Singlet to Triplet Conversion of Metastable He Atoms during Deexcitation at a Cs-Covered Surface

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Electron emission from a Cs monolayer on a Cu(110) surface by impact of metastable ^3S He* atoms is caused by Auger deexcitation as demonstrated by identification of Cs $5p$- and $6s$-derived levels in the electron energy distribution curves. Such curves recorded with ^1S He* are almost identical, and it turns out that only a small fraction of the singlet atoms undergo direct Auger deexcitation while the major part is converted into the triplet state from where Auger deexcitation occurs. A novel mechanism for this spin-flip process is proposed; it is accompanied by the creation of an electron-hole pair in the target for conservation of energy and total spin.

Recent experiments by Lee *et al.*[1] demonstrated that metastable singlet He*(2^1S) atoms impinging on a K-covered Ni(111) surface may undergo efficient transformation into the triplet (2^3S) state from where Auger deexcitation connected with electron emission occurs. This evidence was based on the observation that the electron energy distributions recorded with the singlet atoms contained certain spectral features which were also pertinent with the triplet atoms, although the excitation energies stored in these two species differ by 0.8 eV and should therefore give rise to a corresponding difference in the kinetic energy of the emitted electrons. In the present Letter we present conclusive evidence that such a singlet → triplet conversion process takes place, in fact, with high probability at a Cs monolayer adsorbed on a Cu(110) surface, and we propose a novel mechanism for this spin-flip process.

The experimental setup has been described in detail elsewhere.[2] Thermal ($\epsilon_{kin} \simeq 60$ meV) beams of metastable ^1S or ^3S He* atoms are created by electron bombardment of He atoms from a nozzle source. The free ^1S He* atom has an excitation energy $E^* = 20.6$ eV and an ionization potential of the electron in the $2s$ level of $I = 3.95$ eV. The corresonding data for the free ^3S He* atom are $E^* = 19.6$ eV and $I = 4.76$ eV.

Cs was evaporated from a SAES getters source onto a clean Cu(110) surface held at room temperature up to saturation. The resulting work function was 1.3 eV as determined by the threshold energy of electron emission in ultraviolet photoemission spectroscopy using He I radiation ($h\nu = 21.2$ eV). Multilayer formation takes place only at substantially lower substrate temperatures.[3]

UPS data from the thus prepared sample are reproduced in Fig. 1. The onset of electron emission at the highest kinetic energies marks the Fermi level E_F

which allows us to convert the kinetic energy scale into the scale of binding energies, as usual:

$$E_B = h\nu - \epsilon_{kin} - \phi. \tag{1}$$

Emission from the sp bands of the underlying Cu substrate extends from $E_B = 0$ to 2 eV, followed by the structures originating from the Cu d bands. The Cs $6s$-derived levels located just below E_F have a very small cross section for excitation by the applied photons[3] so that they are not discernible in this spectrum. (These features become visible, however, if photon energies < 10 eV are used[4] and are very prominent in the metastable deexcitation spectra shown below.) With decreasing ϵ_{kin} the background of secondary elec-
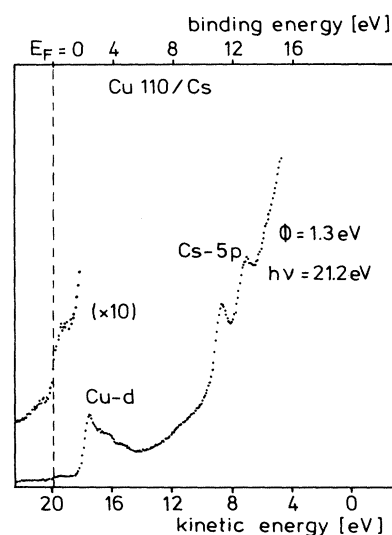

FIG. 1. UPS ($h\nu = 21.2$ eV) data from a monolayer of Cs adsorbed on a Cu(110) surface.

trons rises continuously on which, however, two peaks at $E_B = 11.2$ and 12.7 eV ($\epsilon_{kin} = 8.7$ and 7.2 eV) are superimposed which are due to ionization of the spin-orbit–split Cs $5p$ levels.[5]

Figure 2(a) displays the energy distribution of electrons emitted by deexcitation of ^3S He* atoms. Because of the low work function of the surface this spectrum is clearly due to the one-electron Auger deexcitation (AD) rather than the mechanism of two-electron resonance ionization plus Auger neutralization.[6] The absence of any spectral features due to deexcitation at Cu(110)[7] demonstrates that the underlying substrate is completely shielded by the overlayer. In analogy to Eq. (1) the relation between ϵ_{kin} and E_B now reads

$$\epsilon_{kin} = E_{eff}^* - E_B - \phi, \tag{2}$$

where the photon energy $h\nu$ is replaced by the effective excitation energy E_{eff}^* (which may differ from the value E^* of the free atom as a result of the He*-surface interaction by a few tenths of an electronvolt[8]).

