Fingerprints of level depletion in the photoelectron spectra of small Na clusters in the ultraviolet domain

P M Dinh$^{1,2}$, S Vidal$^{1,2}$, P-G Reinhard$^3$ and E Suraud$^{1,2}$

1 Université de Toulouse, UPS, Laboratoire de Physique Théorique (IRSAMC), F-31062 Toulouse, France
2 CNRS, LPT (IRSAMC), F-31062 Toulouse, France
3 Institut für Theoretische Physik, Universität Erlangen, D-91058 Erlangen, Germany
E-mail: dinh@irsamc.ups-tlse.fr

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Abstract. In the framework of time-dependent density functional theory (TDDFT), we study electronic emission from small Na clusters after irradiation by an intense femtosecond laser pulse. Photoelectron spectra (PES) are compared with level depletion, i.e., the electron loss at each single-electron level. Laser frequencies in the UV range (from 9 to 19 eV) are explored. We find a clear correlation of the peak areas in the photoelectron spectra with the state depletion. This thus allows experimental access to the ionization mechanism. This correlation, moreover, demonstrates that one can find a physical interpretation of the Kohn–Sham orbitals in PES, as in real-time TDDFT.

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1. Introduction

Photons provide a very convenient tool for the analysis of the structure and dynamic properties of clusters and molecules [1]. Laser irradiation of clusters and molecules leads to electronic emission, the kinematic properties of which provide key information on the emitting system [2–4]. Pulses in the femtosecond (fs) range have opened up a wide area of fs spectroscopy. This allows a detailed tracking of ionic dynamics in molecules and clusters; see, e.g., [5–8]. The availability of coherent light beyond the visible, ranging from ultraviolet (UV) up to x-rays, offers a new, interesting option for such studies. Free electron lasers (FEL) provide here a particularly versatile source [9] that can be tuned to deliver fs pulses at high frequency and simultaneously high intensity. It is thus now within the reach of experiments to study, in great detail, photoemission even from possibly deep-lying electronic states in neutral or cationic molecules and clusters. At the side of observables, photoelectron spectroscopy and angular distributions of emitted electrons [2] provide an invaluable tool for the investigation of the system’s properties. Experimental tools for such an analysis, especially photoelectron spectra (PES), have indeed been further developed recently and are increasingly being used (for an overview in cluster physics, see [10]).

Electronic emission mechanisms are highly sensitive to laser frequency [4, 10]. This can even be analyzed by studying the level depletion of electronic levels [11], namely how much of the total emission stems from a given electronic state. Such an analysis is quite interesting as it reveals underlying emission mechanisms in the course of a laser irradiation. Still, as such, it remains a purely theoretical object. A natural observable for the analysis of electronic emission is provided by PES. It is thus a natural candidate to check whether level depletion can be ‘visualized’ on an experimentally accessible basis. In the regimes from perturbative up to moderate excitations, PES provide a direct mapping of the energies of occupied electronic levels [12], to the extent that these levels are actually emitting electrons. One can thus expect that the PES could also give some indication of the level of depletion of a given single-electron level. The purpose of this paper is to tackle this question. For this we use time-dependent density functional theory (TDDFT) at the level of the local density approximation (LDA). The defect of LDA with respect to the self-interaction problem leads us to augment LDA by a self-interaction correction (SIC) to describe emission properties correctly. This TDDFT scheme (coupled to classical molecular dynamics of ions) has been extensively used for the description of cluster dynamics in many regimes [10, 13].

In this paper, we shall analyze PES spectra as computed from our model in relation to depletion from occupied electronic levels. We will show that there is a strong correlation between level depletion and PES peak amplitude, which confirms the consistency of this observable in our calculations and which provides a direct experimental clue to the ionization mechanism. We consider as test cases Na clusters in the regime of vacuum ultraviolet (VUV) radiation and show that the PES provides a printout of the actual ionization mechanism, as a function of laser frequency.

2. Theoretical framework

We describe the laser-induced electron dynamics by means of real-time TDDFT in the standard manner [10, 13]. We solve the (time-dependent) Kohn–Sham equations for the cluster electrons on a grid in coordinate space, using time splitting for the time propagation [14] and accelerated
We have pursued the simulations up to $2 \times N$ all states finally gives the total average ionization of the considered clusters such that we are dealing with predominantly one-photon processes,

$$\nu$$

point where the occupation number $n$ is large enough to avoid any non-physical spurious ionization. We have also chosen the laser intensity $I$ so low that $N_{\text{esc}}$ remains small, guaranteeing that we stay in the perturbative regime and that the electronic emission scales with $N_{\text{esc}}$ or equivalently with $I$. In practice, $I$ is about $10^{11} \text{ W cm}^{-2}$ at lower frequencies, and reaches at most $3 \times 10^{12} \text{ W cm}^{-2}$ for the highest frequencies. In all cases, the final ionization is of the order of $10^{-3}$. The laser frequencies $\omega_{\text{las}}$ are all above the IP of the considered clusters such that we are dealing with predominantly one-photon processes throughout.

