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Mechanism of metastable $^1S_0$ He* deexcitation on the Pd(111) surface with adsorbed NO

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A mechanism of metastable $^1S_0$ He* deexcitation is proposed for a NO-covered Pd(111) surface in competition with the resonance ionization of the excited noble-gas atom, based on potential-energy curves (transition matrix elements are not calculated). The quantum-mechanical and electrostatic interactions between He and NO and their interaction with the semi-infinite Pd(111) surface are fully accounted for within a spin-unrestricted screened Hartree-Fock theory. For the system He*-NO/Pd(111) resonance ionization of metastable He* dominates at large distances. Close to the classical turning point of the projectile the strong interactions in the system will lead to an electronic configuration of lowest energy which corresponds to the formation of a NO^- negative ion He^+-NO^-/Pd(111). Penninglike transitions can occur in the complex He^+-NO^-/Pd(111) even though the metastable helium atom has been resonantly ionized. In this complex the negative NO^- ion is in a triplet configuration. An interesting aspect of the experimental metastable deexcitation spectrum is that a structure due to the NO $2\pi^*$ electron appears only for $^1S_0$ He* and not for $^3S_1$ He*. In the present theory this is explained by a spin-selection mechanism, which relies on the reflection of the metastable thermal He* atom, if its $2s$ electron has antiparallel spin orientation relative to the unpaired $2\pi^*$ electron of adsorbed NO. For parallel spin orientation of the He* $2s$ and NO $2\pi^*$ electrons the approach of the He* projectile towards the target is nonactivated. In this way the $1s$ electron of He* retains the information of whether it originates from singlet $^1S_0$ He* or triplet $^3S_1$ He* atomic beams despite the resonance ionization of the metastable helium atom at closer distances.

I. INTRODUCTION

Metastable deexcitation spectroscopy (MDS, surface Penning spectroscopy) together with the recently developed scanning tunneling spectroscopy (STS) are the only experimental techniques yielding surface specific spectroscopic data without averaging over several atomic layers of the sample. MDS in the case of NO adsorbed on the Pd(111) surface is especially attractive due to the possibility to render spin-resolved spectra.[1] The interpretation of the spectra is, however, difficult in view of the uncertainty in the deexcitation mechanism of the metastable noble-gas atoms.

The problem is rather complex in the case of the interaction of He* thermal beams with transition-metal surfaces covered with molecular adsorbates, which do not lead to a significant decrease of the work function. Considering the high work function of these targets ($\phi > 4$ eV) there is no physical argument against the involvement of the resonance ionization (RI) of He*($1s^1 2s^1$) competing with the Penning ionization of the adsorbate. An *ad hoc* argument against RI of He* on transition-metal surfaces saturated with molecular adsorbates (CO, NO) has been suggested: the screening of the substrate surface through the adsorbate layer.[2–5] The screening of the interaction between the projectile and the metal surface is supposed to lead to larger classical turning points for He*, compared to the clean transition-metal surface, accompanied by an exponential decrease of the rate of RI so that the Penning transitions dominate. The mechanism of deexcitation of metastable He* atoms in the case of transition-metal surfaces saturated with molecular adspecies (NO, CO) has been assumed to involve cross Auger electron transitions from the occupied adsorbate-derived electron states into the singly occupied $1s$ orbital of He*, accompanied by the ejection of its $2s$ electron, which is detected (Auger deexcitation, AD). This mechanism can be possible only if the He* projectile retains its $2s$ electron in the initial state, i.e., resonance ionization must not occur. However, an important point has been missed. As our extensive studies of molecular adsorption on transition-metal surfaces show, chemisorption interaction can be strong, leading to a significant broadening of the unoccupied adsorbate states into resonances.[6,7,8] The interaction of He* with the adsorbed species can be rather strong as well (the $2s$-wave function of He* is rather diffuse and singly occupied, so that He* chemically resembles a Li atom). The interaction of He* $2s$ with the diffuse unoccupied adsorbate-derived states may lead to near-resonant ionization of the metastable He* atom even at large distances between the projectile and the substrate surface. In this way the molecular adsorbed species does not screen the interaction between the projectile and the metal surface, but rather mediates the RI of He*. This is the major result of our theory of the rate of He* resonance ionization on clean and NO-covered Pd(111).[9]

Gaining insight into the mechanism of He* deexcitation in front of metal surfaces saturated with molecular adsorbates is important, if we want to understand the spectra obtained with the help of MDS. Unresolved questions, concerning the interaction of metastable He* atomic beams with the NO-covered Pd(111) surface, that needed to be answered can be summarized as follows.

