimum of $r(E_{\text{kin}})$ at each intensity level. The squares with the vertical bar on each curve indicate the point where the kinetic energy reaches $2U_p$.

minimum. The position of the minimum shows a dependence on the intensity of the laser pulses. It slightly shifts towards larger kinetic energies with increasing light intensity. Also the minimum gets shallower with increasing intensity. Towards $E_{\text{kin}} = 0$, the ratio for Xe₂ always increases steeply. In the low-energy region $E_{\text{kin}} \lesssim 1$ eV, this increase may in large parts be attributed to shake-off of a Rydberg electron as a result of charge oscillation in the ion core after frustrated tunnel ionization of Xe₂ [15]. Figure 4 also shows that, after passing the minimum, the photoelectron yield ratio further increases also in the kinetic-energy range where rescattered photoelectrons predominate ($E_{\text{kin}} > 2U_p$).

The yield ratio for the ArXe dimer also shows a certain variation with the kinetic energy in the range below $E_{\text{kin}} = 2U_p$ with a shallow minimum developing close to $E_{\text{kin}} \approx 5.5$ eV. However, the ratio approaches a nearly constant value below $E_{\text{kin}} \approx 3$ eV whereas the ratio for the Xe₂ dimer steeply increases towards $E_{\text{kin}} = 0$. Beyond $E_{\text{kin}} = 2U_p$, the ratio for ArXe also continuously increases with increasing E_{kin} ; however, at a rate much smaller than that for Xe₂ SFI at the same light intensity (see Fig. 4).

Before we further discuss the possible origin for the development of the minimum in the yield ratio for SFI of Xe₂ and its dependence on the laser pulse intensity, we calculate this ratio for the model molecule. As will be seen, the calculation results suggest a reasonable origin for the experimental findings.

B. Model calculation

With the assumptions made in Sec. III on the model homonuclear dimer, we calculate the SFA transition probabilities $|M_{(+,-),i}^{(1)}(\mathbf{p})|^2$ in Eq. (7) at a fixed internuclear separation of

$R = 8.3$ a.u., the equilibrium internuclear separation of Xe₂. We restrict ourselves to determining the transition probability for photoelectrons emitted along the direction of linear polarization of the laser pulse, which is assumed to be pointing along the z axis of a suitably chosen laboratory frame of reference. A laser pulse with $n = 42$ optical cycles and a $\cos^2(\pi t/nT)$ pulse envelope for the electric-field strength is assumed, where T is the oscillation cycle width and $-nT/2 \leq t \leq nT/2$. This number of cycles corresponds approximately to the actual pulse width used in the experiment. The photon energy is chosen in accordance with the experimental value $\hbar\omega = 1.55$ eV, and the ionization potential to be that of the Xe atom. For the energy-level splitting of the ionic state pair ϕ_+^I and ϕ_-^I , which corresponds to the $\tilde{\phi}_+^D$ and $\tilde{\phi}_-^D$ Dyson orbital pair (4), we use $\epsilon = \epsilon_+ - \epsilon_- = -0.4$ eV. This splitting closely resembles the actual energy-level splitting of the Xe₂⁺ ionic electronic state pair $I(1/2)_u - I(1/2)_g$ (notation according to Ref. [21]) at the equilibrium internuclear separation of Xe₂. The state $I(1/2)_u$ is the Xe₂⁺ electronic ground state. To keep the SFA transition matrix element in its simple form (7), with the two-center interference explicitly revealed, the dipole transition moment is chosen to be $\mathbf{d} = -\mathbf{R}/2$. This value is close to the actual one for the $I(1/2)_u - I(1/2)_g$ state pair [22]. The experimental random alignment of the internuclear axis with respect to the laser pulse polarization direction is taken into account by determining $|M_{(+,-),i}^{(1)}(\mathbf{p})|^2$ for a set of alignment angles and averaging over this set. The presence of a distribution of electric-field peak amplitudes in the focal spot of the laser pulse is accounted for by adding transition probabilities $|M_{(+,-),i}^{(1)}(\mathbf{p})|^2$ calculated for a set of peak amplitudes weighed with the respective spatial volume where they are present (assuming a Gaussian laser beam profile).

