Singlet-to-triplet conversion of metastable He atoms at alkali-metal overlayers

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Energy distributions of electrons emitted from alkali-metal surfaces by impact of metastable He atoms reveal that there is a high probability for transformation of singlet atoms (excitation energy $E^* = 20.6$ eV) into triplet atoms ($E^* = 19.8$ eV) prior to deexcitation into the ground state. The conversion probability (as expressed by the ratio R of the intensities of valence-band emission due to triplet and singlet He* deexcitation, respectively) increases with increasing alkali-metal coverage on a Ru(0001) substrate, and in turn decreases with increasing oxygen exposure at a fixed alkali coverage. These findings indicate that R is a qualitative measure for the degree of "metallization" of the adlayer. R also increases with temperature due to broadening of the nearest-neighbor distribution whereby, on the average, a larger part of the adlayer becomes metalliclike. For Cs overlayers exhibiting work functions <2 eV the mechanism of deexcitation changes and may proceed via He^{*-} ($1s^1 2s^2$) formation as reflected by the R data as well as by the widths of the electron spectra.

I. INTRODUCTION

Metastable He atoms in the singlet state ($[1s2s\,^1S_0]$, excitation energy $E^* = 20.6$ eV) undergo a very efficient transformation into the lower-lying triplet state ($[1s2s\,^3S_1]$, $E^* = 19.8$ eV) upon scattering with free thermal electrons.[1] Likewise, this process was found to occur with high probability prior to deexcitation into the ground state if singlet He* collide with alkali-metal surfaces.[2-5] Evidence in the latter cases stems from the recorded energy distributions of emitted electrons resulting from Auger deexcitation in which a valence electron from the surface fills the hole of the ground state of the He* and the electron in the 2s level is ejected.[6] These metastable deexcitation spectra (MDS) then typically exhibit a small peak at highest kinetic energies originating from interaction of $^1S_0$ species with the surface valence levels, followed by a considerably more intense peak at somewhat lower kinetic energies due to deexcitation of $^3S_1$ species which had previously been created in the collision process of the incident $^1S_0$ He* atoms (see Fig. 1). Two mechanism have been proposed for this singlet-to-triplet conversion process.

Mechanism A:[3] A valence electron from the surface fills the hole in the 2s level of the incident He* whereby in an Auger process the already present 2s electron with opposite spin is lifted to an energy above the Fermi level E_F from where it tunnels into the solid. The spin-flip process competes with deexcitation into the ground state where an electron from the target fills the hole in the 1s level and the energy is transferred in an Auger process to the 2s electron which eventually is ejected. This mechanism obviously requires a high enough density of states above E_F and a work function Φ which is low enough to prevent resonance ionization into He^+ of the incident He* when the energy of its 2s electron crosses the Fermi level. These conditions are fulfilled with alkali-metal surfaces, but, e.g., not with transition-metal surfaces where deexcitation via Auger neutralization causes a complete

change of the character of the measured electron distributions.[7] Several theoretical treatments[8-10] reported in the literature are consistent with mechanism A and suggest that it might occur at fairly large distance from the surface.

Mechanism B:[5,11] If the work function of the sample is low enough the affinity level of the incident He* (being
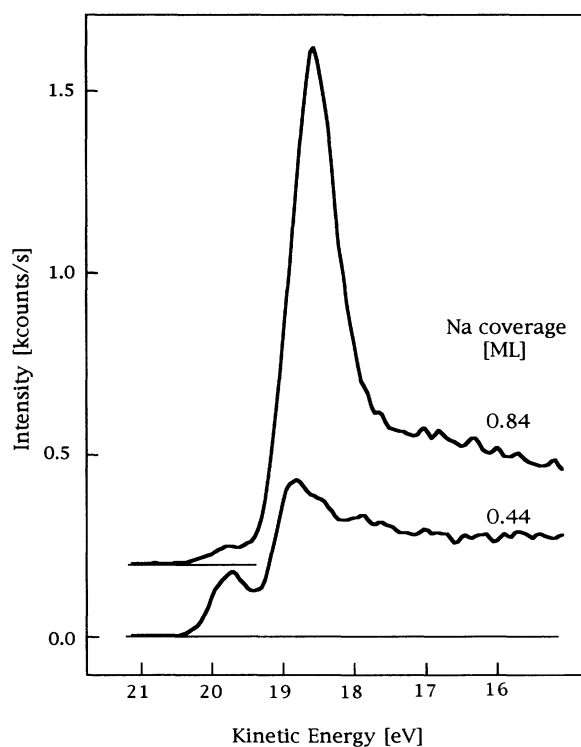

FIG. 1. Valence region of $He^*(2^1S_0)$ deexcitation spectra taken at Na coverages of 0.44 and 0.84 ML. On a macroscopic scale both situations are characterized by the same value of the work function (2.5 eV) but the local electronic structures as probed by MDS are quite different.