The two peaks at low kinetic energies again clearly have to be attributed to the Cs $5p$ levels. The onset of electron emission at high kinetic energies occurs at $\epsilon_{kin} = 18.4$ eV, i.e., 1.5 eV lower than with UPS. This is due to the difference $h\nu - E^* = 21.2 - 19.8 = 1.4$ eV, so that this onset has again to be identified with the Fermi level. Because of the extreme surface sensitivity of metastable deexcitation spectroscopy, emission from the Cu substrate states is now completely suppressed, and instead an intense and about 1.5-eV-

FIG. 2. Metastable deexcitation spectra from a Cs monolayer on Cu(110). (a) ^3S He*; (b) ^1S He*.

wide peak appears just below E_F which has to be attributed to valence states derived from the Cs $6s$ levels. A similar peak is also observed with adsorbed K overlayers ($ = 4s$),[1] and its development as a function of K coverage will be described elsewhere.[9]

A spectrum recorded with ^1S He* atoms is reproduced in Fig. 2(b). The features due to the Cs $5p$ levels as well as the intense Cs $6s$-derived peak occur at exactly the same kinetic energies as in the ^3S He* spectrum, although the excitation energy is now higher by 0.8 eV and therefore—according to Eq. (2)—a corresponding shift of the spectral features on the kinetic energy scale would be expected. The only difference between Figs. 2(a) and 2(b) is that in the latter case an additional *weak* peak starts at precisely 0.8 eV higher kinetic energy: This is obviously the spectral feature arising from singlet He* deexcitation. This observation agrees qualitatively with the findings of Ref. 1 for K/Ni(111). This effect is, however, even more clearly demonstrated with the Cs layer since in this case the additional features from the $5p$ levels (which can directly be compared with the UPS data) are present in the spectra. Further experiments with multilayers of Cs (evaporation at 140 K substrate temperature), or with K and Li adsorbed on Cu(110) revealed quite similar results. The spectra always exhibit only very weak contributions which can be attributed to deexcitation of the singlet species. Since it was observed that this peak at high ϵ_{kin} grows upon adsorption of oxygen[9] it cannot even be ruled out that it is caused by the presence of spurious amounts of oxygen and might probably be completely absent with a perfectly oxygen-free surface. In any case the data demonstrate conclusively that a ^1S He* atom approaching an alkali-metal surface is very efficiently converted into a ^3S He* atom before it is deexcited. (It should be mentioned that no indication for such a transformation was found with molecular adsorbates[2,8] or with large–band-gap insulators[10] where the spectral structures obtained with ^1S He* and ^3S He* were found to be displaced on the ϵ_{kin} scale with respect to each other by the expected amount of 0.8 eV.)

Lee *et al.*[1] proposed the following mechanism for the singlet → triplet transformation process: The singly occupied $2s$ level of a ^1S He* atom approaching the surface is located above E_F, while that of the ^3S He* is 0.8 eV lower in energy and lies below E_F. As a consequence the $2s$ electron of ^1S He* tunnels into an empty state of the solid, and the intermediately formed He$^+$ is rapidly neutralized by transition of a target electron into the $2s$ level with opposite spin, thus forming a ^3S He* which subsequently undergoes Auger deexcitation. That the He$^+ \rightarrow {}^3S$ He* transformation does indeed very effectively take place at an alkali-metal–covered surface had been previously demonstrated by Hagstrum.[6]
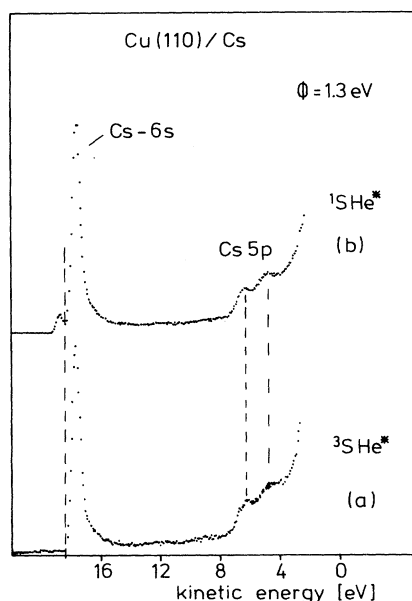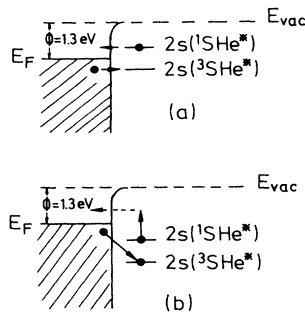
FIG. 3. Two possible mechanisms for the singlet → triplet conversion at a surface (for explanation see text).