Representative calculated momentum distributions $[|M_{(+,-),i}^{(1)}(\mathbf{p})|^2]$; see Eq. (7)] for photoelectrons emitted along the laser beam polarization axis (z axis) are shown in Fig. 5 at a light pulse peak intensity of 8×10^{13} W/cm². The full (black) curve represents $|M_{+,i}^{(1)}(\mathbf{p})|^2$ with the ion left finally in the electronic state ϕ_+^I . The dashed (red) one shows $|M_{-,i}^{(1)}(\mathbf{p})|^2$. It has the ion finally in the electronic state ϕ_-^I . The photoelectron yield (arb. units) is plotted on a logarithmic scale. The momentum interval displays ranges from zero to one atomic unit. It covers the range up to the classical upper momentum limit of directly emitted photoelectrons being located at about 0.84 a.u. Significant differences are observed for the momentum distributions. At $p_z = 0$, the transition probability $|M_{+,i}^{(1)}(\mathbf{p})|^2$ is approximately one order of magnitude larger than the transition probability $|M_{-,i}^{(1)}(\mathbf{p})|^2$ whereas in the range between about 0.3 and 0.7 a.u., $|M_{+,i}^{(1)}(\mathbf{p})|^2$ appears suppressed compared with $|M_{-,i}^{(1)}(\mathbf{p})|^2$. According to the transition matrix elements $M_{(+,-),i}^{(1)}(\mathbf{p})$ [see Eq. (7)], a result like this can be provided by the $\cos(\mathbf{R} \cdot \mathbf{p}/2)$ term in Eq. (7), in case the ionic state ϕ_+^I is chosen to be the final one. By contrast, the $\sin(\mathbf{R} \cdot \mathbf{p}/2)$ term can give rise to the opposite behavior in the case ϕ_-^I is the final state. A suppression (ϕ_+^I) or, on the other hand, an enhancement (ϕ_-^I) should be observable close to $Rp_z = \pi$. With the internuclear separation being $R = 8.3$ a.u., the corresponding momentum p_z amounts to just 0.38 a.u. It is close to the position of the suppression

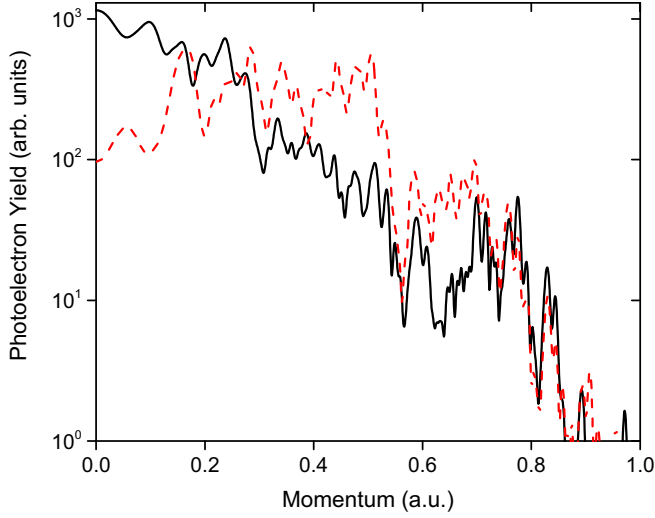


FIG. 5. Representative calculated momentum distributions $[|M_{(+,-),i}^{(1)}(\mathbf{p})|^2]$, see Eq. (7)] for photoelectrons emitted directly (without rescattering) along the direction of polarization of the laser pulse. The light pulse intensity is 8×10^{13} W/cm². The full (black) curve shows $|M_{+,i}^{(1)}(\mathbf{p})|^2$ [final ionic state ϕ_+^I , (+) according to Eq. (4)], the dashed (red) curve shows $|M_{-,i}^{(1)}(\mathbf{p})|^2$ [final ionic state ϕ_-^I , (-) according to Eq. (4)].

found in the momentum distribution for the situation where the ionic state ϕ_+^I is chosen to be the final one.