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continuously lowered in energy by image force field effects) eventually crosses the Fermi level so that resonance ionization with formation of a negative ion He*$^-$ ($1s^1 2s^2$) may take place. This species may undergo rapid autoionization leaving back the triplet He* species. This 2^3S species may be resonantly ionized and autoionized again. The difference to mechanism A consists in a resonance ionization rather than an Auger-like autoionization of the He atom process involving substrate electrons in the deexcitation steps. Mechanism B will necessarily be restricted to samples with very low function ($\Phi \le 2$ eV) and is supported by the results of recent theoretical work.[12,13]

At this point it has to be noted that with both mechanisms efficient singlet to triplet conversion involve a high densities of occupied as well as unoccupied states in the range of Fermi level. The present work reports on a series of systematic experiments on this effect carried out with alkali-metal overlayers at varying coverages as well as under the influence of the subsequent exposure to oxygen, and the results will be shown to provide additional information about the electronic properties of the surface probed.

II. EXPERIMENTAL

The experimental arrangement is essentially the same as that used in a series of previous studies and as described in detail elsewhere.[14] In brief, it consists of an atomic beam system in which thermal metastable He* atoms (typically $\sim 95\%$ in the singlet state) are created by electron bombardment of He atoms emitted from a nozzle source and subsequently impinge onto the sample surface. The main UHV system contains standard facilities for surface cleaning and characterization as well as a hemispherical electron energy analyzer for recording the energy distributions of the electrons emitted. A He discharge lamp enabled the simultaneous recording of ultraviolet photoelectron spectra (UPS) with $h\nu = 21.2$ eV. The total width of these spectra offers a convenient means for determination of the work function Φ. Alkali-metal overlayers were evaporated onto a clean Ru(0001) substrate from commercial SAES getter sources; their characterization again has been described elsewhere.[15]

III. RESULTS AND DISCUSSION

Figure 1 shows energy distributions (=MDS data) for electrons emitted by impact of an almost pure ^1S He* beam from the Ru(0001) sample covered with different concentrations of Na. The latter is referred to the monolayer (ML) capacity which corresponds to an absolute coverage (i.e., ratio of adatoms over substrate atoms) of $\theta = 0.58$ or a density of 9×10^4 Na atoms/cm^2. Both spectra exhibit different ratios of the heights of the two peaks originating from the valence levels probed by deexcitation of ^1S and ^3S He* species, respectively. For the sake of qualitative arguments presented in the following, it suffices to analyze these data in terms of the ratio of heights of the triplet over the singlet peak which is considered as a measure for peak heights the efficiency of the singlet $\rightarrow$ triplet conversion process. The change of this

quantity R with Na coverage is reproduced in Fig. 2 together with the variation of the work function Φ. The latter data exhibit the typical behavior of alkali-metal overlayers, namely, a strong decrease followed by a minimum and an increase to the value of the bulk metal. Simply speaking, this effect is attributed to the continuous transition of the "ionic" state of the adsorbate with strong dipole-dipole repulsions into the "metallic" state with pronounced lateral overlap of the valence orbitals leading to electronic states highly delocalized in the directions parallel to the surface. This "metallization" is considered to begin roughly around the work-function minimum and to be completed at about two monolayers where the electronic properties of the bulk are reached.[16] As the data of Fig. 2 show, the singlet-triplet conversion efficiency R starts to increase just in the range of the $\Delta\Phi$ minimum and reaches a saturation value around 0.8 ML where the overlayer has to be considered to be essentially metallic in nature. It is evident that this effect is not simply a consequence of the varying work function since, e.g., the data of Fig. 1 were recorded for identical Φ values, but are quite different in shape. It is rather suggested that R reflects the nature of the electronic structure of the alkali-metal overlayer, in that a high value for R indicates metallic, i.e., delocalized properties.