FIG. 4. Variation of the ionization potential of ^1S and ^3S He* atoms with distance d from the surface according to image-force effects (Ref. 11).

While this mechanism [illustrated by Fig. 3(a)] appears to be rather plausible if the work function is not too low, it is difficult to reconcile it with the data for the sample with $\phi = 1.3$ eV: Since the ionization potential of a free ^1S He* atom is $I = 3.95$ eV, it would be necessary that the singly occupied 2s level of the ^1S He* is shifted upwards in energy by more than 2.6 eV in order to enable resonance ionization.

Since a metastable noble-gas atom approaching a surface is electronically similar to an alkali-metal atom an estimate of such level shifts may be obtained from the literature on alkali-metal adsorption. At larger distance the ionization potential is decreased essentially because of image-force effects, i.e., $I_{eff} = I - e^2/4d$.[11] Here I is the ionization potential of the free atom, and I_{eff} that in front of a surface at a distance d, where d is the separation between the jellium edge and the center of the impinging atom. Although this image formula will no longer be valid if the particle is very close to the surface[12] it should be applicable for qualitative discussion.

The variation of I_{eff} as a function of d for ^1S and ^3S He* is shown in Fig. 4. At a distance d^+, I_{eff} becomes equal to the work function ϕ, and resonance ionization of He* will take place if $d < d^+$. The dashed lines mark the work function for the present adlayer of Cs (1.3 eV) as well as for a multilayer (2.1 eV). For $\phi = 1.3$ eV we arrive at $d^+ = 3.0$ Å for ^1S He* and $d^+ = 2.7$ Å for ^3S He*. This means that resonance ionization (RI) of ^1S He* and Auger deexcitation (AD) of ^3S He* would have to take place almost exclusively within a range of 0.3 Å in order to reconcile the experimental findings with the proposed model. With the multilayer sample ($\phi = 2.1$ eV), on the other hand, d^+ is shifted to 3.6 and 3.0 Å, respectively.

Although it might well be that the electronic transitions take place while the particle passes a 0.3-Å distance, it is difficlut to find a physical reason for a displacement of this range if the work function changes. In particular, if for $\phi = 2.1$ eV RI + AD is completed at 3.0 Å, there is no reason why for the $\phi = 1.3$-eV sample AD of the singlet species (without previous
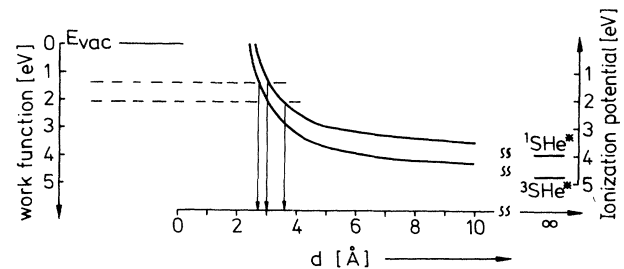
RI) should not also take place very efficiently before it enters the 2.7–3.0-Å region—which is not observed.

It appears therefore to be more likely that the spin-flip process in the ^1S He* atom approaching a surface with very low work function is of the type illustrated by Fig. 3(b). The 2s levels of both the ^1S and the ^3S He* are below E_F. The conduction electrons are scattered at the 2s electron whereby the spin of the latter is flipped. The energy gain due to the exchange interaction on the He* atom leads to creation of an electron-hole pair in the solid with a compensating change of spin. More specifically, this mechanism is equivalent to an AD process where the target electron undergoes a transition into the singly occupied 2s level whereby the already present 2s electron with opposite spin is shifted upwards in energy and tunnels into the solid. The competing AD process with the He 1s hole will take place with much lower probability because the 1s wave function is much more contracted and thus exhibits a much smaller overlap with the metal wave functions than does the 2s. Since this mechanism requires a nonvanishing density of empty states just above E_F at the surface, it becomes clear why it is not operating with molecular adsorbates or insulators as mentioned above. This proposed mechanism bears some similarity with the Kondo effect. On the other hand, it is related with the "superelastic" scattering of thermal electrons at singlet He*[13] and with the occurrence of a He⁻ resonance in He + e gas-phase scattering.[14]

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