Photoionization of a strongly polarizable target

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Abstract
We demonstrate that the angular distribution of photoelectrons from a strongly polarizable target exposed to a laser field can deviate noticeably from the prediction of conventional theory. Even within the dipole–photon approximation the profile of distribution is modified due to the action of the field of alternating dipole moment induced at the residue by the laser field. This effect, being quite sensitive to the dynamic polarizability of the residue and to its geometry, depends also on the intensity and frequency of the laser field. Numerical results, presented for sodium cluster anions, demonstrate that dramatic changes to the profile occur for the photon energies in vicinities of the plasmon resonances, where the effect is enhanced due to the increase in the residue polarizability. Strong modifications of the characteristics of a single-photon ionization process can be achieved by applying laser fields of comparatively low intensities $I_0 \sim 10^{10}$–$10^{11}$ W cm$^{-2}$.

1. Introduction

In this paper, we demonstrate that the profile of angular distribution of electrons emitted in the process of a single-photon ionization from a strongly polarizable target (in particular, a metal cluster anion) exposed to a laser field can be noticeably modified due to the action of the field $U(r, t)$ of alternating dipole moment $D(t)$ induced at the residue by the laser field. The field $U(r, t)$ acts on the escaping electron and, being dependent on the polarization vector of the laser field, brings additional dependence of the cross section on the emission angle. The degree of this dependence is determined by the magnitude of $D(t)$ which, in turn, is proportional to the residue’s dynamic polarizability. Therefore, for a target with large polarizability the effect can be very pronounced even for laser fields of low intensities.

The effect of the laser-field-induced dipole moment in atomic photoionization process was discussed in [1] (where one finds also the references to the earlier works by the authors) and, more recently, in [2]. Both papers were devoted to the study of multiphoton detachment of electrons from atomic negative ions. In [1] the process was analysed by means of the perturbation theory. Numerical analysis was carried out for halogen and alkali metal anions, and it demonstrated that the induced dipole moment influences the magnitude of total cross section of the many-photon detachment. The paper [2] dealt with the process of a strong-field many-photon detachment of an atomic anion. The non-perturbative adiabatic theory, developed in [3], was modified to account for the field of the induced dipole moment. The numerical calculations, performed for Rb$^-$ and Cs$^-$, showed the increase of the detachment rate and essential modification of the angular distribution.

In our paper, we investigate the influence of the induced dipole moment on the angular and spectral distributions of photoelectrons in the process of single-photon ionization (or detachment) occurring in the weak-field regime. Numerical results are presented for sodium cluster anions Na$_N^-$ with $N = 10^1, \ldots, 10^2$. The corresponding residue clusters are characterized by large values of the dynamic dipole polarizability $\alpha(\omega)$, which in the vicinity of plasmon resonances, i.e. at $\omega = 2, \ldots, 3$ eV, can be as large as $10^4, \ldots, 10^5$ au, which by far exceed the maximum values of $\alpha(\omega)$ of individual atoms (e.g., $\alpha(\omega) \approx 400$ au for Cs at the photon energy 0.47 eV [2]).
We demonstrate that dramatic changes to the profile of angular distribution occur in vicinities of the plasmon resonances and for comparatively low intensities \( \sim 10^{10} - 10^{11} \text{ W cm}^{-2} \) of the laser field. These are exactly the ranges used in recent experimental studies [4, 5] of the photodetachment from various metal cluster anions carried out by means of angle-resolved photoelectron spectroscopy. Therefore, the experimental test of the predicted effects seems to be feasible.

The atomic system of units, \( e = m = \hbar = 1 \), is used throughout the paper.

2. Theoretical framework

2.1. Setting the problem

Consider the process of photoionization of a strongly polarizable target (a cluster, a fullerene, a complex molecule, etc) by spatially homogenous linearly polarized laser field

\[
E(t) = E_0 \cos \omega t = \frac{1}{2} (E_0 e^{-i\omega t} + E_0 e^{i\omega t}). \tag{1}
\]

We assume that the field wavelength \( \lambda \) greatly exceeds the characteristic size \( R \) of the target, \( \lambda \gg R \). Thus, the process can be treated within the dipole–photon limit.

The laser field ionizes the target and polarizes the residue. Therefore, in addition to other fields (the static potential of the residue, the long-range polarizational potential) the escaping photoelectron feels the field due to the oscillating dipole moment \( \mathbf{D}(t) \) induced at the residue

\[
\mathcal{U}(r, t) = -\frac{\mathbf{D}(t) \cdot \mathbf{r}}{r^3}. \tag{2}
\]

To simplify the consideration we assume that the residue is spherically symmetric, so that its tensor of polarizability contains only a scalar part which is noted as \( \alpha(\omega) \). Then, the moment \( \mathbf{D}(t) \) reads

\[
\mathbf{D}(t) = \mathbf{d} e^{-i\omega t} + \mathbf{d}^* e^{i\omega t}, \tag{3}
\]

where \( \mathbf{d} \equiv \mathbf{d}(\omega) = \alpha(\omega) \mathbf{E}_0 / 2 \). The field of the induced dipole can be written as follows:

\[
\mathcal{U}(r, t) = U(r) e^{-i\omega t} + U^*(r) e^{i\omega t}, \tag{4}
\]

with \( U(r) = \mathbf{d} \cdot \mathbf{r} / r^3 \). This field is dependent on the direction of \( \mathbf{E}_0 \); therefore, the angular distribution of photoelectrons acquires additional dependence on the polarization of the laser field. The degree of this dependence is determined by the magnitude of \( \mathbf{D}(t) \), which is proportional to the residue dynamic dipole polarizability. Hence, for a target with large polarizability the modification of the angular distribution due to the induced dipole moment can become noticeable even for a laser field of a comparatively low intensity.

