

New Interpretation of Penning Spectra from Alkali-Metal Atoms Chemisorbed on Metal Surfaces

R. Hemmen and H. Conrad

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

(Received 1 May 1991)

Penning deexcitation spectra of alkali atoms adsorbed on metals show an intense peak at the Fermi level for coverages around the work-function minimum. This strong electron emission is assigned to the decay of a core-excited negative He^- ion created by resonance transition of a substrate electron into the affinity level of the metastable rare-gas atom. The formation of this species also easily provides an explanation for the observed He^* singlet-triplet conversion.

PACS numbers: 79.20.Nc, 73.20.-r, 79.80.+w

A revival of the discussion on the electronic structure of chemisorbed alkali-metal layers has been prompted by recent experimental [1,2] and theoretical [3] results concerning the occupation and energetic position of the alkali-metal-atom s state interacting with a metal surface. The previously accepted picture of almost complete ionization of the alkali-metal atom at low coverages followed by a depolarization-induced backdonation of charge with increasing coverage [4,5] has lately been called into question by theoretical [3] and experimental [2] investigations.

A direct observation of occupied alkali-metal s states in photoemission is only possible on metal substrates with a relatively flat sp band at the Fermi level. Previously, alkali-metal-induced features have been reported for photon energies below 5 eV [6]. Only recently, Horn *et al.* [1] have observed at 25-eV photon energy an s -induced feature for potassium adsorbed on Al(111). A more sensitive method for the investigation of the electronic structure of adsorbed alkali-metal atoms, even at very low coverages, is Penning ionization spectroscopy [7,8] (i.e., deexcitation of metastable rare-gas atoms) because of its extreme surface sensitivity and high cross section for s -level deexcitation. The method has already been used for studying potassium adsorption on Ni(111) [9] and Cu(110) [10], and Cs on W(110) [11]. These data were interpreted in terms of considerable s -level occupancy even at very low coverages. The interpretation of the results was, however, complicated by the existence of a very effective transformation process at the alkali-metal-covered surface, which converts the singlet He^* (1S_0) metastable into the triplet (3S_1) species [12]. Since these two metastable configurations have different excitation energies [$E^*(^1S_0)=20.6$ eV; $E^*(^3S_1)=19.8$ eV] the measured spectra consist of a superposition due to both excitations. The conversion rate changes with alkali-metal coverage, and thus the peak intensities cannot directly be related to the density of s states at E_F . In order to circumvent this problem, we present Penning deexcitation spectra of potassium on Pt(111) with a nearly pure He^* triplet beam ($^1S_0/^3S_1 < 0.1$). In the course of the experiments we were able to separate features genuinely induced by Penning transitions, and a narrow intense maximum located directly at the Fermi level which exhibits a resonancelike behavior. We demonstrate

that the appearance of this latter feature is correlated with the work function. In previous publications both of these features have been interpreted as due to a Penning transition involving an alkali-metal s electron. We argue that the sharp emission maximum at E_F originates from the creation of an excited negatively charged He in the configuration ($1s\ ^12s\ ^2S$) which decays into a ground-state He atom and an emitted electron on the time scale of autoionization processes. This intermediate core-excited He^- state also explains the singlet-triplet conversion process in a natural way. An analogous interpretation has been used to explain the existence of emission maxima in the electron spectra observed in collision experiments with medium-energy Ne^+ ions (~ 1 keV) at Mg, Al, and Si surfaces [13]. These structures have been assigned to the decay of the $\text{Ne}^{**}\ 2p\ ^4(^3P, ^1D)3s\ ^2$ autoionizing states created via an intermixing of the electronic states of Ne at the close distances to the surface accessed at these kinetic energies.

