

Limits to the quantitative analysis of multiatom resonant photoemission: The case of $c(2\times 2)\text{O}/\text{Ni}(100)$

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We have investigated multiatom resonant photoemission (MARPE) on an adsorbate system $c(2\times 2)\text{O}/\text{Ni}(100)$. We observe a negligible MARPE enhancement ($2\pm 5\%$) of the O $1s$ photoelectron intensity when the excitation energy is tuned to the Ni L_3 absorption resonance. A strong nonlinearity in our photoelectron detection system is shown to produce artificial MARPE effects of up to 140% for uncorrected spectra. The possibly dominating influence of measurement artifacts in systems besides the studied adsorbates suggests a careful review of the intensity of the MARPE effect and its applicability in general.

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Resonant photoemission is a well-established technique which can, e.g., be used to enhance the signal from a particular element in a multicomponent system.¹ This enhancement is treated in terms of a core-excitation-decay process producing the same final state as the direct photoemission process, where the interference between the two channels leads to Fano-like resonance profiles.^{2,3} Resonant photoemission is treated as an intra-atomic effect; i.e., it occurs on a single atomic site. Recently it was observed that in heteronuclear ensembles, e.g., MnO, the core level photoemission cross section of one elemental species (O) is significantly enhanced (40%) for photon energies matching absorption edges of the other (Mn).⁴ This behavior, which was denoted multiatom resonant photoemission (MARPE), is thought to be mostly caused by the nearest neighbors to the emitter and is therefore proposed as an ideal tool to determine the local geometric structure.⁴ The effect has also been reported for other transition-metal compounds.⁴⁻⁷

The study of atomic adsorbates allows us to investigate a well-defined sample where, due to the low symmetry of the surface, self-absorption effects and the variation of the penetration depth can be minimized. We therefore studied the MARPE effect on $c(2\times 2)\text{O}/\text{Ni}(100)$ as a model system, looking at the O $1s$ intensity when scanning the photon energy through the L_3 (at 852 eV) edge of nickel (corresponding to the $2p_{3/2}\rightarrow 3d$ transitions). We observe a negligible MARPE enhancement ($2\pm 5\%$) in this system. However, in order to obtain this result, careful calibration of the photoelectron detection system at low count rates was necessary to allow for a quantitative analysis. The main obstacle was the strong photoelectron-flux-dependent nonlinearity of the Scienta SES200 detection system.^{8,9} This gives rise to an artificial enhancement of the O $1s$ photoemission cross section through the Ni L_3 absorption resonance, leading to an artificial MARPE effect when no correction to the nonlinearity is made. The influence of this measurement artifact in our system is presented together with conclusions that can be drawn from them.

The experiments were performed at beam line I511 (Ref. 10) at the MAX II storage ring, comprising a Scienta SES200 hemispherical photoelectron analyzer.¹¹ Photoelectrons emitted along the normal to the surface were detected, and the angle of incidence of light was larger than 20° . The photon flux was measured on a freshly evaporated goldmesh, allowing a flux normalization of the x-ray photoemission spectra (XPS). Different combinations of filters and various slit openings were used to change the incoming photon flux, always keeping the photon energy resolution below 0.2 eV. The Scienta detection system was operated in the “gray-scale” mode using 150 eV pass energy and a constant resolution of 0.2 eV. We cleaned the Ni(100) crystal by cycles of Ar-ion sputtering and annealing to 800 °C; low-energy electron diffraction (LEED) and XPS verified the surface crystallinity and the cleanliness. The $c(2\times 2)\text{O}$ overlayer on Ni(100) was prepared by dosing 10 L of O at 200 °C.

Figure 1 shows normalized O $1s$ photoelectron spectra measured below and at the Ni L_3 absorption resonance, collected at different incoming photon fluxes. The spectra are normalized to the photon flux, and a linear background — strongly increased for O $1s$ spectra measured on resonance due to the enhanced absorption at the Ni edge — has been subtracted. Surprisingly, we observe a pronounced variation in the enhancement of the O $1s$ photoemission intensity on resonance (shown in percent) as a function of incident photon flux, which is not expected from current MARPE theory.¹² In particular, the resonant enhancement for the low-photon-flux measurement (A) is negligible within the statistical accuracy, whereas at the high-photon-flux measurement (D) a strong enhancement on resonance of 140% is observed. In order to explain this behavior, either a nonlinear flux dependency of MARPE must be postulated or the observed photon flux dependence stems from a measurement artifact.

To determine the response of the Scienta SES200 as a function of photoelectron flux, we measured the Ni

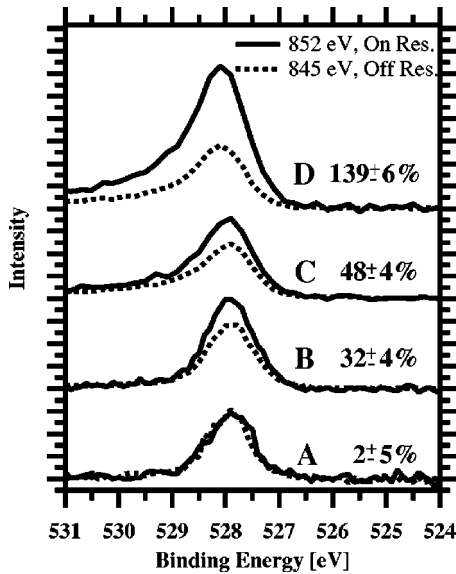


FIG. 1. O $1s$ photoelectron spectra measured off (dashed line) and on (solid line) the L_3 edge of nickel, collected at different incident photon fluxes. The spectra are normalized to the incoming photon fluxes measured with a goldmesh, and a constant background has been subtracted. The integrated O $1s$ enhancement is shown in percent, together with its statistical error. The four sets of measurements are denoted A–D, as referred to in the text.