For the data with Na/Ru(0001) the work function never drops below ~ 2.5 eV, a value which is very likely to rule out mechanism B. With mechanism A, to a first ap-
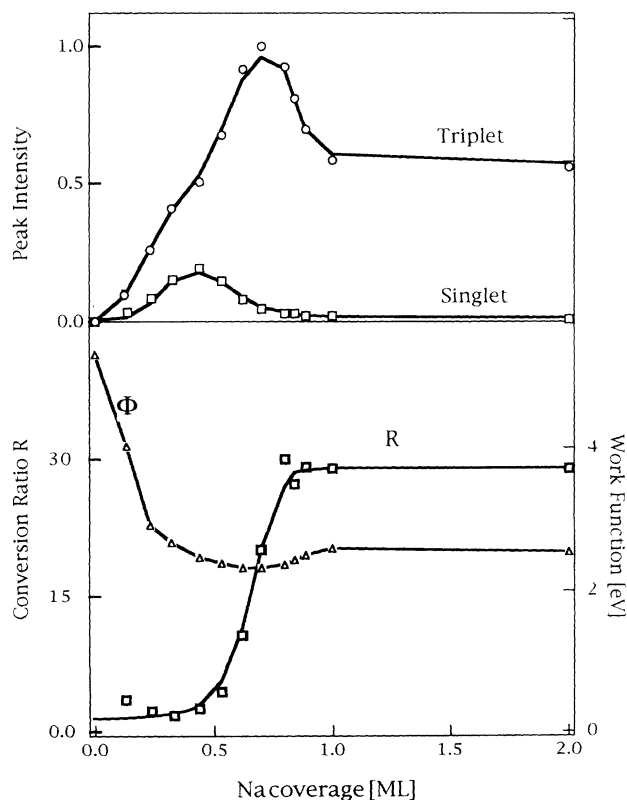

FIG. 2. Intensities of the singlet and triplet peaks as probed by He*(2^1S_0) deexcitation spectroscopy vs Na coverage (upper panel). The lower panel shows the resulting conversion ratio R in comparison and the work function Φ vs the Na coverage.

proximation R will be governed by the competition between filling either the He $1s$ (=deexcitation into the ground state) or the $2s$ hole state (eventually leading to singlet-to-triplet conversion) by a valence electron from the target. Since the wave function of the $2s$ state is spatially much more extended than that of the $1s$ state, $S \rightarrow T$ conversion might be expected to be always very efficient which, however, is not the case. R is not only small for low alkali-metal coverages, but deexcitation at *free* alkali metal atoms was found to exhibit no detectable singlet-to-triplet conversion at all.[17] It is clear that, in addition, the final state of the $2s$ electron also has to be taken into account. For deexcitation into the ground state this will be a free electron which is ejected and detected, while in the case of operation of singlet-to-triplet conversion it will be an empty level above E_F "leaking out" into the vacuum. Free alkali atoms exhibit no levels at the required energy and hence no $S \rightarrow T$ conversion is observed, while for alkali-metal surfaces it is the density of unoccupied states above E_F which will determine the efficiency for conversion. (With scattering by free thermal electrons there exists, of course, a continuum of levels and hence $S \rightarrow T$ conversion is very efficient.[13]) Transition from the "ionic" into the "metallic" state upon increasing the coverage not only alters the density of occupied states and the spatial charge distribution[18] but also the properties of the unoccupied levels as, for example, probed experimentally by inverse photoemission.[19] It becomes hence plausible why this transition is accompanied by a variation of the efficiency for He* singlet-to-triplet transformation.

The data for Li overlayers reproduced in Fig. 3 exhibit the same trend for the variation of R with coverage in that, again, it starts to increase near 50% of the saturation of the first monolayer in the range of the work-function minimum and then levels off beyond about 1 ML. This figure contains, in addition, the variation with coverage of the difference between the effective deexcitation energies E_{eff}^* of the He* ^1S and ^3S species as derived from the cutoffs at high kinetic energies in the MDS spectra viz. $\varepsilon_{kin,max} = E_{eff}^* - \Phi$.[4] The values of E^* for the isolated He* atoms (20.6 eV for the singlet and 19.8 eV for the triplet species) will in general be modified due to the shape of the interaction potential with the target and the range of distances over which deexcitation preferentially occurs.[20] In a previous study with a series of transition metal surfaces covered by molecular adsorbates it was found that E_{eff}^* may be substantially altered and that also the difference $\Delta E_{eff}^* = E_{eff}^*(^1S) - E_{eff}^*(^3S)$ may deviate from the free particle value of 0.8 eV.[21]