The experimental system has been described previously [14]. Penning deexcitation spectroscopy was performed with He^* atoms prepared in a supersonic nozzle beam by electron bombardment. More than 90% of the metastable atoms in the singlet configuration are produced under standard conditions. By setting the impact energy of the electrons to the maximum of the cross section for triplet excitation and quenching the 1S_0 with a He discharge lamp its amount is then reduced to less than 10% [15]. The Pt(111) surface was cleaned using cycles of ion bombardment and heating in oxygen. K was evaporated from a SAES getter source thoroughly outgassed. Any contamination of the alkali layer could easily be detected by Penning spectroscopy. Coverage calibration was achieved by measuring the change of the work function ($\Delta\Phi$ vs Θ) in HeI photoemission spectra. The resulting curve was in good agreement with published data and could be calibrated absolutely by means of the (2×2) LEED pattern at $\Theta=0.25$ [16]. The spectra presented in the figures are normalized to constant He^* flux. All spectra were measured at a 130-K sample temperature.

A sequence of metastable deexcitation spectra produced by impact of singlet He^* is shown in Fig. 1 for various potassium coverages. The smooth electron distribution of the clean Pt(111) surface is induced by an ion neutralization process. Because of the high work function

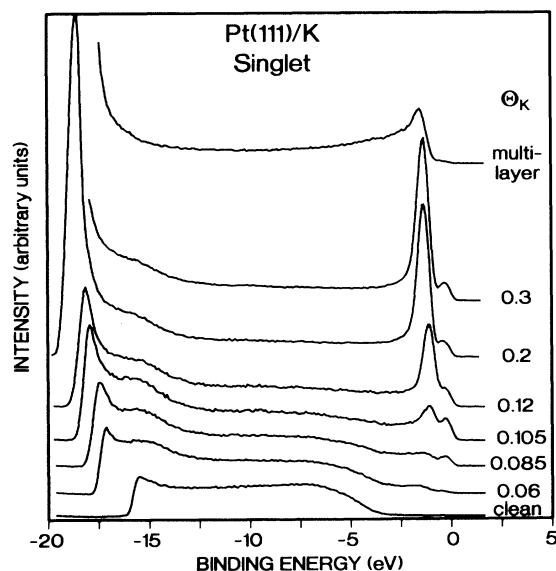


FIG. 1. Penning deexcitation spectra of K adsorbed on Pt(111).

of the clean surface the He^* atom loses its $2s$ electron by resonance ionization and the He^+ ion created at the surface is neutralized via an Auger process [17]. For potassium coverages up to $\Theta=0.1$ the appearance and growth of two structures at low binding energies is observed. These two structures are induced by the interaction between the K-covered surface and the 1S_0 and 3S_1 configurations of He^* at lower and higher binding energy, respectively [9,10]. The energetic separation of the peaks agrees well with the difference of excitation energy. The comparable intensity of the two peaks demonstrates the effect of the conversion process, by which a considerable amount of the primary singlet species is transformed into the triplet. Concomitant with the increase of the K-induced features, the broad emission characteristic of the bare region of the surface [10] is reduced but is clearly discernible up to $\Theta_K=0.1$.

Between $\Theta_K=0.1$ and $\Theta_K=0.2$ a sudden very strong increase of only the triplet-induced peak occurs while the singlet peak intensity remains essentially unchanged. Further increase in potassium coverage leaves the electron intensity distribution virtually unaltered. Only after potassium multilayer formation does the s -induced feature broaden and decrease in intensity due to the formation of bulklike s bands. The tail toward higher binding energy is connected with plasmon losses and Auger transitions characteristic of solid K as discussed elsewhere [18]. The observation of the steplike intensity enhancement at $\Theta_K=0.1$ indicates a change in the interaction of the He^* atom with the alkali layer. It is, however, not clear whether this modification reflects a change in the s density or merely an increase in the conversion rate. We have therefore measured the low-coverage region (up to

