Photoelectron spectra: a tool of analysis of irradiation dynamics

M. Baer\textsuperscript{1}, P. M. Dinh\textsuperscript{2}, P.-G. Reinhard\textsuperscript{1,2} and E. Suraud\textsuperscript{1,2}

\textsuperscript{1}Institut für Theoretische Physik, Universität Erlangen, D-91058 Erlangen, Germany
\textsuperscript{2}Laboratoire de Physique Théorique, Université Paul Sabatier, CNRS, F-31062 Toulouse Cédex, France

E-mail: dinh@irsamc.ups-tlse.fr

Abstract. We explore from a theoretical perspective photoelectron spectra emitted from a Na\textsubscript{8} cluster irradiated by a short laser pulse. We use time-dependent density-functional theory (TDDFT) at the level of the local-density approximation (LDA). That includes a self-interaction correction (SIC) to recover the proper emission threshold. As environments are known to play an important role in irradiation dynamics, we consider the example of Na\textsubscript{8} deposited on a MgO(001) surface and compare it to the case of a free cluster. Anisotropy of emission is also briefly discussed.

1. Introduction

For decades, optical methods have provided a key tool for analyzing cluster structure and dynamics [1–4]. More recently, new insights into the dynamics of irradiation have been gained by measuring the properties of electrons emitted after irradiation by a short laser pulse. The first step in that direction is photoelectron spectroscopy (PES) which measures kinetic energies of emitted electrons. While early attempts in this direction were performed long ago [5,6], steady development of tools allows now to measure fully angular and energy resolved distributions of outgoing electrons [7–10].

The case of clusters in contact with environments (embedded clusters or clusters deposited on a substrate) brings further challenging aspects into play and furthermore allows to understand the impact of an environment on emission properties, a key aspect in many physical situations ranging from materials science to biological systems. Contact with an environment may be compulsory in biological compounds and it is often used for easier experimental handling in molecular and cluster physics. On the other hand, it complicates the physical situation and its theoretical description. For example, deposition on a surface modifies emission properties and furthermore requires to take into account a huge number of degrees of freedom to accommodate an acceptable (possibly dynamical) description of the substrate. The theoretical description of such problems thus constitutes a demanding task. This paper aims at addressing such a question for a rather simple example with a clear-cut separation between optically active system and environment. We thus perform a first theoretical exploration of PES of laser excited metal clusters deposited on an insulating surface MgO(001).

The description is based on density-functional theory [11], which is well adapted for electronic structure and dynamics in clusters [12]. The detailed dynamics of laser excitation and subsequent
electron emission is treated by the time-dependent extension of DFT, namely TDDFT [13,14]. As a test case, we take Na₈ deposited on a MgO(001) surface which is a typical insulator material. We concentrate on a moderate laser excitation in which electronic emission is dominated by direct emission [15–17]. In practice, there is competition between direct and thermal emission, the preferred exit channel depending on pulse duration. For sufficiently short pulses, collisional relaxation and the resulting thermal emission can be neglected. We will use pulses with full width at half maximum (FWHM) of 20 fs.

2. Outline of the model

We use a hierarchical model in which the cluster is described in full microscopic detail while the environment is treated at a lower level of refinement with classical molecular dynamics. This model corresponds to an improved QM/MM approach as frequently used in biochemistry or surface science [18]. The new aspect is that electronic excitations are possible at the side of the substrate by attributing to each substrate atom a dynamical polarization. The details of this model have been presented at many places and we refer the reader to the recent review [19] which summarizes many aspects of the model and applications. For completeness sake, we recall a few key aspects.