Together with the state-wise ionization, we record the kinetic energy of outgoing electrons for $\alpha$. We thus define the time-resolved depletion of the state $\alpha$ by $\nu^{(\alpha)}(t) = 1 - \langle \varphi_{\alpha}(t)|\varphi_{\alpha}(t) \rangle$. When multiplied by the occupation number $n_{\alpha}$, one obtains the average ionization $N_{\text{esc}}^{(\alpha)}$ out of the state $\alpha$. The sum over all states finally gives the total average ionization $N_{\text{esc}}$ (= the number of escaped electrons).

We have pursued the simulations up to $2 \times T_{\text{pulse}}$ in order to collect all ionization, i.e. up to a point where the $\nu^{(\alpha)}(t)$ no longer change [13, 23]. We have also chosen the laser intensity $I$ so low that $N_{\text{esc}}$ remains small, guaranteeing that we stay in the perturbative regime and that the electronic emission scales with $N_{\text{esc}}$ or equivalently with $I$. In practice, $I$ is about $10^{11} \text{ W cm}^{-2}$ at lower frequencies, and reaches at most $3 \times 10^{12} \text{ W cm}^{-2}$ for the highest frequencies. In all cases, the final ionization is of the order of $10^{-3}$. The laser frequencies $\omega_{\text{las}}$ are all above the IP of the considered clusters such that we are dealing with predominantly one-photon processes throughout.

Together with the state-wise ionization, we record the kinetic energy of outgoing electrons to evaluate the PES [12, 24]. We choose a ‘measuring point’ $r_M$ far away from the system and close to the absorbing boundaries. We assume negligible mean field at $r_M$, so that we encounter free particle dynamics there and only outgoing waves will pass the point $r_M$. Thus, we can
Figure 1. Calculated PES of laser-irradiated Na\textsubscript{10} in the linear scale, for two different laser frequencies $\omega_{\text{las}}$ and intensities $I$ as indicated. Solid lines stand for the yield in the forward direction, whereas the dashed lines correspond to that in the sideward direction.

decompose the wave function as radially outgoing waves

$$\psi(\mathbf{r}_M, t) = \int_0^{\infty} dk \tilde{\psi}(k, \Omega_{\mathbf{r}_M}) e^{-i\omega t} e^{ikr_M},$$

where $r_M = |\mathbf{r}_M|$ and $\Omega_{\mathbf{r}_M}$ is the solid angle related to the direction of $\mathbf{r}_M$. We then compute the PES in the direction $\Omega_{\mathbf{r}_M}$ as

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}(E_{\text{kin}}, \Omega_{\mathbf{r}_M}) \propto |\tilde{\psi}(k(E_{\text{kin}}), \Omega_{\mathbf{r}_M})|^2,$$

where $\tilde{\psi}(k(E_{\text{kin}}), \Omega_{\mathbf{r}_M})$ is the Fourier transform (in time) of $\psi(\mathbf{r}_M, t)$. In compliance with the cylindrical box, we consider three 'measuring' points, namely forward, backward and sideward (with respect to the symmetry axis). The first two points are on the $z$-axis and would correspond to the positions of a detector in the direction of the laser polarization. Because of the symmetry, these two measuring points basically give the same yield. The sideward 'point' collects the photoelectron yield over the circle perpendicular to the $z$-axis and centered in the cylindrical box. We have previously studied the influence of the laser frequency in the depletion of Na\textsuperscript{+}\textsubscript{9}, Na\textsubscript{2+}\textsubscript{22} and C\textsubscript{2}H\textsubscript{4} [11]. In this paper, we consider Na\textsubscript{8} and Na\textsubscript{10} in addition to Na\textsuperscript{+}\textsubscript{9}, and complement the analysis of the depletion results by a comparison with the trends of PES.

3. Discussion and results

3.1. An illustrative example

As an illustrative example, we first discuss the case of Na\textsubscript{10} irradiated by a laser of low frequency (9.5 eV) and another one at high frequency (16.3 eV). Na\textsubscript{10} exhibits four non-degenerate electronic states whose energy, respectively, lies at $\varepsilon_{1s} = -5.82$ eV, $\varepsilon_{1p_z} = -4.78$ eV, $\varepsilon_{1p_x} = \varepsilon_{1p_y} = -4.46$ eV and $\varepsilon_{2s} = -3.64$ eV.

Figure 1 presents the PES in the linear scale. Thanks to the relatively low laser intensities, they display sharp peaks corresponding to one-photon emission (on the logarithmic scale, not
shown here, one can also spot two-photon processes that are, however, suppressed by two or more orders of magnitude). One can easily read from the figure the binding energies of Na
_{10} via the relation \( E_{\text{kin}} = \epsilon + n \hbar \omega_{\text{las}} \), where \( n \) denotes the number of photons involved in the process (thus here, \( n = 1 \)). By comparing the low- and the high-frequency cases, we can immediately note that, for a given state, the relative peak heights strongly depend on the laser frequency. The idea of this paper is thus to monitor each peak height as a function of \( \omega_{\text{las}} \) from the one-photon spectra (since the latter exhibit the highest yield) and to compare it with the level depletion. More relevant is the area of each peak. We have thus fitted each peak with a Gaussian and we have reported in the following the ratio between dominant peaks. In particular, the peaks corresponding to the 1p_{x,y} states are always suppressed by at least two orders of magnitude, whatever the cluster and \( \omega_{\text{las}} \). Thus, these states will not be considered on purpose in all the results presented below.