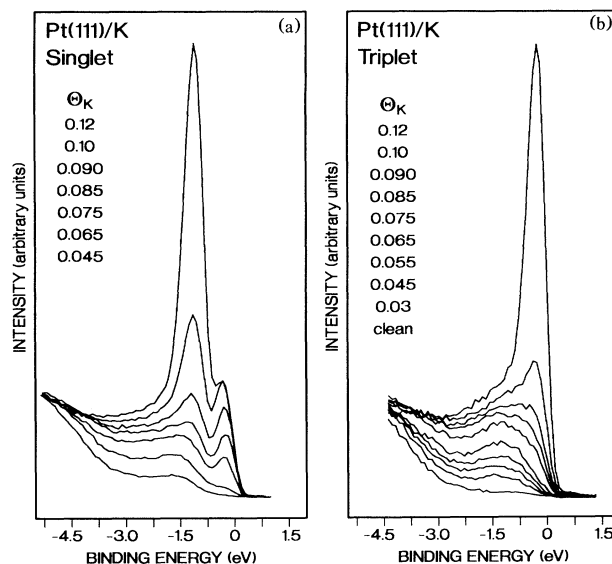


FIG. 2. Penning deexcitation spectra of K adsorbed on Pt(111) from (a) singlet and (b) triplet He^* atoms.

$\Theta_K=0.12$) in more detail for both singlet and triplet configurations. The resulting spectra are presented in Fig. 2. At this point a note on the energy scaling in the figures is appropriate. Penning electron distributions follow the same energy balance as UV spectra, with the photon energy being replaced by the effective excitation energy of the metastable atoms. The onset of electron emission at high kinetic energy is thus identified as the Fermi energy and assigned to the zero of the binding energy for each species separately.

The spectra of Fig. 2(b) (measured with 3S_1) show the development of the low-coverage potassium layer without the interference of the $^1S_0 \rightarrow ^3S_1$ conversion. The K $4s$ -derived emission is visible as a broad maximum at $E_B=1.4$ eV already at the lowest coverages and grows in intensity with increasing Θ_K . From Fig. 2(b) it is evident that the sharp and dramatic increase in the intensity of the triplet feature noted above is actually due to the emergence of an additional, very narrow peak at the Fermi level on top of the broad maximum still present at $\Theta_K=0.12$. The sudden appearance of this sharp peak (over only a very small coverage region) suggests an interpretation other than in terms of a mere charge redistribution in the $4s$ level of K. Moreover, we have observed the same effect with metastable Ne^* and Ar^* (both in the triplet configuration) and for chemisorbed Na, Rb, and Ba [18] also studied. It is concluded that the occurrence of this effect is a very general phenomenon independent of the specific target.

We assign the strong electron emission at E_F to the autoionizationlike decay of a core-excited negatively charged He^- ion in the configuration $1s^1 2s^2 2S$. This is created via a resonance ionization transition near very

low-work-function surfaces where the affinity level of He^* will be occupied by a valence electron from the metal surface. The process is schematically shown in Fig. 3(b) together with the well-known reverse process observed for high-work-function surfaces [Fig. 3(a)]. The energy diagrams of Figs. 3(a) and 3(b) differ only by the position of the Fermi level, i.e., the work function. The left-hand parts indicate the spectral density of the s orbital of the alkali-metal atom on the surface. The right-hand sides show the energy positions of the occupied $2s$ and the affinity level of triplet He^* as a function of distance from the surface. When the He^* approaches the substrate, the image potential interaction will shift the occupied level up and the affinity level down [19]. For the higher-work-function surface [Fig. 3(a)], the filled $2s$ level will cross the Fermi level at some distance and the $2s$ electron will tunnel into the substrate. This well-established resonance ionization leading to a positively charged He^+ ion has commonly been observed at clean surfaces even in cases where asymptotically the excited s electron is below E_F , like Cu(110) with $\text{He}^* \ ^3S_1$ [10]. The resonance process is so effective that virtually no Penning transitions can be detected.