(i) Can the resonance ionization of He* be neglected in the case of NO/Pd(111)?

(ii) If this is not possible, and resonance ionization followed by Auger neutralization (RI+AN) is the dominating mechanism, why are the MD spectra observed not similar to the spectra obtained with He^+ ion neutralization spectroscopy (INS), but rather resemble the spectra obtained with ultraviolet photoemission (UPS)?

The results of our scattering theory for the resonance ionization of He* on a clean and NO-covered Pd(111) surface[9] demonstrated that the argument against RI of He* in front of NO/Pd(111) is not correct. The theoretical evidence is that RI on the NO-covered palladium surface is nearly 35 times faster than on clean Pd(111) at the same distance with respect to palladium. We performed a consistent quantum-mechanical study of the adsorption of He* and NO, and their coadsorption on Pd(111). The scattering theoretical study of He* resonance ionization uses self-consistent transition-inducing potentials and exact scattering states from the adsorption calculation. It was shown that adsorbed NO does not screen the Pd(111) surface for He*. On the contrary, the NO virtual levels above the Fermi level mediate the resonance ionization of the He* 2*s* electron even at larger distances from the metal surface than occur on the clean Pd(111) surface. The cause of the enhanced rate of RI on NO/Pd(111) has been found to lie in the strong interaction between NO and the metal surface and between the two gas particles. In the experimental MD spectra obtained at saturation coverage of NO on the Pd(111) surface at 140 and 300 K, the NO-derived Penning features are also superimposed on an intense structureless background, which is generated by the RI of He* followed by the neutralization of He^+.

The unresolved problems then are the following.

(i) With the 2*s* electron of the metastable helium atom resonantly ionized into the unoccupied metal states, from where is the Penning electron ejected?

(ii) A second unresolved problem with the He* deexcitation spectra of NO/Pd(111) is connected with the different spectra observed with He* singlet $^1S_0$ and triplet $^3S_1$ atomic beams, which have been reported by the same authors.[1] Figure 1 shows the experimentally observed spectrum recorded with $^1S_0$ He* atomic beams and the difference spectrum $^1S_0$ He* $-{}^3S_1$ He*. As on the time scale of Auger transitions, the adsorbed NO molecule behaves as if it has an unpaired electron spin in the $2\pi^*$-derived orbital on many transition-metal surfaces,[1] the additional feature in the $^1S_0$ He* spectrum close to the Fermi level has been attributed to Auger deexcitation, whereby the single electron in the NO-derived $2\pi^*$ state tunnels into the 1*s* hole of the metastable helium atom. The released energy was supposed to be transferred to the excited 2*s* He* electron which is emitted and detected. The difference between the deexcitation spectra of singlet and triplet He* has been explained by a spin-selection mechanism,[1,3] which was based on the following assumptions.

(1) The metastable helium atom retains its 2*s* electron in the initial state, i.e., resonance ionization does not occur.

(2) The interaction between coadsorbed NO and He* is due to the Coulomb electron-electron repulsion between the helium 2*s* electron and the single electron in the $2\pi^*$ orbital of NO. Their quantum-mechanical interaction is ignored. Depending on the relative spin orientation of the two electrons involved, the $2\pi^*$ ionization energy stays below the Fermi level (parallel orientation) or shifts above (anti parallel orientation) resulting in a positive NO^+ ion adsorbed on Pd(111).