In the present case ΔE_{eff}^* was found to be close to 0.8 eV for low coverages, but to increase with coverage to 1.6, 1.5, and 1.2 eV for Li, Na, and Cs, respectively. As can be seen from Fig. 3, this is essentially due to the reduction of E_{eff}^* for the triplet species, while that for the singlet species remains practically unaltered. These findings are rationalized as follows: As long as the adsorbate is "ionic" it will essentially exert an electrostatic interaction on the impinging He* atoms which will not differ too much for the singlet and triplet species, and hence ΔE_{eff}^* is close to the free particle value. In the "me-

tallic" state, on the other hand, the valence electron will be localized more at the alkali-metal atom and its interaction with an impinging He* atom will contain covalent contributions. Theoretical calculations of the interaction potential between a single Na atom and either a ^1S or ^3S He* atom revealed in the latter case a considerably deeper (≈ 0.7 eV) minimum[20] which in effect renders the observed increase of ΔE_{eff}^* for the overlayer plausible. As can be seen from Fig. 3, this increase occurs again in the coverage range around 0.5 ML, which is considered as additional support for the suggested interpretation.

Figure 4 shows the variation of R and of the work function Φ with coverage for Cs overlayers. Now the findings are quite different: Superimposed on the gradual increase of R between ~ 0.4 and 1 ML this quantity exhibits a pronounced maximum at about 0.5 ML. This is just in the range of the work-function minimum which with this system drops to values even slightly below 2 eV. The maximum of R is essentially due to a lowering of the intensity of the singlet peak in this range, while the triplet peak remains practically constant. Such an effect would be compatible with a conversion process of the incident ^1S He* species at a somewhat larger distance from the surface where deexcitation into the ground state is less
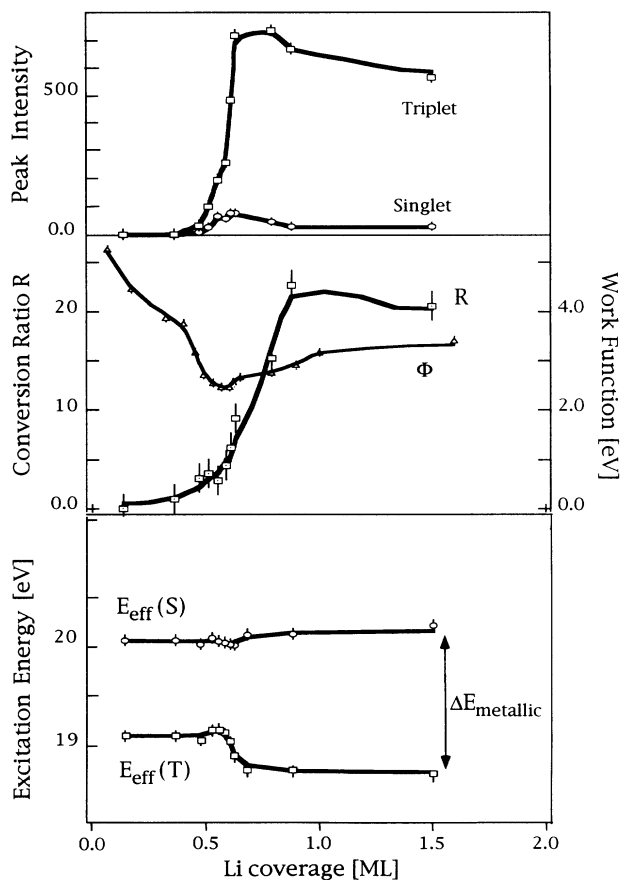

FIG. 3. In analogy to Fig. 2, the singlet and triplet intensities, conversion ratio R, and the corresponding work function as functions of Li coverage (two upper panels). The lower panel shows the changes of the energy separation between singlet and triplet peaks vs coverage.
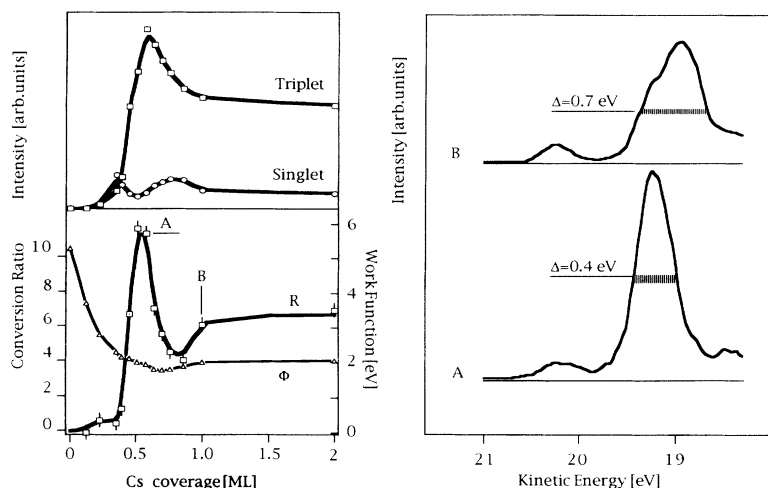
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FIG. 4. Variation of the singlet and triplet intensities, as well as of the conversion ratio R and the work function with Cs coverage (left panel). The MDS data corresponding to points A and B in the R vs Cs-coverage curve are reproduced in the right panel.