2.2. The perturbation series

Let us clearly state the conditions which we impose on the parameters of the laser field. These include the following inequalities:

(I) \( E_0 \ll E_{\text{int}} \),

(II) \( \varepsilon \gg \frac{E_0^2}{4\omega R} \),

(III) \( \omega > |\varepsilon_i| \). \tag{5}

The first condition implies that the laser field strength is much smaller than the strength \( E_{\text{int}} \) of the internal field in the target. This condition allows one to ignore the laser field when constructing the wavefunction of the bound electron with the binding energy \( \varepsilon_i \). Numerical results presented in section 3 refer to the laser field strength \( E_0 \sim 10^{-2} \text{au} \sim 10^6 \text{ V cm}^{-1} \).

The second condition states that the energy \( \varepsilon \) of the escaping electron is large compared to the ponderomotive shift due to the wigging in the laser field. Owing to this condition we do not ‘dress’ the photoelectron wavefunction with the laser field.

The last inequality in (5) indicates that the photon energy exceeds the ionization threshold of the bound electron. Therefore, the process of a single-photon ionization is allowed for which the energy conservation law reads

\[
\varepsilon = \varepsilon_i + \omega. \tag{6}
\]

Combining conditions (I) and (III) one demonstrates that the following inequality is met: \( \gamma = \omega k / E_0 \gg 1 \) where \( \gamma \) is a so-called Keldysh parameter, and \( k = (2|\varepsilon_i|)^{1/2} \). The limit \( \gamma \gg 1 \) defines a weak-field regime (see, e.g., [3]). Thus, in this paper we investigate the influence of the induced dipole moment \( \mathbf{D}(t) \) on the angular and spectral distributions of photoelectrons in the process of single-photon ionization (or detachment) occurring in the weak-field regime. Earlier the role of \( \mathbf{D}(t) \) was studied in the process of many-photon detachment (i.e., when \( \omega \ll |\varepsilon_i| \)) from atomic negative ions. It was done in the weak-field [1] and in the strong-field [2] limits.

Let us note that the weak-field condition (II) does not immediately imply the applicability of the perturbative approach with respect to \( \mathcal{U}(r, t) \). Indeed, from (2)–(4) follows that \( |\mathcal{U}(r, t)| \sim E_0 |\alpha(\omega)| / r^2 \) exceeds \( E_0 r^3 \) by a factor \( |\alpha(\omega)| / r^3 \). For a strongly polarizable target this factor can be large enough in a wide range of radial distances \( r > R \), and this might lead to a non-perturbative treatment of the action of \( \mathcal{U}(r, t) \).

To carry out a quantitative analysis we first postulate that under certain conditions the field (4) can be considered as a time-dependent perturbation which modifies the wavefunction of the escaping electron. The criterion of applicability of this approach will be formulated in the course of calculations.

The matrix element \( \mathcal{M} \), which describes a dipole–photon transition of the electron from the initial bound state \( \psi_i(r, t) = \psi_i(r) e^{-i\varepsilon t} \) to the final state \( \psi_f(r, t) = \psi_p(r) e^{-i\omega t} \) with the asymptotic momentum \( \mathbf{p} \) and energy \( \varepsilon = p^2 / 2 \), can be written in the following form:

\[
\mathcal{M} = \mathcal{M}_0 + \mathcal{M}_1 + \mathcal{M}_2 + \cdots. \tag{7}
\]

The right-hand side of this equation represents the power series in \( \mathcal{U}(r, t) \). The structure of the terms of the series is illustrated by diagrams in figure 1.

The zeroth-order term \( \mathcal{M}_0 \) describes the direct process of photoionization standing for the matrix element of the operator \( \mathbf{E}_0 \cdot \mathbf{D}(\omega) \exp(-i\omega t)/2 \),

\[
\mathcal{M}_0 = \frac{1}{2} \int_{-\infty}^{\infty} dt \psi_p^* (\mathbf{r}, t) \mathbf{E}_0 \cdot \mathbf{D}(\omega) e^{-i\omega t} \psi_i (\mathbf{r}, t) \\
= 2\pi \delta(\varepsilon - \varepsilon_i - \omega) \mathcal{M}_0, \tag{8}
\]

where the second equality follows that \( \int_{-\infty}^{\infty} dt e^{-i\omega t} = 2\pi \delta(\varepsilon - \varepsilon_i - \omega) \).
Figure 1. Diagrammatical representation of a single-photon transition amplitude in a form of perturbation series in $U(r, t)$ (indicated with the dashed vertical lines). The double line represents the escaping electron whose wavefunction is ‘dressed’ with all static fields. The filled circle denotes the vertex of the effective electron–laser-field interaction.

where

$$M_0 = \frac{1}{2} \int dr \, \psi_0^*(-r) E_0 \cdot \tilde{D}(\omega) \psi_1(r).$$

We assume that the wavefunction $\psi_0^*(-r)$ (whose asymptotic form is ‘the plane wave + the incoming wave’) corresponds to the state ‘dressed’ with all static fields. The delta function on the right-hand side of (8) expresses the energy conservation law (6).