Figure 1 also shows the sideward signals as dashed lines. The information one obtains from the figure is that, indeed, the height of the sideward peak also depends on the laser frequency but a comparison with the other states is impossible as such, since this yield is actually very much dominated by emission from the 1p_{z} state only. This has thus motivated us to only discuss in the following the forward (and backward) emission. A more detailed study would require full angular distributions of the photoelectrons (or photoangular distributions (PAD)). In our group we have developed sensitive and efficient techniques to compute PAD within a full 3D treatment of the electronic wave functions \[25, 26\]. These calculations are, however, very expensive. For the exploration study presented in this paper, we chose to use CAPS to be able to perform an exhaustive scan of PES and level depletion as a function of laser frequency.

3.2. Systematic trends

We first present in detail the case of Na\textsuperscript{9}. The 1s state has a binding energy of \(-8.61\) eV, whereas the 1p_{x} and the 2-degenerate 1p_{x,y} are very close in energy \((-7.40\) and \(-7.24\) eV, respectively). In the left panel of figure 2, the level depletion \( \nu_{1s} \) and \( \nu_{1p_{x,y}} \) are compared with the ratio of the 1s peak area over that of the 1p_{z}, for laser frequencies ranging from 9.5 to 19 eV. Both ratios increase monotonically and come very close together over several frequencies. While the ratio of depletion increases almost linearly with \( \omega_{\text{las}} \), the ratio of PES peaks shows higher than linear components. The PES signal, taken at one reference point, combines the trends overall yield with changes in the angular distribution. Anyway, we see here a very clear indication that the PES signal corresponding to a given single-electron level does reflect the level of depletion. To demonstrate that this is a general feature, we show in the right panel of figure 2 the same for the neutral cluster Na\textsubscript{8}. The situation is basically the same.

We now turn to Na\textsubscript{10}. We recall that there are four non-degenerate states with energies \( \epsilon_{1s} = -5.82\) eV, \( \epsilon_{1p_{x}} = -4.78\) eV, \( \epsilon_{1p_{x,y}} = -4.46\) eV and \( \epsilon_{2s} = -3.64\) eV. We found that the 1s peak area or depletion is always higher than that of the 2s state, whatever be the laser frequency. The ratios between s states are thus not presented. Figure 3 compares each s state independently with the 1p_{z} one.

The patterns are at first glance very similar to those observed in Na\textsuperscript{9} and Na\textsubscript{8}. However, the results from PES deviate from a monotonic trend at the low- and high-frequency edges. This is due to changes in the angular distributions which change the weight of the forward direction (measured in these PES). The cluster Na\textsubscript{10} has a strong deformation, which leads to stronger changes in the angular distribution.
Figure 2. The ratio of 1s over 1p\textsubscript{z} depletion (thick curve) and that of PES peak areas (thin line) in Na\textsubscript{9} (left) and Na\textsubscript{8} (right), as functions of laser frequency $\omega_{\text{las}}$.

Figure 3. Ratios of depletions (thick curves) and that of PES peak areas (thin curves) in Na\textsubscript{10}, as functions of laser frequency $\omega_{\text{las}}$. Full lines: 1s over 1p\textsubscript{z}; dashed lines: 2s over 1p\textsubscript{z}.

All the cases discussed above show one interesting feature concerning the frequency where the ratio curves are equal to 1 (see crossing with the dotted horizontal line in figures 2 and 3). This frequency differs, of course, from case to case. But, the crossing frequencies for ratios from depletion and for ratios from PES nearly coincide for all cases. This is most probably not an accident. The reason for such coincidences is not yet clear and has to be worked out in future investigations.

4. Conclusion

We have studied in this work the response of simple metal clusters to laser irradiation in terms of PES. We have compared the behavior of the PES to single-electron level depletion for processes
in the one-photon regime and found that both are strongly correlated. While level depletion is a purely theoretical observable, PES can both be computed and measured. The correlation we observe thus provides an experimental signal to analyze how single-electron levels are depleted in the course of a laser irradiation. It turns out that level depletions, and correspondingly the amplitude of PES peaks, do depend on the laser frequency. While low-frequency lasers favor emission from least bound levels, higher frequencies also significantly ionize more deeply bound states. This effect, clearly visible from the computation of depletion, can now be traced back to the PES signal. This proves once more the relevance of PES computations in relation to the analysis of detailed ionization mechanisms in the laser irradiation of molecules and clusters.

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