For the low-work-function surface the reverse process occurs. The affinity level shifts through the Fermi level and will be filled by a substrate electron via a resonance transition, thereby creating a negatively charged He^- in a core-excited doublet configuration. Such a state has already been detected and assigned in electron-scattering experiments of gas-phase He [20]. The state is bound by 0.5 (1.3) eV relative to the excitation threshold of $\text{He}^* \ ^3S_1$ (1S_0) [20]. These values correspond to the asymptotic level positions relative to the vacuum level in the one-electron picture being used in Figs. 3 and 4. The core-excited He^- decays very fast (on the time scale of au-

toionization processes) into ground-state He under the emission of an electron at the same kinetic energy where in the Penning transition the electrons from the Fermi level are emitted. Since resonance transitions are very efficient, the additional decay channel shows up in the electron spectra as an intense peak at E_F . Its sudden appearance with alkali-metal coverage is correlated with the work-function decrease below a value where the electron transition into the affinity level of He^* becomes possible. At higher coverages, above the work-function minimum, the intensity of the maximum should decrease, in agreement with the experimental findings shown in Fig. 1.

The creation of the negative He^- ion also gives a natural explanation for the observed singlet-triplet conversion process of He^* [12]. Because of the spin-spin interaction in He^* , the occupied $2s$ levels and the affinity levels are different for the triplet and the singlet species in a one-electron picture. In Fig. 4 the asymptotic values are shown together with their variation with the distance to the surface. The resulting curves are identical in shape because the image potential interaction does not differentiate between spin orientations. Starting initially with a He^* singlet it is evident from Fig. 4 that the crossing of the Fermi and the affinity level of $^1S \text{He}^*$ occurs at a larger distance from the surface than for $^3S \text{He}^*$. At that distance, however, two decay channels of the negative He^- ion exist. One leads to the strong electron emission at the Fermi level described above and is to be identified with the narrow peak at the highest kinetic energies in Figs. 1 and 2(a) according to the higher excitation energy of the singlet species. The alternative path-

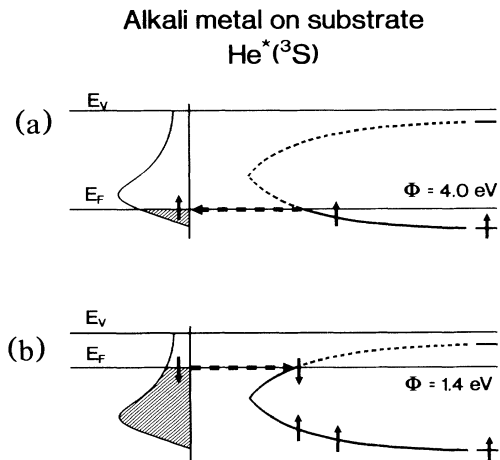


FIG. 3. Energy-level diagrams for surfaces with different work functions as a function of the surface- He^* distance. Broken lines correspond to unoccupied levels. The arrows indicate the spin orientation of the electrons. See text for details.

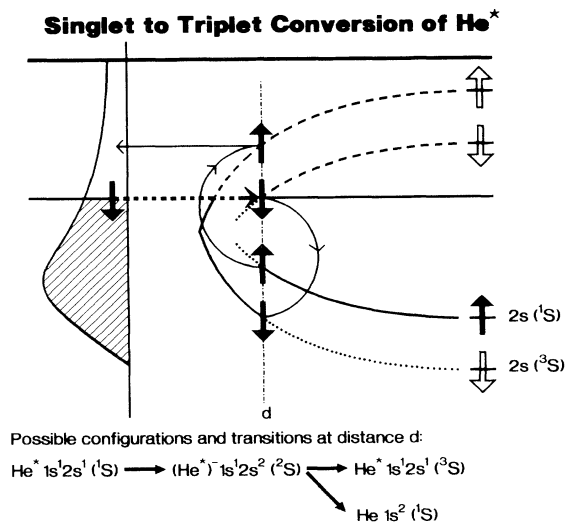


FIG. 4. Energy-level diagram for the possible transitions of singlet He^* in front of a low-work-function surface. The arrows indicate the spin orientation of the electrons. Open arrows indicate the possible spin orientation of unoccupied levels. See text for details.