The constituents of the system and their degrees of freedom are: ϕᵣ(⃗r, t), n = 1, ..., Nᵥ for valence electrons of the Na cluster, i(Na), i(⃗Rₙ), i(⃗Rᵣ) = 1, ..., Nᵣ for the positions of the Na⁺ ions, i(O), i(⃗Rᵣ) = 1, ..., M for the positions of the O cores, i(k), i(⃗Rᵣ) = 1, ..., M for the centers of the O valence clouds, i(k), i(⃗Rᵣ) = 1, ..., M for the positions of the Mg²⁺ cations. The Na cluster is treated in standard TDDFT at the level of local-density approximation, coupled with molecular dynamics, (TDLDA-MD) [12, 20]. The Mg²⁺ cations (label i(k)) are electrically inert and treated as charged point particles. The polarization of O²⁻ anions is described by distinguishing between a valence electron distribution (i(ν)) and a complementing core (i(σ)). All ions of the MgO substrate are described as classical degrees of freedom in terms of positions i(ν), the O²⁻ dipoles dynamically stemming from the difference R(ν) − R(c). The Mg and O ions are arranged in bulk MgO crystalline order (six layers of 784 Mg²⁺ plus 784 O²⁻ ions). The dynamical degrees of freedom for Mg and O are taken into account in an active cell of the MgO(001) surface region underneath the Na cluster (three layers, each with 242 Mg²⁺ plus 242 O²⁻). The active cell is embedded in an “outer region” of MgO material with ions kept fixed, but oxygen dipoles still fully dynamical. Beyond that region, only the Madelung potential is considered. Finally the ions in the lowest layer are fixed to prevent relaxation towards an artificial second surface.

The total energy is composed as E = EₖNa + EₖSurf + Eₖcoupl where EₖNa describes an isolated Na cluster, EₖSurf the MgO(001) substrate, and Eₖcoupl the coupling between the two subsystems. For EₖNa, we take the standard TDLDA-MD functional [12, 20] including an average-density self-interaction correction [21]. The energy of the substrate and the coupling to the Na cluster consists of the long-range Coulomb energy and some short-range repulsion modeled through effective local core-potentials [22–24]. The model parameters were furthermore calibrated to represent results of calculations to a fully quantum-mechanical description of the active MgO cell [25].

The equations of motion are obtained by variation of the above energy in standard manner [12] and are augmented by an external laser field of frequency ωlas, intensity I with sin² pulse profile activated only in the time interval 0 ≤ t ≤ Tpulse which corresponds to a full width at half (intensity) maximum as FWHM= Tpulse/3. The laser polarization is perpendicular to the surface (z-axis). The TDDFT equations are solved on a grid in coordinate space in full three dimensions [20].
3. Results

Experimentally, it is possible to measure the kinetic energy of the electrons which were ionized from the cluster by a laser pulse. For not too strong laser pulses, the resulting spectra allow to directly analyze the single-particle structure of the cluster. The theoretical calculations in [17, 26], which used the same technique as employed in this work, have confirmed that, at least for free clusters and not too intense pulses, the simple single-particle picture is valid. This is demonstrated in figure 1 (upper panel) for the case of a free \( \text{Na}_8 \) cluster irradiated by a laser with frequency \( \omega = 0.18 \text{ Ry} \), which is slightly below the plasmon frequency of the cluster.

![Figure 1](image_url)  
Figure 1. Kinetic energy distribution of emitted electrons from free \( \text{Na}_8 \) (top) and \( \text{Na}_8 \) on \( \text{MgO}(001) \) (bottom). The laser frequency is \( \omega = 0.18 \text{ Ry} \) (top) and \( \omega = 0.205 \text{ Ry} \) (bottom). The three curves correspond to laser intensities \( 10^8 \), \( 10^9 \) and \( 10^10 \text{ W/cm}^2 \) (same ordering from bottom to top in each panel) and have been shifted up/down for better visualization. The Roman numbers denote the multi-photon order responsible for the peak and the vertical lines display the peak position expected from the single-particle spectrum, identifying the orbitals from which the electron density was emitted (dotted line for 1s, dashed-dotted for 1p).

Figure 1 shows results from calculations using three different laser intensities, \( I = 10^8, 10^9 \) and \( 10^{10} \text{ W/cm}^2 \). The photon energy is smaller than the ionization potential of the cluster, so that one photon does not suffice to lift up an electron into the continuum. Two- or more-photon processes are required. At moderate intensities, total ionization remains small, and the residual cluster does not charge up significantly, leaving the ground-state mean-field practically unchanged. In this case, peaks can be found in the spectrum at

\[
E_{i,n} = \varepsilon_i + n \cdot \omega > 0 ,
\]  