This mechanism is only possible if indeed the quantum-mechanical interaction between the two gas particles can be ignored and if (1) the He*-NO complex has a He 2*s* orbital grossly occupied up to close distances; (2) the exchange interaction between the two electrons involved is big enough ($\sim$0.5 eV); or (3) the $2\pi^*$-penetration integral, i.e., the sum of He-core attraction and 2*s* electron repulsion, which controls the shift of the $2\pi^*$ level of NO, is repulsive.

However, none of these assumptions proves to be correct. The *ab initio* value of the exchange integral $(2s2\pi^*|2\pi^*2s)$ is 0.17 eV at a distance 1.5 Å between He* and the oxygen end of NO. The $2\pi^*$-penetration integral

$$(2\pi^*2\pi^*|R_{\rm He}) = \left\langle 2\pi^* \left| -\frac{1}{R_{\rm He}} \right| 2\pi^* \right\rangle + (2\pi^*2\pi^*|2s2s) - (2\pi^*2s|2s2\pi^*) , \quad (1)$$

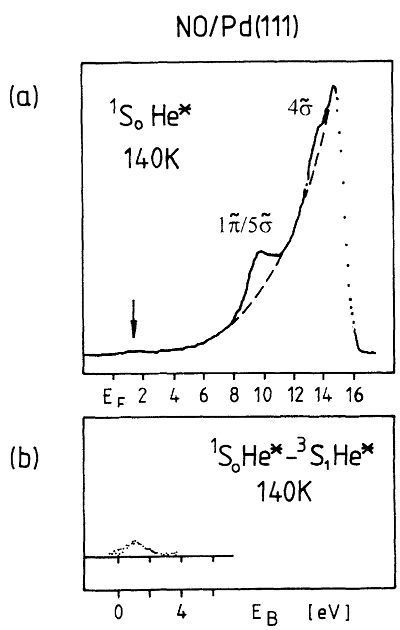

FIG. 1. (a) MDS ($^1S_0$ He*) data for NO adsorbed on Pd(111) at 140 K up to saturation. (b) Difference MD spectra taken with $^1S_0$ He* and $^3S_1$ He* in the energy range close to the Fermi level from a Pd(111) surface saturated with adsorbed NO at 140 K (experimental data due to Sesselmann *et al.* reported in Ref. 1). The tilde in the notation of the one-electron orbitals denotes that they are derived from the respective nonperturbed gas phase molecular orbitals.

is attractive at all distances, with the following definition of the two-electron integrals:

$$(AB|CD)=\int\int \phi_A^*(\mathbf{r}_1)\phi_C^*(\mathbf{r}_2)r_{12}^{-1}\phi_B(\mathbf{r}_1)\phi_D(\mathbf{r}_2)dr_1^3dr_2^3 \ . \tag{2}$$

This is illustrated in Fig. 2, which in addition displays the repulsive contribution from the He* image. Even the sum of these two penetration integrals is strongly attractive. The quantum-mechanical and electrostatic interactions between the two adsorbates are strong and lead to changes in the electronic configuration.

Both the MD experiments of Sesselmann *et al.*[1] and the theory of resonance ionization of He* on NO/Pd(111) (Ref. 9) show that resonance ionization of He* does occur. The theory gives evidence that the rate of RI is much higher on Pd(111) covered with NO than on the clean palladium surface. Once the metastable helium atom has lost its 2*s* electron, the difference between singlet and triplet He* in the atomic beam should vanish. What then is the reason for the different $^1S_0$ He* and $^3S_1$ He* MD spectra of NO/Pd(111)?

In this paper we present potential-energy curves resulting from a quantum-mechanical calculation of the interaction of a metastable $^1S_0$ He* atom with a NO molecule adsorbed at equilibrium on a Pd(111) surface (Sec. II). The theoretical model assumes that the isolated He* species is stable, i.e., the presence of the 1*s* hole is neglected. At large distances the ground state of the interacting system corresponds to a positively ionized He* atom. The results suggest that at closer distances the quantum-mechanical and electrostatic interactions between the two adsorbates lead to conversion from the asymptotic ground state He$^+$-NO to He$^+$-NO$^-$. For brevity we shall call the He* projectile an adsorbate in the following. The Penning ionization of adsorbed NO (Sec. III) then occurs as an Auger transition.

$$\mathrm{NO}_a^- + \mathrm{He}_a^+ \rightarrow \mathrm{NO}_a^+ + \mathrm{He}_g + e^-$$

between the two particles. (The subscript *g* is used for gas phase species *a*, for adsorbed particles.) It is accompanied by the ejection of the additional electron in the $2\pi^*$ level of the negative ion NO$_a^-$ instead of the 2*s* electron of He*, as was assumed earlier. The spin selection mechanism, operating despite the resonance ionization of the metastable atom, is described in Sec. IV.