The quantity $\tilde{D}(\omega)$ is the operator of the effective dipole moment of an ionized electron. In a complex system, in addition to the ‘bare’ dipole moment, $-r$, this quantity accounts for the many-electron correlations which modify the interaction with the external field. The calculation of $\tilde{D}(\omega)$ can be performed, for example, within the framework of random-phase approximation. For a strongly polarizable target the main contribution to $\tilde{D}(\omega)$ comes from the interaction of the ionized electron with the dipole moment induced by the laser field on the core. In its nature, this interaction is similar to the potential $U(r, t)$. The difference between the two interactions is that the latter modifies the wavefunction of the outgoing photoelectron in the outer region, whereas the former modifies the electron–photon vertex responsible for the direct photoionization process. For the purpose of our paper it is important to compare $M_0$ with the correction terms due to the field $U(r, t)$. Below in the paper we demonstrate that to estimate the relative magnitude of the correction terms the actual evaluation of $M_0$ is not needed.

The terms $\mathcal{M}_n$ with $n \geq 1$ are the corrections to the transition amplitude due to the $n$-times interaction of the photoelectron with $U(r, t)$. Since this field explicitly depends on $t$ (see (4)) then in each act of the interaction the electron energy is changed (increased or decreased) by $\omega$. As a result, not all terms on the right-hand side of (7) represent the correction to the direct amplitude $M_0$, which implies the validity of (6). For example, evaluating $M_1$ (the second diagram in figure 1) one finds that it contains the terms proportional to $\delta(\epsilon - \epsilon_i)$ and to $\delta(\epsilon - \epsilon_i - 2\omega)$, which conflict with the conservation law (6). Therefore, the term $M_1$ must be ignored when constructing the correction to $M_0$.

The lowest-order correction originates from the amplitude $\mathcal{M}_2$ (the last diagram in figure 1), which contains the terms proportional to $\delta(\epsilon - \epsilon_i - \omega)$. Applying the standard technique of the time-dependent perturbation theory, one derives the following expression for this contribution:

$$\mathcal{M}_2|_{\omega=\epsilon_i+\omega} = 2\pi \delta(\epsilon - \epsilon_i - \omega) M_2,$$
It is important to note that the correction term (16) depends on the ratio of the amplitudes $M_2$ and $M_0$. Thus, one can expect that it is less sensitive to the approximation chosen to describe the photoelectron wavefunction than the cross section $d\sigma_0/d\Omega_2$. Therefore, to estimate the influence of the target polarization one can calculate $K(\omega, \theta)$ within the framework of a comparatively simple approximation, which is described in the following section.

To conclude this section let us mention that the action of the field $U(r, r)$ on the photoelectron can lead to the processes other than single-photon detachment. In particular, the second diagram in figure 1 describes the process of two-photon detachment in which the energy of photoelectron equals to $\varepsilon_i + 2\varepsilon_0$. One can easily show the corresponding cross section, being proportional to $(|\alpha(\omega)|^2 E_0^2$, is of the same order of magnitude as the correction $K(\omega, \theta)d\sigma_0$ to the cross section of the single-photon process, which implies the validity of equation (6). Generally speaking, all the corrections must be treated on equal terms. However, in the present paper, we restrict ourselves to the analysis of the cross section of the single-photon process, which implies

$$K(\omega, \theta) = -\frac{e}{\varepsilon_i} \sum_{l,m} \frac{g_{\delta l}(r_1, r) Y_{lm}(n_1) Y_{lm}^*(n)}{r_1 r} \approx 2\varepsilon_0 \sum_{l,m} \frac{X_{pl}(r_1) \chi_{pl}(r)}{r_1 r} Y_{lm}(n_1) Y_{lm}^*(n).$$

(19)

Here $r_1 / r_2$ is the largest/smallest of $r_1, r$, $X_{pl}(r)$ stands for the irregular solutions of the radial Schrödinger equation for the energy $E = p^2/2$. The quantity $g_{\delta l}(r_1, r) = X_{pl}(r_1) \chi_{pl}(r_2)/p^2 r_2 r_3$ is the exact radial Green’s function corresponding to the multipolarity $l$. The first equality in (19) states the partial-wave expansion of Green’s function. The approximate equality is based on the assumption $r_1 > r$.

Strictly speaking, the radial Green’s function can only be written as a product of two solutions if the potential acting on the electron is local. Meanwhile, the interaction of the escaping photoelectron and the residue includes the non-local exchange potential. To justify the use of (19) we refer to the analysis of the exchange effects in elastic electron-cluster scattering carried out in [8, 9]. From these papers it follows that for electron energies about 1 eV and higher the results obtained within the LDA (local density approximation) [10, 11] do not differ much from the calculations within the many-body perturbation theory. In the process of photodetachment from metallic cluster anions the most pronounced correction to the angular distribution occurs for the photon energies in the vicinity of the plasmon resonance. The corresponding range of energies of photoelectron is $\sim 1$ eV (see the data and the results presented in section 3). Hence, the exchange effects can be accounted for within the LDA scheme, which operates with effective local potentials.

Using (19) in (11) one notes that the radial integral over $r$ reduces to that from (18). Therefore, the amplitude $M_2$ acquires the form

$$M_2 \approx -\gamma(\omega, \theta) M_0,$$

(20)

with

$$\gamma(\omega, \theta) = |\alpha(\omega)|^2 E_0^2 \frac{e^{-i\delta}(p)}{8\pi} \int \int dr_1 dr_2 \psi_{pl}^*(-r_2) \times \frac{\mathbf{e}_0 \cdot \mathbf{n}_2}{r_2^2} (G_{\varepsilon \to \alpha}(r_2, r_1) + G_{\varepsilon \to \alpha}(r_2, r_1)) \frac{(\mathbf{e}_0 \cdot \mathbf{n}_1)^2}{r_1^2} X_{pl}(r_1).$$

(21)

Here the integration is carried out over the spatial region $r_1, r_2 > R$.