(1)
where $\varepsilon_i$ are the single-particle energies of the occupied Kohn-Sham orbitals of the ground state, and $n$ is the multi-photon order. These energies are plotted as vertical lines in figure 1. The Roman numbers indicate the multi-photon order $n$. Obviously, for the two lower laser intensities, as mentioned above, the simple single-particle approach correctly describes all peaks in the spectra. The identification can further be confirmed by watching the motion of the peaks with changing $\omega$: Changing $\omega$ by $\Delta\omega$ moves the peak $E_{i,n}$ by $\Delta E_{i,n} = n \cdot \Delta\omega$. For higher intensities (upper curve in figure 1) peaks are broadened and the whole spectrum is red-shifted, due to changing the mean-field (cluster charging). The reason is the changed mean-field in this case. The strong laser pulse ionizes considerably more electrons (about 0.7 in this case), charging the residual cluster, so that the remaining electrons are deeper bound. Going over to even higher intensities would completely wipe out the single-particle structure in the spectrum [26].

The same technique is now applied for the deposited cluster but with a laser frequency of 0.205 Ry instead. The first main question here is whether the single-particle picture is still valid. Figure 1 (bottom) indicates that this is indeed the case. All dominant peaks in the spectra can be clearly identified with multi-photon transitions from the ground-state single-particle Kohn-Sham orbitals. Note that the degeneracy of the $1p$ level is removed by the substrate (two close-by vertical lines instead of one for free Na$_0$) and that this $1p$ splitting is also found in the PES. The second question in focus is what happens when the outgoing electron wave hits the substrate and is reflected. The repulsive interface potentials prevent the electron wave from penetrating the surface, but it could possibly exchange energy with the surface dipoles. It is thus conceivable that the electronic scattering at the substrate is not elastic. If that was the case, one would expect that the peaks in the kinetic energy spectrum would broaden or satellite peaks would show up. However, in all computed cases, no peak broadening nor further dominant peaks, which cannot be explained by the single-particle structure or excitations spectrum, were found. So the inelasticity of the scattering process seems to be small. This is not so surprising as both the laser and the electronic frequencies involved reside in a frequency domain where the dielectric response of MgO is very small. Above $\sim$ 0.6 Ry, however, the dielectric function of MgO possesses a broad resonance, but the contributions of the outgoing electron wave in this energy region are quite small. Our model qualitatively reproduces the appearance of the resonance in the dielectric response (triggered by the oxygen shell mass), but not the details. So the model is probably not very reliable if the laser frequency is well above 0.6 Ry.

In the case of the deposited cluster, the kinetic energy distribution is expected to strongly depend on the direction of emission, i.e. on the location of the measuring points used to calculate the energy spectra. The distributions in figure 1 have been obtained by averaging over all measuring points. Figure 2 shows the spectra as calculated at three individual measuring points, one far above the surface on the positive $z$-axis ($\theta = 0$, later called A), another one 5 $a_0$ above the surface on the $x$-axis ($\theta = \pi/2$, called B), and finally one deeply below the surface on the $z$-axis ($\theta = \pi$, called C). Note that, since the substrate is modeled as a finite slab, the measuring point is located below the slab in empty space. The spectrum measured at A is very similar to that measured at B, apart from the fact that the relative weight of emission between the split 1p orbitals changes slightly. Anyway, the $n$-photon processes mapping the single-particle spectrum still dominate the distribution. The electron yield decreases with increasing photon order $n$ as intuitively expected. This is clearly different for the spectrum measured at C: the electron yield does not decrease with increasing $n$. For instance, the figure shows that a 3-photon process from a 1p state ($E_{\text{kin}} = 0.26$ Ry in the figure) is two orders of magnitude more probable than a 2-photon process from the same 1p state ($E_{\text{kin}} = 0.08$ Ry). This result is due to the insulating properties of the MgO substrate. The electrons do not gain enough energy by absorbing two photons in order to override the transmission barrier (at 0.125 Ry in figure 2), whereas absorption of 3 photons suffices because the emitted electrons have now acquired sufficient kinetic energy.
Figure 2. Kinetic energy distribution of emitted electrons from Na$_8$ exposed to a laser pulse with $\omega = 0.18$ Ry as calculated from three different measuring points (see text for detail). The spectrum corresponding to $\theta = 0$ has been shifted up by a factor of 10 for better visualization.