A reasonable question to ask is why can we establish this mechanism without calculating transition matrix elements. The answer is that only resonant processes are involved in order to reach the configuration He$^+$-NO$^-$, and they are much faster than Penning and ion neutralization processes. Our argument is that at any distance between the projectile and the Pd(111) surface smaller than approximately 6 Å, the system is in its state of lowest energy (with the He 1*s* hole still present, of course), which is reached by resonant processes.

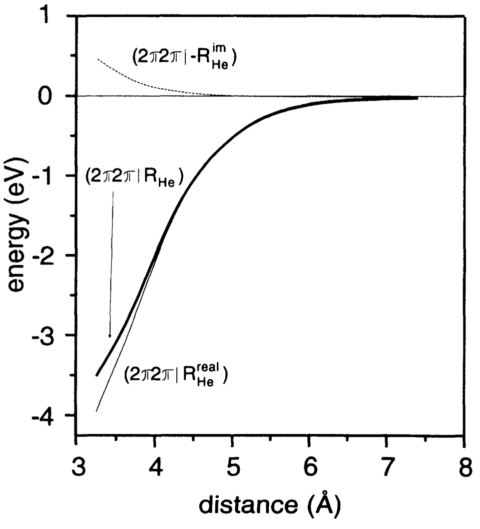

FIG. 2. Distance dependence of the penetration integrals of the $2\pi^*$ NO orbital due to the potential supplied by He* and its image in the metal surfaces $(2\pi^*2\pi^*|R_{He}^{real})$ and $(2\pi^*2\pi^*|-R_{He}^{im})$ and their sum $(2\pi^*2\pi^*|R_{He})$ for He* approaching the NO/Pd(111) surface in the threehold hollow site closest to NO.

II. THE INTERACTION OF METASTABLE He* WITH NO ADSORBED ON Pd(111)

A. The model

In this paper we do not explicitly treat the Auger deexcitation of the metastable helium atom to its ground state. Therefore in this investigation we do not include the 1*s* shell of He* specifically. The 1*s* electron and the hole in the 1*s* orbital are too contracted to be of any significance for the adsorption interaction. This means that the basis set contains only wave functions describing the 2*s* electrons, but the Hamiltonian matrix elements are determined in such a way as to reproduce the spectroscopic data for the electronic configuration $^1S_0(1s^1 2s^1)$. The essential quantity reproduced is the energy of the He* 2*s* level, which is 3.972 eV below the vacuum level (for $^3S_1$ He, which we do not study, it would be 4.768 eV). The absorption of the single adsorbates $^1S_0$ He* and NO on Pd(111) and their coadsorption is studied with the Hamiltonian:

$$H=H_{\mathrm{He}^*}+H_{\mathrm{NO}}+H_{\mathrm{Pd}(111)}+H_{\mathrm{He}^*\text{-}\mathrm{Pd}(111)}+H_{\mathrm{NO}\text{-}\mathrm{Pd}(111)}$$
$$+H_{\mathrm{image}}+H_{\mathrm{core\text{-}core}}+H_{\mathrm{He}^*\text{-}\mathrm{NO}} \ . \tag{3}$$

The first three terms in the first line of this equation describe the noninteracting gas particles and the metal surface. The last two terms specify the interaction of the adsorbates with the substrate in the absence of direct adsorbate-adsorbate overlap, and neglecting image forces. These interactions are included in the terms of the last line together with the core-core repulsion. The model has been described before, and used extensively for the study of different adsorption systems and phenomena at the gas-solid interface.[6-14] It is based on the spin-unrestricted screened Hartree-Fock theory, and explicitly takes into account electron-electron, electron-core, core-core, and image interactions in a self-consistent manner.