The influence of two-center interference, present in relation (7) for $M_{(+,-),i}^{(1)}(\mathbf{p})$ through $\cos(\mathbf{R} \cdot \mathbf{p}/2)$ and $\sin(\mathbf{R} \cdot \mathbf{p}/2)$, can be more precisely quantified by calculating the ratios

$$r_+(\mathbf{p}) = \frac{|M_{+,i}^{(1)}(\mathbf{p})|^2}{|M_{+,i}^{(1)}(\mathbf{p})|^2 + |M_{-,i}^{(1)}(\mathbf{p})|^2},$$

$$r_-(\mathbf{p}) = \frac{|M_{-,i}^{(1)}(\mathbf{p})|^2}{|M_{+,i}^{(1)}(\mathbf{p})|^2 + |M_{-,i}^{(1)}(\mathbf{p})|^2}, \quad (14)$$

for the final ionic state states ϕ_+^I and ϕ_-^I , respectively. In the denominator of Eqs. (14), two-center interference is eliminated since it represents the total transition probability without accounting for the final state, ϕ_+^I or ϕ_-^I . The result for r_+ for photoelectrons emitted along the direction of polarization of the laser pulse is shown in Fig. 6 plotted as a function of the kinetic energy of the photoelectron $E_{\text{kin}} = p_z^2/2$ ($p_x = p_y = 0$ is assumed). The basis for the calculation are the parameters of the model dimer defined above and the light intensities used in the experiment. To emphasize the effect of the $\cos(\mathbf{R} \cdot \mathbf{p}/2)$ and $\sin(\mathbf{R} \cdot \mathbf{p}/2)$ terms appearing in $M_{(+,-),i}^{(1)}(\mathbf{p})$, which vary slowly with the kinetic energy, a low-pass filter was applied to the ratio functions. It eliminates narrow features that would otherwise mask the effect of interference.

At all light intensities between 5×10^{13} and 11×10^{13} W/cm² the ratio r_+ (ϕ_+^I being the final ionic state) in Fig. 6 shows a pronounced local minimum located in the kinetic-energy range between ≈ 2 eV and ≈ 7 eV. It is accompanied by the shape of the ratio function changing with the light intensity in the vicinity of the minimum. Towards $2U_p$, the classical upper limit for the kinetic energy of directly emitted electrons (indicated in Fig. 6 by the vertical bars),

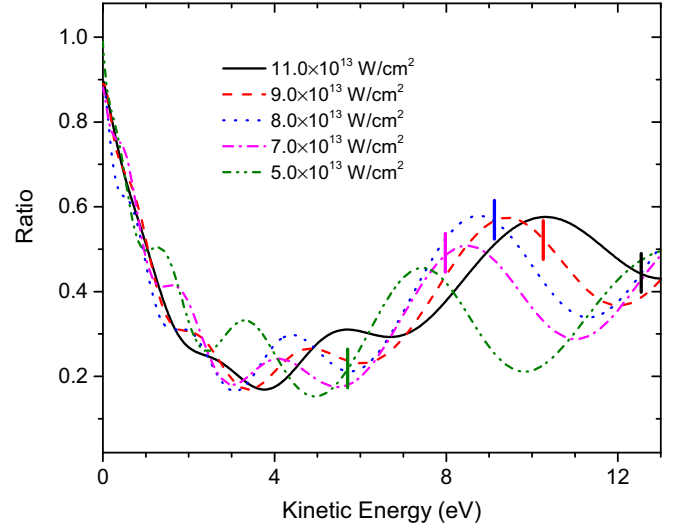


FIG. 6. Calculated ratio $r_+(E_{\text{kin}})$ [see relation (14)] for electrons emitted along the direction of polarization of the laser beam ($p_x = p_y = 0$, $E_{\text{kin}} = p_z^2/2$) at the light intensities used in the experiment. The calculations were done for the model homonuclear dimer parameters specified in Sec. IV B. The vertical lines indicate the $2U_p$ positions for the different light intensities.