Vice versa, the plot indirectly shows that the inelasticity in the scattering process between electron and MgO surface is only small. The electron density which has gained enough energy from the laser to penetrate the material, can pass the whole substrate slab and leave it on the lower side, where the point C resides. Even after passing the MgO layers, the principal kinetic energy distribution of the electron density is still dominated by the original electronic structure of the cluster, so that the electron has obviously not coupled to the oxygen dipoles. This, however, is not surprising, as the dielectric response of MgO is small in this energy/frequency domain. Resonances become important only for larger frequencies, see the discussion above.

4. Conclusions and perspectives
We have presented photoelectron spectra (PES) of a small sodium cluster deposited on an insulator MgO(001) surface and compared the properties of emitted electrons to the case of a free cluster. This serves as a simple archetype example for the analysis of the effects of an environment on PES. In both cases, there remains a relevant map of the single-particle energies of occupied states. Nonetheless, the surface significantly affects the energies of emitted electrons. That is to a large extent due to a shift of the single-particle energies emerging by deposition on a surface. The effect is even larger when considering angular distributions of emitted electrons, as suggested by comparing emission properties at various points in space. This is due to the fact that transmission of free electrons into the substrate is strongly suppressed by the large band gap of MgO(001). A next step is obviously to consider a full description of angular distributions of emitted electrons [27]. Another interesting aspect is to study PES in the case of irradiated organic molecules and to study the impact of the environment (for example water) in such cases. Work in this direction is in progress.

Acknowledgments
This work was supported, by Agence Nationale de la Recherche (ANR-06-BLAN-0319-02), the Deutsche Forschungsgemeinschaft (RE 322/10-1) and the Humboldt foundation.
References
[1] Brack M 1993 Rev. Mod. Phys. 65 677
[2] de Heer W 1993 Rev. Mod. Phys. 65 611
[3] Kreibig U and Vollmer M 1995 Optical Properties of Metal Clusters, Springer Series in Materials Science 25 (Berlin: Springer)
[4] Haberland H 1994 Clusters of Atoms and Molecules 1- Theory, Experiment, and Clusters of Atoms, Springer Series in Chemical Physics 52 (Berlin: Springer)
[5] McHugh K M et al 1989 J. Chem. Phys. 91 3792
[6] Lichtenberger D L 1991 et al Chem. Phys. Lett. 176 203
[7] Pinaré J C 1999 et al Eur. Phys. J. D 9 21
[8] Baguenard B et al 2001 Phys. Rev. A 63 023204
[9] Verlet J R R et al 2004 J. Chem. Phys. 121 10015
[10] Kostko O et al 2007 J. Phys. Conf. Ser. 88 012034
[11] Dreizler R M and Gross E K U 1990 Density Functional Theory: An Approach to the Quantum Many-Body Problem (Berlin: Springer)
[12] Reinhard P G and Suraud E 2003 Introduction to Cluster Dynamics (New York: Wiley)
[13] Runge E and Gross E K U 1984 Phys. Rev. Lett. 52 997
[14] Marques M A et al 2006 Time Dependent Density Functional Theory, Lecture Notes in Physics 706 (Berlin: Springer)
[15] Campbell E E B et al 2000 Phys. Rev. Lett. 84 2128
[16] Schlipper R et al 2001 Appl. Phys. A 72 255
[17] Pohl A et al 2004 J. Phys. B 37 3301
[18] Altoe P et al 2007 Theor. Chem. Acc. 118 219
[19] Dinh P M et al 2010 Phys. Rep. 485 43
[20] Calvayrac F et al 2000 Phys. Rep. 337 493
[21] Legrand C et al 2002 J. Phys. B 35 1115
[22] Nasluzov A et al 2001 J. Chem. Phys., 115 8157
[23] Reza Ahmadi G et al 1995 Chem. Phys. 199 33
[24] Dupl`aa F and Spiegelmann F 1996 J. Chem. Phys. 105 1492
[25] Bär M et al 2007 Eur. Phys. J. D 45 507
[26] Pohl A et al 2000 Phys. Rev. Lett. 84 5090
[27] Wopperer P et al 2010 Phys. Rev. A 82 063416