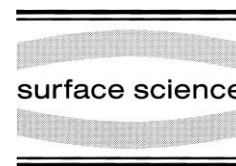




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# Symmetry properties of an electronic alkali excitation at a noble metal surface as investigated by two-photon photoemission

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## Abstract

We report a Two-photon Photoemission study of an excited state of cesium adsorbed on a Cu(111) single crystal surface at sub-monolayer cesium coverage. The dependence of cesium excitation on the laser polarization enables us to make statements about the symmetry of the intermediate as well as the initial state of the 2PPE process. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The unoccupied electronic structure of alkali-induced states at metal surfaces has been thoroughly investigated in the last decade, mainly by means of Inverse Photoemission (IPE) [1–4]. Within the low sub-monolayer coverage regime, however, only the change in energetic position as a function of coverage has been discussed so far. As has been pointed out by Thowallda et al. [5] and Fischer et al. [6], the higher energy resolution of 2PPE compared to IPE allows a much deeper insight into this kind of state. In addition, the possibility of changing the orientation (polarization) of the exciting laser-field with respect to

surface symmetries enables investigations on the orbital character of states involved in the 2PPE process. This paper uses the latter property of 2PPE to achieve additional insight into symmetry properties of a cesium derived unoccupied adsorbate state as observed on a Cu(111) single crystal surface.

## 2. Experimental

The photon source for the two step excitation process is a commercial Ti–sapphire system delivering 40 fs pulses in the wavelength region between 750 and 890 nm. After frequency doubling in a BBO crystal, the beam is divided into two separate paths by means of a beam-splitter. The vector potential  $A$  of the two laser fields is chosen to be s- and p-polarized, respectively (see Fig. 1). Experiments are performed either with just one

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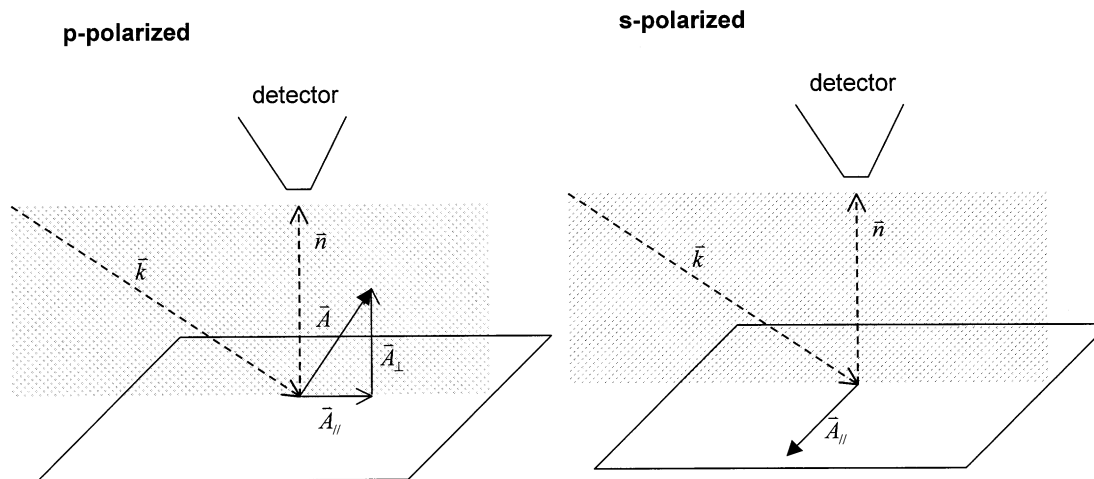


Fig. 1. Geometry for p- and s-polarized excitation within the 2PPE experiment. The shaded area displays the plain given by the incident beam  $\vec{k}$  and the surface normal  $\vec{n}$ . Only in the case of p-polarized light does the vector potential  $\vec{A}$  contain a component perpendicular to the surface plane of the sample.

beam (i.e. the second one blocked) or both beams focused collinearly on to the sample, which is mounted in a UHV chamber. In the latter case, a perfect temporal overlap is ensured by a computer-controlled optical delay line, which the temporal distance between the two pulses to be controlled within  $\pm 2$  fs (corresponding to  $\pm 0.6$   $\mu\text{m}$  optical pathway difference). The angle of incidence of the laser is  $45^\circ$  with respect to the surface normal. The photo-emitted electrons are detected within an angle of  $\pm 6^\circ$  with respect to the surface normal by a cylindrical sector energy analyzer with an energy resolution of 80 meV at 4 eV pass energy.

The copper single crystal was cleaned by repeated argon ion sputtering and annealing (1 kV, 800 K). Cesium was deposited from a commercial SAES getter source. The pressure during evaporation was maintained in the low  $10^{-10}$  mbar range. The coverage investigated is about 0.1 ML with respect to a closely packed Cs monolayer at the copper surface.