the increase of the ratio systematically shifts to higher kinetic energies with increasing laser pulse intensity. Towards zero kinetic energy, the ratio always increases in a similar way. According to Eq. (6), $r_-(\mathbf{p}) = 1 - r_+(\mathbf{p})$. Thus, $r_-(\mathbf{p})$, where ϕ_-^I is the final ionic state, shows the opposite behavior. Here a minimum develops at $E_{\text{kin}} = 0$ and a maximum where $r_+(E_{\text{kin}})$ reaches its minimum value.

The result we find means that, depending on the final ionic state, ϕ_+^I or ϕ_-^I , either the integral I_1 or I_2 in relation (10), remains small. In the case ϕ_+^I is the final ionic state at the end of the laser pulse, the absolute value of the time-dependent amplitude $|c_1(t)|$ remains smaller than $|c_2(t)|$ during the whole laser pulse, since in our case the energy-level splitting between the two ionic states ϕ_+^I and ϕ_-^I of 0.4 eV is significantly smaller than the photon energy (1.55 eV). This, however, is not sufficient to render $|I_1(\mathbf{p})|$ small or alternatively large compared with $|I_2(\mathbf{p})|$. Additionally, it is necessary that the second summand in the integrand of the integrals $I_{1,2}(\mathbf{p})$ [the term proportional to $\tilde{\phi}_{n,l,m}(\mathbf{p} + \mathbf{A}(t)/c)$, the Fourier transform of the atomic orbital] contributes only little to the integral compared with the first one. The calculation actually shows just this behavior.

An approximate expression for the transition matrix element (7) would thus be

$$M_{(+,-),i}^{(1)}(\mathbf{p}) \approx -\sqrt{2} \cos\left(\frac{\mathbf{R} \cdot \mathbf{p}}{2}\right) \int_{T_i}^{T_f} dt \exp[i\tilde{\chi}] c_2^*(t) \times \frac{\partial}{\partial t} \left[\tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right] + \sqrt{2} \sin\left(\frac{\mathbf{R} \cdot \mathbf{p}}{2}\right) \int_{T_i}^{T_f} dt \exp[i\tilde{\chi}] c_1^*(t) \times \frac{\partial}{\partial t} \left[\tilde{\phi}_{n,l,m}\left(\mathbf{p} + \frac{\mathbf{A}(t)}{c}\right) \right]. \quad (15)$$

The corresponding monomer SFA transition matrix element for ionization of the same atomic Dyson orbital $\tilde{\phi}_{n,l,m}(\mathbf{p})$ used for construction of the dimer orbitals for directly emitted electrons just reads

$$M_{f,i}^{(1)}(\mathbf{p}) \propto \int_{T_i}^{T_f} dt \exp[i\tilde{\chi}] \frac{\partial}{\partial t} \left[\tilde{\phi}_{n,l,m} \left(\mathbf{p} + \frac{\mathbf{A}(t)}{c} \right) \right]. \quad (16)$$

Comparing this to the approximate dimer, transition matrix element (15) shows that the main difference between monomer and dimer SFA is actually the presence of interference due to the cosine and sine functions and the driving of ionic transitions represented by $c_1(t)$ and $c_2(t)$ in Eq. (15). This applies to the off-resonance situation ($\hbar\omega$ is larger than the ionic energy-level difference $|\epsilon_+ - \epsilon_-|$) discussed here. It changes under close resonance conditions where the amplitudes $c_i(t)$, $i = 1, 2$ reach similar values or even exchange significance in certain time intervals while the laser pulse is applied. Under these conditions, the approximation (15) to the SFA matrix element for the dimer no longer applies.