way is indicated in Fig. 4 by the thin arrowed lines. The spin orientation of the additional electron corresponds to the triplet configuration and the negative He^- ion can decay into the triplet He^* under emission of the electron with the reverse spin into the substrate. In a recent theoretical investigation the $^1S_0 \rightarrow ^3S_1$ conversion was explained by virtual processes through the He ionic states [21], while in our interpretation a real state is created. The triplet He^* thus created can further approach the surface and decay as described above. As a result, the typical double-peak intensity distribution in the electron spectra in Figs. 1 and 2(a) is observed, with the singlet-induced feature building up at lower coverages, i.e., higher work function, than the triplet maximum.

Obviously, Penning ionization occurs in addition to the processes discussed above and gives rise to the broad features near E_F present in all spectra. It is these small spectral features which are related to the alkali-metal s states. Previous work [7-12,17] neglecting the possibility of additional decay channels had assigned the whole structures at E_F to s -level emission.

In summary, we have identified the formation of a negatively charged core-excited He^- ion at low-work-function surfaces created by resonance transitions of substrate electrons into metastable rare-gas atoms. This observation requires a reinterpretation of two experimental observations in a coherent scheme, i.e., the presence of a dominating emission peak in the Penning spectra at low work function and the process of the singlet-triplet conversion.

[1] K. Horn, A. Hohlfield, J. Somers, T. Lindner, P. Hollins,

- and A. M. Bradshaw, Phys. Rev. Lett. **61**, 2488 (1988).
 [2] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **64**, 571 (1990).
 [3] H. Ishida, Phys. Rev. B **40**, 1341 (1989).
 [4] R. W. Gurney, Phys. Rev. **47**, 479 (1935).
 [5] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 212 (1976).
 [6] S. A. Lindgren and L. Wallden, Solid State Commun. **28**, 283 (1978); **34**, 671 (1980).
 [7] F. Boszo, J. T. Yates, J. Arias, H. Metiu, and R. M. Martin, J. Chem. Phys. **78**, 4256 (1983).
 [8] H. Conrad, G. Ertl, J. Küppers, S. W. Wang, K. Gerard, and H. Haberland, Phys. Rev. Lett. **42**, 1082 (1979).
 [9] J. Lee, C. Hanrahan, J. Arias, F. Bozso, R. M. Martin, and H. Metiu, Phys. Rev. Lett. **54**, 1440 (1985).
 [10] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. Lett. **55**, 1231 (1985).
 [11] W. Maus-Friedrichs, M. Wehrhahn, S. Dieckhoff, and V. Kempter, Surf. Sci. **237**, 257 (1990).
 [12] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. Lett. **55**, 611 (1985).
 [13] G. Zampieri, F. Meier, and R. Baragiola, Phys. Rev. A **29**, 116 (1984).
 [14] K. Besenthal, G. Chiarello, M. E. Kordesch, and H. Conrad, Surf. Sci. **178**, 667 (1986).
 [15] H. Morgner and A. Niehaus, J. Phys. B **12**, 1805 (1979).
 [16] H. P. Bonzel, Surf. Sci. Rep. **8**, 43 (1987), and references therein.
 [17] H. Conrad, G. Ertl, J. Küppers, W. Sesselmann, and H. Haberland, Surf. Sci. **100**, L461 (1980).
 [18] R. Hemmen, T. Nern, and H. Conrad (to be published).
 [19] See, for example, J. W. Gadzuk, and H. Metiu, Phys. Rev. B **22**, 2602 (1980).
 [20] G. J. Schulz, Rev. Mod. Phys. **45**, 378 (1973).
 [21] K. Makoshi, A. Yoshimori, and B. I. Lundqvist, Surf. Sci. **230**, 350 (1990).