The Hamiltonian is defined in a basis set description, which means that the one-electron eigenfunctions are linear combinations of basis orbitals. The basis set of wave functions describes the separated system (isolated gas particle and metal surface) and is taken from first-principles calculations. The extension of the model to study the coadsorption of two gas particles (He* and NO) was recently described.[9] Both direct (electrostatic and quantum-mechanical) and indirect substrate-mediated interactions between the two adsorbing species are included, as well as cross image interactions. The diagonal electron-electron and electron-core integrals between He* and NO are evaluated *ab initio*. The hopping terms of the Hamiltonian between basis wave functions centered on the two adsorbates are chosen in a semiempirical way, in analogy to the treatment of the adsorbate-metal hopping terms.

B. Potential-energy curves

The adsorption of NO on Pd(111) will be described in detail in a forthcoming paper.[7] The most favorable adsorption site for NO above the hexagonal (111) face of palladium is in the bridge position between two adjacent Pd surface atoms. The binding energy of the equilibrium adsorption complex with the nitrogen atom 2 Å away from the surface plane equals 1.2 eV (to be compared to the experimental value of 1.6 eV reported by Wickham, Banse, and Koel).[15] At high NO coverages [$\Theta=0.75$ monolayer (ML)], where the Penning transitions in NO/Pd(111) have been observed by Sesselmann *et al.*[1] Bertolo and co-workers[16,17] have found that only one third of the NO molecules are adsorbed at bridge sites, and two thirds at on-top sites. The experimental and theoretical values of the binding energy at equilibrium on top of a Pd atom, the N end closer to the palladium atom, equal 0.9 eV.[7,15] In the following we will concentrate on this adsorption form of NO, since it is the relevant one for the Penning processes. The axis of the NO molecule lies parallel to the surface normal, and the NO interatomic distance is kept fixed at the gas phase value (1.1505 Å).

A noteworthy theoretical result is that within the spin-unrestricted Hartree-Fock formalism NO adsorbed at equilibrium on many transition-metal surfaces (Cu, Ag, Ni, Pd) is predicted to retain its gas phase electron configuration with a single electron in the $2\pi^*$-derived orbital.[7,10]

In order to study the interaction of $^1S_0$ He* with the above-described adsorption complex, we calculated the potential-energy curves for the ground state and several excited states corresponding to different numbers of electrons on the adsorbates. In these calculations the adsorbed NO molecule is always kept fixed at its equilibrium position in the absence of the He projectile. The energy zero in the displayed total energy curves refers to NO adsorbed on Pd(111), with the He* atom at infinity.

The ground state of the system at distances of the projectile larger than 4 Å from the first layer of Pd atoms involves a positively ionized He atom. The energy changes of this system as a function of the perpendicular distance between the He projectile and the first atomic layer of Pd(111) are plotted in Figs. 3 and 4 as thick solid lines for two different impact parameter α [curves (a)]. Figure 3 refers to impact parameter $\alpha=0$, i.e., the He ion approaches the target along the N-O molecular axis above the oxygen end. The total energy change for impact parameter $\alpha>0$ is plotted in Fig. 4. In this case the He ion approaches the target above the threefold hollow site of the hexagonal Pd(111) plane, in close proximity to the adsorbed NO molecule. The direction connecting the NO molecular axis defines the z direction, and this lateral impact position of He is defined as the x axis.

In order to calculate electronically excited states, we need to have a tool for preventing electrons from escaping into the metal. The procedure developed involves the definition of basis wave functions which define a local adsorbate complex ("surface molecule"). Excited states are then represented by having occupied eigenstates of this local complex above the Fermi level. The eigenstates are selected by having the largest coefficient on the respective gas particle orbital ($2s$ for He and $2\pi^*$ for NO). A Green-function method is then used to couple the surface molecule to the continuum of metal states.