A simple situation arises for a degenerate ionic electronic state pair ϕ_+^I and ϕ_-^I [$\epsilon = 0$ in Eq. (8)]. According to Eq. (8), the amplitudes c_1 and c_2 then become time independent. Provided the approximation (15) to the dimer SFA transition matrix element applies, it just reduces to a simple product of the interference factor $\cos(\mathbf{R} \cdot \mathbf{p}/2)$ with the corresponding atomic transition matrix element (16) for ϕ_+^I being the final dimer ion electronic state. By contrast, if ϕ_-^I acts as the final ionic state, one just gets the product of $\sin(\mathbf{R} \cdot \mathbf{p}/2)$ with the atomic transition matrix element (16). Different from the nondegenerate situation, the interference pattern then becomes stationary, i.e., completely independent of the intensity of the laser pulse. A similar result has been found earlier for the ionization of a one electron homonuclear molecule with a degenerate initial gerade or ungerade electronic state pair at large internuclear separation [33].

V. DISCUSSION

Comparing the experimentally determined ratios $r(E_{\text{kin}}) = Y_{\text{Xe}_2}(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$ (see Sec. IV A and Fig. 4) for photoelectrons detected together with Xe_2^+ and Xe^+ ions with the calculated ratios for the model dimer with the ion left in the ionic state ϕ_+^I (ungerade ionic state, Fig. 6), one observes striking similarities in the kinetic-energy range where directly emitted photoelectrons are found. The minimum in the ratios develops at comparable kinetic energies. Also, the energy range where the ratio is low becomes wider in both cases, and the rising of the ratio towards high kinetic energies becomes less steep with increasing light intensity. It may thus be concluded that two-center interference and the dynamical evolution in the ion, driven by the laser pulse, which is responsible for this behavior of the ratios for the model dimer, explains the experimental observation. Reasoning in this way, one has to keep in mind that there are subtle differences in the ways the ratios are calculated from the experimental momentum distributions and in the model calculation.

The experiment provides momentum distributions for photoelectrons detected either together with Xe_2^+ or with Xe^+ ions. Since Xe and Xe_2 have practically the same ionization

potential, and the atomic constituents of the dimer are only slightly perturbed Xe atoms in the Xe_2 electronic ground state, the main difference between Xe and Xe_2 SFI is the presence of the two-equivalent-center structure of the dimer and the presence of closely spaced ionic states with large transition dipole moments at the ionization threshold of Xe_2 which are absent for the atom. This conclusion is supported by the photoelectron momentum distribution of the ArXe dimer. It is very similar to that of the Xe monomer at the light intensities used here, where SFI of the Ar site of the dimer is practically negligible (see Figs. 2 and 3). The experimentally determined ratio $r(E_{\text{kin}}) = Y_{\text{Xe}_2}(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$ is thus expected to reveal just this difference; namely, interference and driving of ionic transitions. In the experiment, this ratio is the only way to access these effects since we are not able to detect photoelectrons in coincidence with specific Xe_2^+ electronic states.

Two-center interference can affect the experimental photoelectron momentum distributions only when the laser pulse does not create an equal distribution of the detected Xe_2^+ ions over any accessible gerade and ungerade ionic electronic state pair. This disparate distribution may either be induced by the SFI process itself or by subsequent dissociation of Xe_2^+ into Xe^+ and Xe before Xe_2^+ reaches the ion detector. The second possibility may be the most significant one, since several of the relevant ionic electronic states are either purely dissociative or have only a shallow potential minimum [21]. The shapes of the experimentally determined ratios $r(E_{\text{kin}}) = Y_{\text{Xe}_2}(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$ (Fig. 4) and the shapes of the calculated ones (Fig. 6) for the model dimer thus imply that the photoelectrons detected together with Xe_2^+ ions have the ion overwhelmingly in an ungerade electronic state; that is, probably in the electronic ground state $I(1/2)_u$, which has the deepest potential well [21].