efficient. The results strongly suggest that under these conditions mechanism B is dominating: The affinity level of the impinging He* atom crosses the Fermi level if the work function is small enough (≤ 2.0 eV) at a distance longer than required for efficient operation of mechanism A, and resonance ionization into a short-lived He*$^-$ ion may take place which subsequently decays into ^3S He* plus an electron into the substrate.[5] The latter process requires again overlap with the wave functions of empty levels above E_F and will hence also be affected by the electronic structure of the substrate. This is possibly the reason why R decays in the transition region from the "ionic" to the "metallic" state even before the work function has reached its minimum value. In other words, it is not only the absolute value of Φ which determines the efficiency of mechanism B.

If mechanism B is operating, the measured electron energy distribution resulting from autoionization of the atomic He*$^-$ species should be considerably narrower than with mechanism A which reflects the valence band of the alkali-metal surface. Inspection of the right panel of Fig. 4 shows that this is indeed the case: In the range of high R values (point A) the full width at half maximum of the triplet peak amounts only to 0.4 eV (this value is governed by the instrumental resolution) while it is considerably larger outside (point B), which presumably represents a superposition of contributions from both mechanisms.

The data presented so far were all recorded at 300 K. Interestingly, there is an additional effect of the temperature on R. Figure 5 shows a typical set of MDS data for 0.3-ML Cs on Ru(0001) recorded at different sample temperatures. The work function is about 2.5 eV under these conditions so that singlet-to-triplet conversion will be dominated by mechanism A. Over a temperature range of 260 K the singlet-triplet conversion probability increases by a factor of 2. This effect is completely reversible. Low-energy-electron-diffraction (LEED) observations reveal the transformation of a liquidlike configuration characterized by a ring-type diffraction pattern, signaling the existence of short-range order, into a pattern with diffuse background as characteristic for complete disorder of the adlayer. That means that a rela-

tively narrow distribution of nearest-neighbor separations becomes broader upon increasing the temperature. In particular, there will be an increasing fraction of fluctuating ensembles with atomic distances already closer to the "metallic" state which may qualitatively account for the observed increase of R.

Since the efficiency for singlet-to-triplet conversion of metastable He atoms at alkali-metal overlayers was shown to be sensitively influenced by the local electronic structure of the adsorbate it seems to be obvious that there exists also a pronounced influence of coadsorbed species. A series of experiments in which "metallic" overlayers were exposed to O_2, NO, or H_2 revealed a continuous decrease of R, reflecting progressing "demetallization" due to formation of mixed adlayers in which neighboring alkali-metal atoms were partly screened from each other. As an example, Fig. 6 shows the results of an experiment in which a Cs monolayer was exposed to increasing doses of O_2. At first R decreases continuously with oxygen exposure, but again exhibits a pronounced maximum in the region of the work-function minimum where Φ drops below 2 eV and presumably again mecha-
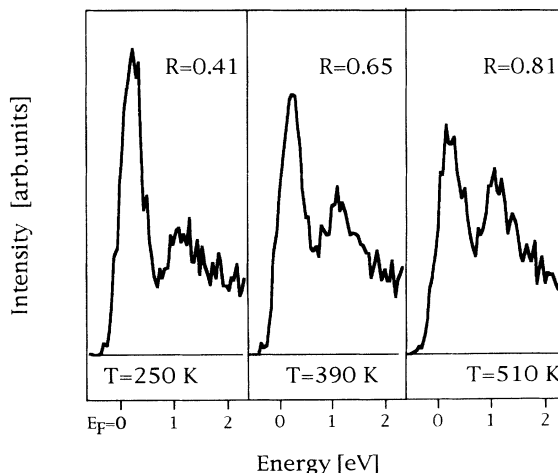