$L_3M_{4,5}M_{4,5}$ Auger lines at $h\nu = 900$ eV as a function of the incident photon flux. The photocurrent I_0 measured on the gold grid reference monitor is a linear function of the photon flux, and the cross section of the Ni $L_3M_{4,5}M_{4,5}$ Auger decay is known to be independent of photon flux. In Fig. 2, the Ni $L_3M_{4,5}M_{4,5}$ Auger intensity, determined from the peak maximum, is plotted versus the photocurrent I_0 as a measure of

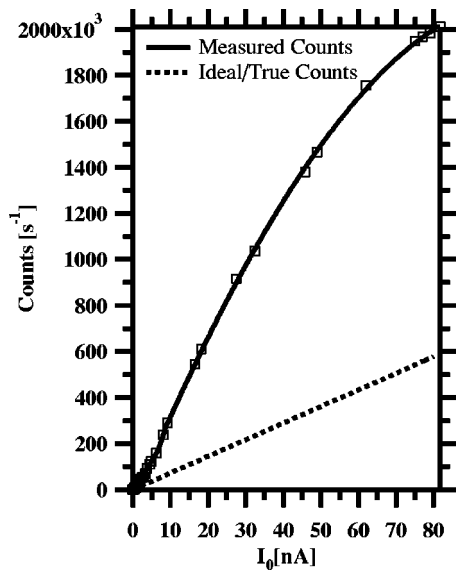


FIG. 2. Ni $L_3M_{4,5}M_{4,5}$ Auger intensity measured at $h\nu = 900$ eV plotted vs the photocurrent as a measure of incident photon flux. A polynomial fit (solid line) to the experimental points (open squares) is made, and a linear fit (dashed line) of the very low count rate region is shown (see Fig. 3 for a blowup of this region).

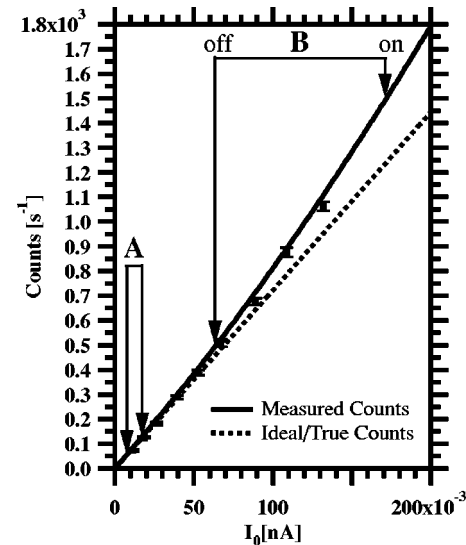


FIG. 3. Blowup of the detector curve (Fig. 2) in the region where measurements A and B in Fig. 1 were detected. Indicated with arrows are the count rates on the background for the on- and off-resonance spectra of the measurements A and B in Fig. 1. The experimental points of the detector curve are plotted with statistical error bars (68%).

incident photon flux. For low photon flux we observe a linear relationship between photon flux and detected Auger intensity passing through the origin, which turns into an increasing slope for higher photon flux. For even higher photon flux the slope becomes linear again but with a constant amplification factor of approximately 4 until detector saturation sets an upper limit to the detectable count rate.

The nonlinear detector response immediately explains the observed photon flux dependence for the resonant enhancement of the O $1s$ photoemission intensities shown in Fig. 1. To see this, in Fig. 3 we have zoomed the very low count rate part of the detector curve (Fig. 2) in which the measurements A and B in Fig. 1 were obtained. Indicated with arrows are the count rates at the background for the spectra measured on and off resonance. For the low-photon-flux measurement (A in Fig. 1), both the off- and on-resonance measurements are taken in the linear detection region, as can be seen in Fig. 3. We here observe a negligible MARPE enhancement of $2 \pm 5\%$. In contrast, the O $1s$ on-resonance spectrum showing a clear enhancement in Fig. 1 (B) has been measured in the nonlinear region (see arrows in Fig. 3), producing an artificial 32% increase of the O $1s$ intensity.

The problem arises because the O $1s$ photoemission is measured on a very large background in the on-resonance case compared to the off-resonance spectrum. Only at very low overall count rates can the on- and off-resonance spectra be both measured with the same linear detector response. In order to overcome this problem, different correction schemes for the detector nonlinearity can be conceptualized on the basis of our measurements in Fig. 2. However, as no analytical function of the detector response exists, curve fitting of the detector response yields additional uncertainty in a quantitative analysis. We have performed three different fits using polynomials of different order, from which we derived a

system-dependent variance of approximately 10% in the corrected O 1s intensity enhancement.

In conclusion, nonlinear detector response has been identified as a major complication in the performance of MARPE measurements on adsorbate systems. Our measurements of $c(2\times 2)\text{O}/\text{Ni}(100)$ give an upper limit to the interatomic O 1s–Ni L_3 resonance of less than $2\pm 5\%$, whereas uncorrected spectra produce artificial MARPE effects of up to 140%. These results suggests a careful review of the inten-

sity of the MARPE effect and its applicability, in general, to identify the possibly dominating influence of measurement artifacts due to nonlinear photoelectron detection systems. In the light of these findings, application to systems besides the investigated adsorbates has recently been reconsidered.¹³

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