In comparing any details of the experimentally determined and the calculated ratios, one should also keep in mind that they do not represent the same quantity. Experimentally, the denominator of the ratio is the photoelectron momentum distribution for SFI of the Xe atom, whereas the calculation uses $|M_{+,i}^{(1)}(\mathbf{p})|^2 + |M_{-,i}^{(1)}(\mathbf{p})|^2$ [see Eqs. (14)]. Both denominators share the feature of not being influenced by two-center interference effects. However, the denominator in the model calculation still incorporates the effect of transitions between the two electronic states ϕ_+^I and ϕ_-^I of the dimer ion induced by the applied laser pulse. This contribution is absent when calculating the experimental ratio. Moreover, the model is restricted to the most basic situation which allows interference effects to appear; namely, one gerade and ungerade molecular Dyson orbital pair together with the accompanying ionic state pair. On the other hand, the actual Xe_2^+ dimer shows altogether six closely spaced electronic states split by spin-orbit interaction with large transition dipole matrix elements between most of these states at the equilibrium internuclear separation of the Xe_2 dimer [21,22]. Also, the Xe_2^+ states are based not only on σ orbitals as assumed in the calculation but also π orbitals are present [21]. Nevertheless, the reduced model is able to attribute experimentally observed features to two-equivalent-center interference and tentatively to driving ionic transitions during application of the laser pulse.

VI. CONCLUSION

In conclusion, a simplified SFI model for homonuclear dimers, based on an ionic two-level system, which we presented here, reproduces the overall behavior of the experimentally found photoelectron yield ratio $r(E_{\text{kin}}) = Y_{\text{Xe}_2}(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$ below the classical $2U_p$ limit of the kinetic energy where mainly directly emitted photoelectrons are found after SFI of Xe_2 . The ratio and its dependence on the laser pulse intensity reveal two-equivalent-center interference and indicate the presence of driving ionic transitions during SFI. To be able to describe the experimental results at large internuclear separation R correctly, specifically two-equivalent-center interference in homonuclear molecules by employing the length gauge in the calculation, as we did, it is necessary to take into account ionic state pairs of gerade and ungerade symmetry. At large R , always closely spaced pairs of this kind are found at the ionization threshold of homonuclear molecules. In employing the length gauge these pairs of ionic states are coupled by a large dipole matrix element which tends to be proportional to R with increasing internuclear separation. Because of this coupling restricting the SFA to only one ionic final state cannot correctly account for two-equivalent-center interference in SFI in this gauge (see, for example, also a similar situation in Ref. [33]). A complete calculation for the noble gas dimers would need to take into account two ionic state pairs; namely, $^2\Sigma_{g,u}$ and $^2\Pi_{g,u}$, together with the spin-orbit interaction coupling these states. The main features, however, are already present in the simplified calculation used here to model the experimental result. We thus are convinced that the differences found in the experimental photoelectron momentum distributions originating from SFI of Xe_2 and Xe up to $E_{\text{kin}} \approx 2U_p$ are actually due to two-equivalent-center interference for directly emitted photoelectrons. The dependence of the experimentally determined ratio $r(E_{\text{kin}}) = Y_{\text{Xe}_2}(E_{\text{kin}})/Y_{\text{Xe}}(E_{\text{kin}})$ (Fig. 4) on the photoelectron kinetic energy combined with the model calculation indicates that the corresponding detected ion is left mainly in an ungerade electronic state. This state is probably the ion ground electronic state $\text{I}(1/2)_u$.

Deeper insight into the interference phenomenon for photoelectrons emitted directly by SFI can be gained by aligning the noble gas dimers prior to SFI. According to the expression (7) for the SFA transition matrix element, one expects to get significantly different photoelectron momentum distributions for the internuclear axis either being aligned parallel or perpendicular with respect to the electric field of the laser pulse.