FIG. 5. MDS data from a surface covered by 0.3-ML Cs recorded at different temperatures.
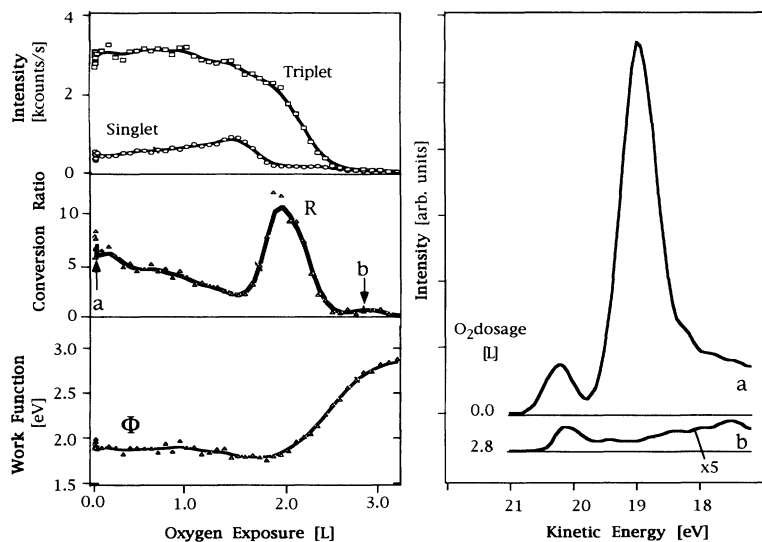
FIG. 6. Changes of the conversion ratio R induced by progressing oxidation of a Cs monolayer at room temperature. The local maximum R around the oxygen exposure of 2 L stems from the rather abrupt decrease of the singlet peak intensity accompanied by a much weaker decrease of the triplet intensity. The panel at the right presents two valence spectra taken at the beginning of oxidation (a) and at the final oxidation stages (b).

nism B dominates. Beyond 1.5-L O_2 the total intensity of valence-band emission from the Cs atoms decays rapidly due to complete oxidation.

However, as can be seen from the right panel of Fig. 6, at this stage still an appreciable singlet peak is found, while triplet emission is practically completely suppressed. This suggests the presence of individual not yet completely ionized Cs atoms which are embedded into oxidic surroundings and which can no longer allow singlet-to-triplet conversion, similar to free alkali-metal atoms.[17] This interpretation is supported by the results of a recent study of the vibrational properties of this system by means of high-resolution electron-energy-loss spectroscopy.[22] The oxidized Cs monolayer exhibits a signal at about 8 meV due to vibration of individual Cs atoms against the Ru substrate, which is completely absent due to screening by the delocalized valence electrons for the oxygen-free Cs overlayer. The metallic character is then reflected by the appearance of a plasmon loss.

Parallel to the continuous decrease of R with progressing oxidation (without taking into consideration the maximum of this context) of the adlayer there is also a continuous decrease of the difference of the effective excitation energies, ΔE^{*}_{eff}, from 1.2 to 0.7 eV. These data again reflect a gradual transition from the "metallic" to the "ionic" state of the adsorbed alkali-metal atoms, quite in analogy to the findings with varying coverage of pure alkali-metal adlayers as mentioned above.

IV. CONCLUSIONS

Upon interaction with alkali-metal surfaces, metastable $1s2s$ He* atoms in their singlet state may undergo transformation into the lower-lying triplet state prior to deex-

citation into the ground state. The latter process leads to electron emission and the resulting spectra (MDS data) reflect the efficiency of this transformation through the intensity ratio R of the valence-band emission arising from triplet and singlet deexcitation, respectively. Experiments with Li, Na, and Cs atoms chemisorbed on a Ru(0001) surface revealed a pronounced increase of R at intermediate coverages in the range of the work-function minimum which is attributed to the transition from the "ionic" to the "metallic" state of the adsorbate with increasing coverage. In addition, the difference of the effective deexcitation energy of singlet and triplet He* increases from 0.8 eV (=the value for the free metastable species) by more than 0.5 eV in this transition range. With Cs overlayers a marked maximum of R is observed over a narrow range of coverages where the work function drops below ~2 eV. This is attributed to the operation of a alternative mechanism proceeding through intermediate formation of a negative-ion resonance as recently proposed by Hemmen and Conrad.[5]

The efficiency for singlet-to-triplet conversion is also affected by coadsorption of other particles such as oxygen which influence the electronic coupling between neighboring alkali-metal atoms, as well as by increasing the temperature by which the lateral distribution and hence also the average electronic coupling is altered.

In summary, the parameter R may be regarded as a sensitive probe of the local and dynamic electronic character of alkali-metal overlayers.

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