### 3. Results and discussion

In general, the alkali state investigated is considered to be derived from the atomic  $p_z$ -alkali valence state [1–4]. This deduction is based mainly on the

energy position with respect to the Fermi level as compared to theoretical calculations on alkali adsorption [7]. Other authors suggest that it is more likely that this state is derived from an s- $p_z$  hybridization of different atomic alkali states [8–10]. However, contributions to the measured feature, e.g. from the atomic  $p_x$  and  $p_y$  orbitals, cannot be excluded a priori. One approach obtaining more information on the respective orbital character of the excitation would be to investigate its symmetry properties with respect to the crystal surface, namely its excitation dependence on the polarization of the exciting photon field. Fig. 2a shows 2PPE spectra of Cs/Cu(111) at normal emission, recorded with p- and s-polarized laser light, respectively. The pronounced peak in the upper spectrum corresponds to the alkali state of interest induced by the adsorption of cesium [8]. This feature arises from the excitation of a normally unoccupied state as can be easily obtained by the dependence of the kinetic energy  $E_{\text{kin}}$  of the corresponding photoemitted electrons as a function of the photon energy  $h\nu$ . When varying the photon energy by  $\Delta h\nu$ , a shift of the peak by  $\Delta E_{\text{kin}} = \Delta h\nu$  is observed, as expected for a normally unoccupied state [11]. The data show that only p-polarized light supports the observation of the alkali peak in our spectrum. However, since two

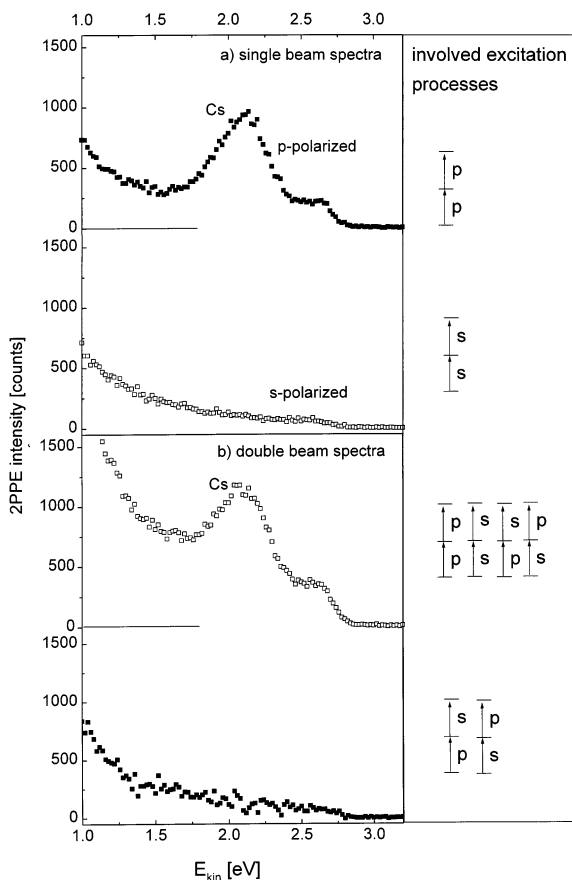


Fig. 2. Light-polarization dependence of the cesium feature as observed at a Cu(111) surface. Upper two spectra: comparison of spectra as taken with p-(■) and s-polarized (□) light, respectively. Lower two spectra: Simultaneous spectrum (□) and difference spectrum (■) as described in the text. The icons on the right summarize the possible excitation processes between initial, intermediate, and final states for the respective spectrum.

different excitation steps are involved, we have not been able to determine the step within the 2PPE process responsible for the lack of the feature in the s-polarized spectrum. An excitation process involving a different laser polarization acting on the different excitation steps might clarify the situation. By directing both beams (p- and s-polarized) simultaneously on to the sample, our spectrum contains, in addition to the single polarization terms, contributions of sp- and ps-types of excitation. A spectrum measured under this condition is shown in Fig. 2b (top). To separate the single-polarization contributions from this

spectrum, we subtracted the two spectra as given in Fig. 2a from the simultaneous spectrum, resulting in the difference spectrum shown in Fig. 2b (bottom). Note that the contribution of sp- and ps-types of excitation is clearly larger than the ss count rate, as shown in Fig. 2a. The lack of an alkali feature in this spectrum, however, suggests that neither an alkali excitation from the initial state nor an excitation from the alkali state into the final state can be induced by s-polarized light. This means, for the given geometry (see Fig. 1), that the field component perpendicular to the surface must be responsible for both excitation steps involving the excited alkali state.

For normal emission detection, the final state of a photoemission process has to be invariant under rotation about the surface normal to be observed by the analyzer [12]. As both excitation steps are induced by the field component perpendicular to the surface, we conclude that also the wave function of the alkali state as well as the initial state must be invariant under rotation about the surface normal. Therefore, the alkali state must be derived from atomic orbitals orientated in the  $z$ -direction (defined as the direction perpendicular to the surface), e.g. the  $6p_z$ ,  $6d_z$  orbitals, and/or the  $6s$  valence level. Contributions from states oriented parallel to the surface ( $6p_x$ ,  $6p_y$ ) must be excluded. Regarding the initial state of the 2PPE process, a bulk excitation from the  $A_1$  bulk band can fulfil this symmetry requirement. In addition, occupied states derived from  $z$ -oriented alkali orbitals as well as the  $6s$  alkali-orbital may also serve as the initial state.

#### 4. Conclusion

We investigated an excitation of cesium adsorbed at a Cu(111) surface as observed within a 2PPE spectrum on its dependence on the orientation of the electrical field vector of the exciting photon-field with respect to the surface normal. Spectra taken by directing simultaneously p- and s-polarized light on to the surface enabled us to make specific statements on the polarization dependence of each excitation step. This allows us to make conclusions on symmetry properties with respect to the initial state as well as the cesium

state involved within the 2PPE process. In the present case, both states have to be invariant under rotation about the surface normal. For the case of the cesium state, we can exclude contributions of the  $6p_x$  and  $6p_y$  valence level to the observed feature.

### Acknowledgements

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