APPENDIX: STRONG-FIELD APPROXIMATION TRANSITION MATRIX ELEMENT

The general SFA transition matrix element $M_{f,i}$ for directly emitted electrons from an initial state ϕ_i to a final continuum state ϕ_f at the end of a laser pulse is given by (see, for example, Refs. [34,35])

$$M_{f,i}^{(1)} = -i \int_{T_i}^{T_f} dt \langle \phi_f | \tilde{U}_0(T_f, t) V(t) U_0(t, T_i) | \phi_i \rangle, \quad (\text{A1})$$

where $\tilde{U}_0(t, t_0)$ and $U_0(t, t_0)$ are two time evolution operators for two different partitionings of the Hamiltonian $H(t)$ of

the atomic system into “zero-order” terms $H_0(t)$, $\tilde{H}_0(t)$ and interaction terms (“perturbations”) $V(t)$, $\tilde{V}(t)$ [35]. $U_0(t, t_0)$ satisfies the time-dependent Schrödinger equation

$$i \frac{\partial U_0(t, t_0)}{\partial t} = H_0(t) U_0(t, t_0), \quad (\text{A2})$$

and $\tilde{U}_0(t, t_0)$ a corresponding one. According to the SFA, we choose $H_0(t)$ to be the time-independent Hamiltonian of the unperturbed neutral atomic system $H_0(t) = H_N$ with $U_0(t, T_i) \phi_i = \exp[-i E_i(t - T_i)] \phi_i$. Here, E_i is the energy of the initial ground state ϕ_i where SFI starts. Then $V(t)$ represents the interaction of the atomic system with the laser pulse which we will treat in the length gauge $V(t) = -\mathbf{E}(t) \cdot \sum_{k=1}^n \mathbf{x}_k$ for n electrons [$\mathbf{E}(t)$ is the electric field of the laser pulse, $\mathbf{x}_k$ is the position vector of electron k]. The final state ϕ_f at the end of the laser pulse represents an ion core in a specific bound state ϕ^{ion} and an electron in the ionization continuum, which will be represented by a plane wave $\phi_{\mathbf{p}}^n = (2\pi)^{-3/2} \exp(i\mathbf{p} \cdot \mathbf{x}_n)$ with the assumption that electron n is ionized. For the continuum electron, this corresponds to the usual SFA assumption. Ignoring antisymmetrization, the final state is then the product of the ionic and plane-wave states $\phi_f = \phi_f^{\text{ion}} \phi_{\mathbf{p}}^n$. $\tilde{H}_0(t)$ is chosen to be

$$\tilde{H}_0(t) = \left[H_I - \mathbf{E}(t) \cdot \sum_{k=1}^{n-1} \mathbf{x}_k \right] + \left[\frac{\mathbf{p}_n^2}{2} - \mathbf{E}(t) \cdot \mathbf{x}_n \right]. \quad (\text{A3})$$

The first square bracket on the right-hand side represents the complete ionic Hamiltonian H_I and the ion–laser-pulse interaction. The second one represents a free-electron interacting with a laser pulse. The interaction term $\tilde{V}(t)$ would thus be the Coulomb interaction of the continuum electron with the ion core. This will then not affect the basic SFA transition matrix element (A1). According to Eq. (A3), the ion core and the continuum electron in the externally applied field can thus be propagated independently. For the final state in Eq. (A1), this means

$$\tilde{U}_0(t, T_f) \phi_f = [\tilde{U}_{I,0}(t, T_f) \phi_f^{\text{ion}}] [\tilde{U}_V(t, T_f) \phi_{\mathbf{p}}^n]. \quad (\text{A4})$$