The correction term (16) is related to $\gamma(\omega, \theta)$ as $K(\omega, \theta) = -2 \Re \gamma(\omega, \theta)$.

Let us comment on the evaluation of the right-hand side of (21). Introducing the expansion (17) and representing Green’s functions $G_{\varepsilon}(r_2, r_1)$ and $G_{\varepsilon \to \alpha}(r_2, r_1)$ in terms of the partial-wave series similar to (19), one carries out the angular integration by means of the standard methods (see, e.g., [12]) evaluation the right-hand side of (11) one takes into account that $r_1, r_2 > R > r$. This allows one to relate $M_2$ to the amplitude $M_0$. To do this let us approximate Green’s function $G_{\varepsilon}(r_1, r)$ as follows:

$$G_{\varepsilon}(r_1, r) = 2\pi p \sum_{l,m} g_{\delta l}(r_1, r) Y_{lm}(n_1) Y_{lm}^*(n) \approx 2\pi \sum_{l,m} \frac{X_{pl}(r_1) \chi_{pl}(r)}{r_1 r} Y_{lm}(n_1) Y_{lm}^*(n).$$

(19)
and arrives at
\[
K(\omega, \theta) = -2 \text{Re} \gamma(\omega, \theta) = -\frac{2}{3} |\alpha(\omega)|^2 E_0^2 \sum_{l \delta_0} \delta_1 \left( \delta_{l0} + \frac{4}{5} \delta_{l2} \right)
- \frac{1}{6} \delta_{3l2} P_3(\cos \theta) \text{Im} B_{1l}.
\]
(22)

The Kronecker symbols \(\delta_{ij}\), which reduce the allowed values of the orbital momenta to \(l = 1, 3\) and \(l' = 0, 2\), reflect the dipole selection rules applicable to each of the vertices to the last diagram in figure 1. The ratio \(P_3(\cos \theta) / \cos \theta\) reduces to \((5P_3(\cos \theta) - 2)/3\) with the help of the recurrence relation for the Legendre polynomials.

The quantities \(B_{1l}\) stand for the following radial integrals:
\[
B_{1l} = \frac{e^{ik(p)-k_0(p)}}{p} \int_{R} dr_1 \int_{R} dr_2 \frac{X_{pl}(r_1) X_{pl}(r_2)}{r_1 r_2}
\times \left[ g_{rl}(r_2, r_1) + g_{rl}(r_1, r_2) \right].
\]
(23)

For any realistic target the exact evaluation of these integrals can be done by numerical means only, implying the computation of the regular \(X_{pl}(r)\) and the irregular \(X_{pl}(r)\) functions as well as of Green’s functions \(g_{rl}(r_2, r_1)\) and \(g_{rl}(r_1, r_2)\). To carry out the approximate integration one can substitute these quantities with the leading terms of their asymptotic representations. For \(X_{pl}(r)\) and \(X_{pl}(r)\) this results in \(X_{pl}(r) \sim \sin(pr-\pi/2+b_0(p))\) and \(X_{pl}(r) \sim -e^{i(pr+b_0(p))}\).

The leading terms in the expansions of the radial Green’s functions are
\[
\begin{align*}
g_{rl}(r_2, r_1) & \sim -i P \frac{e^{iPr_1}}{r_1} S_l(p) e^{-iPr_2} e^{-iPr_2}, \\
g_{rl}(r_1, r_2) & \sim -i P \frac{e^{-iPr_1}}{r_1} S_l(p) e^{-iPr_2} e^{-iPr_2}.
\end{align*}
\]
(24)

Here \(P = \sqrt{2(e+\omega)}\), \(p_1 = \sqrt{-2b_2} S_l(p)\) and \(S_l(p)\) are the elements of the scattering matrix. For the real argument \(p\) this quantity reads as \(S_l(p) = e^{i\beta(p)}\).

By using the asymptotic formulæ one carries out analytical evaluation of the integrals from (23). The final result (the leading term) for \(B_{1l}\) is as follows:
\[
\text{Im} B_{1l} = \frac{(-1)^{(l-1)/2}}{2\pi^2} \left[ \xi^{-1} \frac{\xi^2 + 1}{(\xi^2 - 1)^2} + \xi^{-1} \frac{\xi^2 + 1}{(\xi^2 + 1)^2} + \xi^{-1} \frac{\xi^2 + 1}{(\xi^2 - 1)} \right] \frac{\text{Re} S_l(p) S_l(p) e^{2i(l+1)x}}{(\xi^2 - 1)} + \xi^{-1} \frac{\xi^2 + 1}{(\xi^2 + 1)} + \xi^{-1} \frac{\xi^2 + 1}{(\xi^2 - 1)} \right]
\]
(25)

where \(X = pr, \xi = p/r\) and \(\xi_i = p_i/r_i\) It follows from the approximations formulated above that formula (25) is valid if the photoelectron momentum \(p\) and the ground-state energy \(\epsilon_i\) satisfy the conditions
\[
pR > 1, \quad 2\sqrt{-2\xi R} > 1.
\]
(26)

Letting \(\delta_i(p) = \delta_F(p) = 0\) in (25) one finds the plane-wave Born limit of \(\text{Im} B_{1l}\).

The presence of oscillatory terms on the right-hand side of (25) is physically clear. Indeed, in the limit \(pR > 1\) the wavelength of the photoelectron is less than the size of the target, which is supposed to have a well-pronounced edge (e.g., the edge of an ionic core in a cluster). Thus, the electron experiences a diffraction at the edge when leaving the core. This diffraction leads to the oscillatory character of the cross section. This phenomenon was discussed previously in connection with various processes involving metallic clusters and fullerenes: the radiative electron capture by metallic clusters [13], the electron scattering [14], the polarizational bremsstrahlung [15].

Carrying out obvious summations in (22), one writes correction factor as follows:
\[
K(\omega, \theta) = E_0^2 (\kappa_0(\omega) + \kappa_2(\omega) P_2(\cos \theta)),
\]
(27)
where
\[
\kappa_0(\omega) = -\frac{2}{3} |\alpha(\omega)|^2 \text{Im} \left( B_{10} + \frac{4}{5} B_{12} + \frac{4}{5} B_{32} \right).
\]
(28)

Formula (27) stresses the proportionality of \(K(\omega, \theta)\) to the laser field intensity (which is proportional to \(E_0^2\)) and exhibits explicitly its dependence on the emission angle \(\theta\), which enters, as well as in (15), via the second-order Legendre polynomial.

As a function of \(\theta\) the modulus of \(K(\omega, \theta)\) attains its maximum either at \(\theta = 0^\circ\) (and \(\theta = 180^\circ\)) or at \(\theta = 90^\circ\), depending on the sign of the product \(\kappa_0(\omega)\kappa_2(\omega)\) and on the relative magnitudes of \(\kappa_0(\omega)\) and \(\kappa_2(\omega)\). For further reference let us define the quantity
\[
|\kappa(\omega)|_{\text{max}} = |\kappa_0(\omega) + \kappa_2(\omega) P_2(\cos \theta)|_{\text{max}}
\]
\[
= \begin{cases} 
|\kappa_0(\omega)| + |\kappa_2(\omega)|/2 & \text{if } \kappa_0(\omega)\kappa_2(\omega) > 0, \\
|\kappa_0(\omega)| - |\kappa_2(\omega)| & \text{if } \kappa_0(\omega)\kappa_2(\omega) < 0 \text{ and } 4|\kappa_0(\omega)| > |\kappa_2(\omega)|, \\
|\kappa_2(\omega)| - |\kappa_0(\omega)| & \text{if } \kappa_0(\omega)\kappa_2(\omega) < 0 \text{ and } 4|\kappa_0(\omega)| < |\kappa_2(\omega)|,
\end{cases}
\]
(29)

which allows one to estimate the laser field strength needed to achieve a noticeable correction to the angular distribution (see the discussion in section 3).

Substituting (27) into (13), taking into account (15) and expressing \(P_2^2(\cos \theta)\) via \(P_0(\cos \theta)\) and \(P_1(\cos \theta)\), one derives the following formula for the differential cross section within the lowest order of perturbation theory in \(\mathbf{U}(r, t)\),
\[
\frac{d\sigma}{d\Omega} = \frac{a_0}{4\pi} (a_0(\omega) + a_2(\omega) P_2(\cos \theta) + a_4(\omega) P_2(\cos \theta)).
\]
(30)
The coefficients \(a_{0,2,4}\) are related to the asymmetry parameter \(\beta\) and to \(\kappa_{0,2}\) via
\[
a_0 = 1 + E_0^2 \left( \kappa_0 + \frac{\beta\kappa_2}{5} \right), \\
a_2 = \beta + E_0^2 \left( \kappa_2 + \left( \kappa_0 + \frac{2\kappa_2}{7} \right) \beta \right), \\
a_4 = \frac{18}{35} E_0^2 \beta \kappa_2.
\]
(31)

The right-hand side of (30) suggests that not only the profile of the angular distribution can be changed, but the magnitude of the cross section, integrated over the emission angles, is scaled by the factor \(a_0\) which can be greater or lower than one depending on the signs and magnitudes of \(\beta\) and \(\kappa_{0,2}\).

If the action of \(\mathbf{U}(r, t)\) is ignored then \(a_0 \to 1, a_2 \to \beta\) and \(a_4 \to 0\), and equation (30) reduces to (15).
3. Numerical results

Numerical analysis of the influence of the induced dipole moment on the profile of the angular distribution was carried out for the process of photodetachment of sodium cluster anions Na\textsubscript{N}. The results presented below in this section refer to \( N = 8, 20, 40, 58 \) and 92. The corresponding neutral clusters are spherically symmetric which makes applicable the theory described in section 2.

The parameters of sodium clusters and their anions, used in our numerical calculations, are summarized in table 1. Let us comment on these data.

The ionic core radius was calculated using the standard relation \( R = r_s N^{1/3} \) with the Wigner–Seitz radius \( r_s \) set to 4 au. The values of electron affinities \( I_a \) are taken from a recent work by Kostko [5] which contains, in particular, an excellent collection of reference data on various metal clusters. The other data presented in the table refer to the polarizability of the core and the parameters of the plasmon peak. We considered the dynamic dipole polarizability \( \alpha(\omega) \) of the clusters within the framework of the resonance plasmon approximation (see, e.g., [15, 16]),

\[
\alpha(\omega) = \alpha(0) - \frac{\omega^2}{\omega^2 - \omega_0^2 + i\omega \Gamma}. \tag{32}
\]

Here \( \alpha(0) \) is the static polarizability, \( \omega_0 \) is the surface plasmon energy and \( \Gamma \) is the linewidth of the plasmon resonance.