$\tilde{U}_V(t, T_f) \phi_{\mathbf{p}}^n$ is the Volkoff state of a free electron in a laser pulse. In the length gauge used here, it reads

$$\begin{aligned} \tilde{U}_V(t, T_f) \phi_{\mathbf{p}}^n = & (2\pi)^{-3/2} \exp \left[i \left(\mathbf{p} + \frac{\mathbf{A}(t)}{c} \right) \cdot \mathbf{x}_n \right] \\ & \times \exp \left[-\frac{i}{2} \int_{T_f}^t dt' \left(\mathbf{p} + \frac{\mathbf{A}(t')}{c} \right)^2 \right], \end{aligned} \quad (\text{A5})$$

where $\mathbf{A}(t)$ is the vector potential corresponding to the electric field $\mathbf{E}(t)$. They are related by $\mathbf{E}(t) = -(1/c) \partial \mathbf{A}(t) / \partial t$ (c is the velocity of light).

For our purposes, we restrict the ion to a system of M bound eigenstates ϕ_j^I , $j = 1, \dots, M$ of the unperturbed ionic Hamiltonian H_I ($H_I \phi_j^I = E_j^I \phi_j^I$), and the final state ϕ_f^{ion} is supposed to be one of these. $\tilde{U}_{I,0}(t', T_f) \phi_f^{\text{ion}}$ then can be expressed as

$$\tilde{U}_{I,0}(t, T_f) \phi_f^{\text{ion}} = \sum_{j=1}^M a_j(t) \phi_j^I, \quad (\text{A6})$$

with $a_j(t)$, $j = 1, \dots, M$ being a solution of the ionic time-dependent Schrödinger equation restricted to the subspace spanned by $\{\phi_1^I, \dots, \phi_M^I\}$ and $\phi_f^{\text{ion}} = \phi_{j_0}^I$ for some $j_0 = 1, \dots, M$.

With these assumptions, the SFA transition matrix element (A1) is finally approximated by

$$M_{f,i}^{(1)}(j_0, \mathbf{p}) \cong - \sum_{j=1}^M \int_{T_i}^{T_f} dt a_j^*(t) \exp[i\chi(t, \mathbf{p}, T_f, T_i)] \frac{\partial}{\partial t} \left[\tilde{\phi}_j^D \left(\mathbf{p} + \frac{\mathbf{A}(t)}{c} \right) \right], \quad (\text{A7})$$

with $\tilde{\phi}_j^D(\mathbf{p})$ being the Fourier transform of the Dyson orbital $\phi_j^D(\mathbf{x}_n)$ defined by

$$\tilde{\phi}_j^D(\mathbf{p}) = \frac{1}{(2\pi)^{3/2}} \int d^3\mathbf{x}_n \exp(-i\mathbf{p}\mathbf{x}_n) \phi_j^D(\mathbf{x}_n), \quad (\text{A8})$$

$$\phi_j^D(\mathbf{x}_n) = \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_{n-1} \phi_j^{I*}(\mathbf{x}_1, \dots, \mathbf{x}_{n-1}) \phi_i(\mathbf{x}_1, \dots, \mathbf{x}_n), \quad (\text{A9})$$

and the phase $\chi(t, \mathbf{p}, T_f, T_i)$ being given by

$$\chi(t, \mathbf{p}, T_f, T_i) = \frac{1}{2} \int_{T_f}^t dt' \left(\mathbf{p} + \frac{\mathbf{A}(t')}{c} \right)^2 - E_i(t - T_i). \quad (\text{A10})$$

The SFA transition matrix element (A7) depends on the final bound ionic state $\phi_{j_0}^I$ and on the momentum $\mathbf{p}$ of the continuum electron. The amplitudes $a_j(t)$ in Eq. (A7) will result in an effect of driving ionic transitions on the momentum distribution, specifically if several dipole coupled ionic states are found close to the ionization threshold with energy-level spacings close to the photon energy. The matrix element (A7) is the starting point for calculating the effect of two well-separated emission centers on the momentum distribution of directly emitted photoelectrons for model homonuclear noble gas dimers.

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