Due to the spill-out effect the static polarizability of a metallic cluster of a radius \( R \) exceeds the classical value \( \alpha_{cl} = R^3 \), which characterizes a metallic ball of the same radius. In the table, we present the ratio \( \alpha(0)/\alpha_{cl} \) calculated within the RPA [17] and the LDA [18] as well as the experimentally measured values [19]. The \( \omega_0 \) values were obtained with the help of the relation proposed in [20] to account for the size dependence of the plasmon energy: \( \omega_0 = \omega_{Mie}(1 - 1.58/R) \), where \( \omega_{Mie} = 3.27 \) eV is the Mie plasmon energy in a sodium metallic sphere, and \( \delta = 0.54 \) Å takes into account the spill-out effect.

The size dependence of the width \( \Gamma \) of the plasmon resonance for neutral sodium clusters with \( N \) up to several hundreds was analysed in [21] within the RPA scheme and in [22] within a semiclassical approach. These two methods, being consistent for \( N > 58 \), deviate noticeably for lower values. The RPA calculations reproduce the \( 1/R \) scaling law, which is inadequate when compared to the experimental data for \( N \lesssim 58 \) (see the discussion in [21]). The semiclassical calculations [22] seem to be consistent with the experimental data in the whole region \( N = 10, \ldots, 100 \). The values of \( \Gamma \), presented in the table, were deduced from figure 1 in [22].

It is seen from the table that for all \( N \) the plasmon energy exceeds the electron affinity. This fact justifies the choice of cluster anions in a view of the present study. Indeed, the inequality \( \omega_0 > I_a \) leads to the additional enhancement of \( K(\omega, \theta) \) owing to the pronounced increase of the modulus of the dynamic polarizability in the region \( \omega \approx \omega_0 \).

To conclude the discussion on the parameters of the chosen targets let us note that both criteria from (26) can be easily met for Na\textsubscript{N}. The first inequality fails only in the narrow near-threshold region \( \omega - I_a \ll I_a \) but is well fulfilled for \( \omega \approx \omega_0 \). The validity of the second condition one proves by introducing \( \epsilon_a = -I_a \).

The results of calculation of the quantities relevant to the correction term \( K(\omega, \theta) \) are presented in figures 2 and 3. For each anion the calculations were performed for the photon energies above the ionization threshold \( I_a \) and in the vicinity of the plasmon peak. The latter manifests itself as a resonance in the dependence of \( |\alpha(\omega)|^2 \) on \( \omega_0 \) as it is seen from the upper panel in each graph. The dynamic polarizabilities were calculated via (32) with the parameters \( \omega_0 \) and \( \Gamma \) as indicated in table 1. Given the differences between the calculated and experimentally measured values of the static polarizabilities \( \alpha(0) \), as well as the absence of the experimental data for Na\textsubscript{58} and Na\textsubscript{92}, for the ratio \( \alpha(0)/R^3 \) we used the values close to the theoretical data (see the figure captions).

The dependences of the coefficients \( k_0(\omega) \) and \( k_2(\omega) \) on \( \omega \) are presented in the middle panels. They were computed from (28) and (25). To calculate the right-hand side of the latter formula beyond the plane-wave Born approximation one must know the scattering phaseshifts \( b_1(p) \) and \( b_2(P) \). To determine the phaseshifts we solved numerically the phase equation (see, e.g., [23, 24]) for an electron moving in a local potential. The model potential, which was used to describe the interaction between the photoelectron and the neutral residue, accounted for the following three terms: (a) the short-range potential due to the Coulomb interaction with the core’s electrons and the ionic Jellium core, (b) the exchange-correlation term, which was treated within the Gunnarsson–Lundqvist approximation [25] and (c) the polarization potential was considered in the form \( U_{pol}(r) = -\alpha(0)/2\epsilon_r + R^3 \) for \( r > R \) and \( U_{pol}(r) = 0 \) if otherwise. Inclusion of the polarization term is important for an adequate description of the low-energy electron scattering from metallic clusters (e.g., [10]). A more rigorous treatment accounts for the many-body correlations, which may
be considered, for example, within the Dyson equation scheme [9]. However, for the purpose of our paper it is sufficient to treat the polarization potential in the simple form described above.

Comparing the middle panels in the graphs from figures 2 and 3 one notes that the behaviour of \( \kappa_{0,2}(\omega) \) (and of \( |\kappa(\omega)|_{\text{max}} \) as well) exhibits some general trends along with the specific features determined by the dynamic and geometrical properties of an individual target. Common to all clusters is the existence of extrema for \( \kappa_{0,2}(\omega) \) at \( \omega \approx \omega_s \), which is due to the factor \( |\alpha(\omega)|^2 \), see (28). The extremum can be clearly defined (see the curves \( \kappa_0(\omega) \) for Na\(_8\) and \( \kappa_2(\omega) \) for Na\(_{58}\) which have distinct maxima) or less pronounced (both curves for Na\(_{40}\)) or barely seen (the case of Na\(_{92}\)). The variation in the shape of the extremum, as well as the

Figure 2. Calculation of the correction term for Na\(_8\) and for Na\(_{40}\) as indicated. In each graph the upper panel represents the dependence of \( |\kappa(\omega)|^2 \) on \( \omega \); the middle panel—dependences \( \kappa_{0,2}(\omega) \) and \( |\kappa(\omega)|_{\text{max}} \), equations (28) and (29); the lower panel—dependence of \( E_{\text{corr}}(\omega) \), equation (33). Parameters \( \omega_0 \) and \( \Gamma \) are as indicated in table 1. The data refer to the \( \alpha(0)/R^2 \) ratio equal to 1.45 for Na\(_8\) and to 1.30 for Na\(_{40}\).

Figure 3. Same as in figure 2 but for Na\(_{58}\) and Na\(_{92}\). For both clusters the ratio \( \alpha(0)/R^2 \) is set to 1.20.

behaviour of the curves in the regions below and above the plasmon resonance, can be understood by analysing the \( \omega \)-dependence of the right-hand sides in (28) and (25). The non-oscillatory part of the latter depends on the photon energy mainly through the factor \( (pR)^{-4} = 4R^{-4}(\omega - \omega_s)^{-2} \). This leads to \( \kappa_{0,2}(\omega) \propto |\alpha(\omega)|^2/(\omega - \omega_s)^2 \). Therefore, a symmetric resonance profile of \( |\alpha(\omega)|^2 \) is distorted due to the factor \( (\omega - \omega_s)^{-2} \). For a powerful and narrow resonance (as in the case of Na\(_{58}\)) the distortion is comparatively small, whereas for a wide resonance the disproportion between the low- and the high-\( \omega \) shoulders may completely change the behaviour of the curve in the vicinity of the resonance, as it happens for Na\(_{40}\). In either case the factor \( (\omega - \omega_s)^{-2} \) results in a faster decrease of \( |\kappa_{0,2}(\omega)| \) with \( \omega \) beyond the resonance. In the region \( I_s < \omega < \omega_s \) the curves \( \kappa_{0,2}(\omega) \), being enhanced by the factor, exhibit a non-monotonous oscillatory character (most clearly seen in Na\(_{40}\), Na\(_{58}\) and Na\(_{92}\) graphs). This is due to the second and the third terms on the right-hand side of (25), which contain the oscillating factors \( \exp(iPR) \) and \( \exp(iPR) \), dependent on the cluster size, and the factors
points, the critical strength of the laser field $E_{\text{crit}}$, the ponderomotive energy $E_0(\tilde{\omega})/4\tilde{\omega}^2$; $E_0$ is the internal anionic field.

### Table 2. The minima $\tilde{\omega}$ of the functions $E_{\text{crit}}(\omega)$ (bottom panels in the graphs in figures 2 and 3), the values of $\kappa_0$, and $|\kappa|$ in these points, the critical strength of the laser field $E_{\text{crit}}(\tilde{\omega}) = (|\kappa(\tilde{\omega})|_{\text{max}})^{-1/2}$ and the corresponding intensity $I_{\text{crit}}(\tilde{\omega})$, the ponderomotive energy $E_0(\tilde{\omega})/4\tilde{\omega}^2$

| Cluster | $\tilde{\omega}$ (eV) | $\kappa_0$ (10^3) | $\kappa_0(\tilde{\omega})$ (10^3) | $|\kappa(\tilde{\omega})|_{\text{max}}$ (10^3) | $E_{\text{crit}}(\tilde{\omega})$ (10^{-3} au) | $I_{\text{crit}}(\tilde{\omega})$ (10^{11} W cm^{-2}) | $E_0(\tilde{\omega})/4\tilde{\omega}^2$ (10^{-3} eV) |
|---------|----------------------|------------------|------------------|------------------|-----------------|-----------------|------------------|
| Na8     | 2.64 -0.470 -0.031 0.501 1.41 | 0.66 | 17.5 | 1.44 |
| Na20    | 2.73 0.021 0.022 0.043 4.82 | 7.67 | 30.8 | 15.7 |
| Na58    | 2.72 0.022 -0.100 0.078 3.58 | 4.23 | 37.0 | 8.64 |
| Na88    | 2.89 0.151 -0.160 0.231 2.08 | 1.43 | 44.9 | 2.61 |
| Na92    | 2.98 0.128 -1.589 1.461 0.83 | 0.23 | 50.1 | 0.39 |

$S_\gamma(p) = \exp(i\delta(p))$, $S_\eta(P) = \exp(i\delta(P))$, dependent on the phaseshifts.

The solid curves in the middle panels of each graph represent the dependences $|\kappa(\omega)|_{\text{max}}$ defined in (29). For a given photon energy the quantity $E_0^2|\kappa(\omega)|_{\text{max}}$ stands for the maximum value of $|K(\omega,\theta)|$ within the interval $\theta = [0^\circ, 180^\circ]$. It was already mentioned that the correction term must satisfy the condition $|K(\omega,\theta)| < 1$. Thus, taking into account that $|K(\omega,\theta)| \approx E_0^2|\kappa(\omega)|$, one can introduce a critical value $E_{\text{crit}}(\omega)$, which defines the upper boundary for the laser field strength consistent with the perturbative approach adopted in this paper.

$$E_{\text{crit}}(\omega) = (|\kappa(\omega)|_{\text{max}})^{-1/2}. \quad (33)$$

The corresponding intensity of the laser field (in W cm^{-2}) can be calculated from the relation $I_{\text{crit}} = 3 \times 10^{16} E_{\text{crit}}^2$, where $E_{\text{crit}}$ is measured in atomic units.

In the limit $E_0 \ll E_{\text{crit}}(\omega)$ a strong inequality $|K(\omega,\theta)| \ll 1$ is valid, so that the photoionization process is not affected by the induced dipole moment. The influence of the latter can become pronounced for $E_0 \lesssim E_{\text{crit}}(\omega)$ resulting in $|K(\omega,\theta)| \sim 1$.

Dependences $E_{\text{crit}}(\omega)$ are plotted in the lower panels in figures 2 and 3. For all clusters this function attains its minimum in the point $\tilde{\omega} \approx \omega_0$ in the vicinity of the plasmon resonance. The values of $\tilde{\omega}$, as well as of other quantities calculated in this point, are presented in table 2. It is instructive to compare the critical field $E_{\text{crit}}(\tilde{\omega})$ with the strength $E_\omega$ of the internal anionic field. The latter can be related to the ionization potential $I_\omega$ through $E_\omega = (2I_\omega)^{1/2}$. It is seen that $E_\omega$ exceeds $E_{\text{crit}}(\tilde{\omega})$ by the order of magnitude. The strong inequality $E_\omega \gg E_{\text{crit}}(\tilde{\omega})$, being in accordance with the first condition from (5), justifies the approximation adopted in this paper to neglect the modification of the ground-state orbitals due to the laser field. The last column in the table contains the values of ponderomotive energy of the photoelectron in the critical laser field. Comparing the ponderomotive shifts and the kinetic energies $\epsilon = \tilde{\omega} - I_\omega \sim 1$ eV, one notes that the latter is larger by several orders of magnitude. Therefore, the second condition in (5) is also well fulfilled.

Hence, one can expect that for the intensities $I_0 \lesssim I_{\text{crit}}(\tilde{\omega}) \sim 10^{11}$ W cm^{-2} the modification of the spectral-angular distribution due to the action of the field of the induced dipole moment can be quite pronounced. To carry out the corresponding quantitative estimates one can use the formulae obtained within the framework of perturbation theory.

### Figure 4. Profiles $F(\theta)$ of the angular distribution (35), corresponding to the asymmetry parameter $\beta = 2$, calculated for different sodium cluster anions and for several values of the ratio $\eta = I_\omega/I_{\text{crit}}$, see the legend in the graph. Thick black curves represent the field-free distribution $F_{\gamma}(\theta)$, equation (34). The length of line segment connecting the origin and a given point on the curve is equal to the value of $F(\theta)$ or $F_{\gamma}(\theta)$ (in absolute units) in the corresponding direction. The emission angle $\theta$ is measured with respect to $E_0$, which in each graph is aligned with the horizontal dashed line. In each graph, the spacing between ticks is equal to 1 for both directions.

The calculated profiles of the angular distributions are presented in figure 4. In the present paper, we have not made an attempt to compute the angular asymmetry parameter $\beta(\tilde{\omega})$ for sodium anion clusters (neither have we found its values in the literature). Aiming to illustrate the modification of the profile we carried out the calculations for $\beta = 2$, which is consistent with the assumption of the $s$-wave initial state made in the beginning of section 2.3.

In each graph from figure 4 the thick solid curve represents the unperturbed profile

$$F(\theta) \equiv 1 + \beta P_s(\cos \theta)) / \beta \approx 3 \cos^2 \theta. \quad (34)$$

The emission angle $\theta$ is measured with respect to the vector $E_0$, which in each graph is aligned with the horizontal dashed
Figure 5. Ratio \( \sigma(\omega)/\sigma_0(\omega) \) (see (36)) calculated for different sodium cluster anions and for \( \beta = 2 \). The data refer to the laser field intensity \( I_0 = 2.1 \times 10^{10} \) W cm\(^{-2} \).

In summary, we have demonstrated that the dipole moment, induced at the residue by the incoming laser field, can strongly influence the photoionization process. The additional time-dependent long-range field due to the induced moment, acting on the escaping electron, modifies the spectral-angular and spectral distributions of photoelectrons.

The effect itself, as well as its quantitative treatment, is quite sensitive to the choice of the target and to the parameters of the laser field. We have demonstrated that for a strongly polarizable target (e.g., metallic cluster anions) strong modifications of the characteristics of a single-photon ionization process in the vicinity of the plasmon resonance (typically, \( \omega_s \approx 2–3 \) eV) can be achieved by applying laser fields of comparatively low intensities \( I_0 \sim 10^{10–10^{11}} \) W cm\(^{-2} \).

From a theoretical viewpoint, the advantage of this regime is that the field of induced dipole moment can be treated perturbatively, whereas the influence of the laser field on the photoelectron (a ponderomotive effect) and on the ground state of the target can be ignored. We have shown that even in this weak-field regime one can expect dramatic changes in the profile of angular distribution of photoelectrons as well as in the \( \omega \) dependence of the photoionization cross section. To a great extent, these changes depend on the parameters of the target, like its radius, the static and dynamic polarizabilities, the energy of the plasmon resonance peak and the affinity (or, the ionization potential in the case of a neutral target). Additional variety can be obtained by changing the intensity and the frequency of the laser field.

The analysis, which we have carried out, is based on simple models adopted for the description of the photodetachment process (the plasmon resonance approximation) and of the interaction of the escaping electron with the static field of the residue (via the LDA + long-range polarization potential). We have also restricted ourselves to the case of spherically-symmetric targets. A more accurate quantitative treatment must include more sophisticated approaches, which take into account the many-body correlation effects intrinsic to both the photodetachment and the plasmon resonance.
and the electron escape. However, these will leave untouched the physics behind the basic phenomenon discussed in our paper.

It is possible to study the predicted phenomena by means of modern experimental techniques. The latter include the production and manipulation of the beams of cluster anions of various types and sizes, the energy and angle-resolved photoelectron spectroscopy, the availability of the laser fields of various intensity, frequency and pulse duration [4, 5]. We believe that with all these components at hand, soon it will become possible to test the theory against experimental data.

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