The results for excited states depend on the relative orientations of the electron spins. We have two unpaired electron spins in our system: those of the He $2s$ and the NO $2\pi_y^*$. In our screened Hartree-Fock treatment only the z component of the total spin is a good quantum

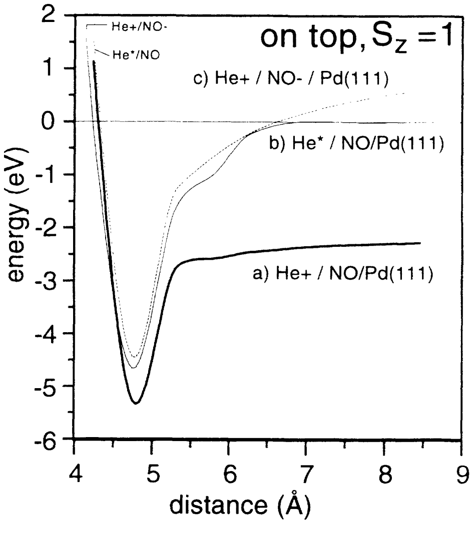

FIG. 3. Energy changes (eV) in the systems (a) He^+-NO/Pd(111), (b) He*-NO/Pd(111) ($S_z=1$), and (c) He^+-NO^-/Pd(111) ($S_z=1$) vs the perpendicular distance (in Å) between He* (He^+) and the first atomic layer in the (111) face of palladium. NO is adsorbed at equilibrium on top of a Pd atom with the N end down, and He* (He^+) approaches the target on top of the oxygen end of NO (impact parameter $\alpha=0$). The distance between N and the underlying Pd atom equals 2 Å, the oxygen atom lies at 3.3 Å in the vacuum, and the molecular axis of NO is parallel to the surface normal. The zero of the energy scale has been chosen to be the He*-NO/Pd(111) system at an infinite distance between He* and the target.

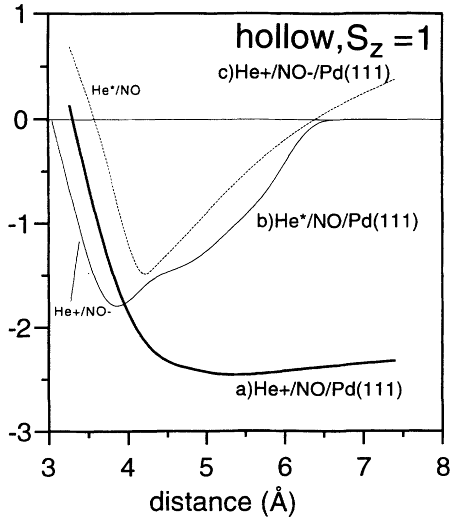

FIG. 4. The same as in Fig. 3 for impact parameter $\alpha > 0$ and $S_z = 1$. The He* projectile approaches the target in the threefold hollow site of Pd(111) close to the NO molecule.

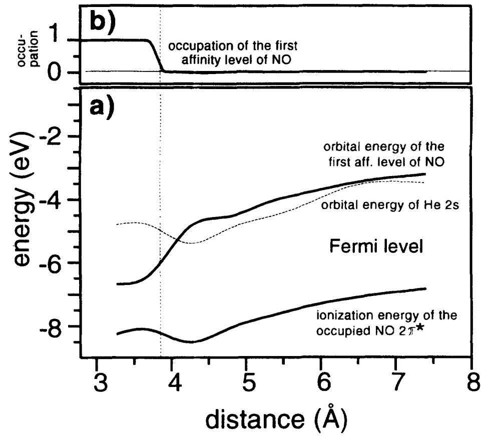

FIG. 5. (a) Variation of the one-electron energy (in eV) for the lowest affinity level ($S_z = 1$), and the ionization energy (full curves) for the electron in the singly occupied $2\pi^*$ orbital of NO_a adsorbed above a metal atom in Pd(111) vs the distance between He^+ and the first metal layer. The orbital energy of the helium 2*s*-derived level is plotted with a dashed curve. (b) Distance dependence of the electron occupation number of the lowest NO-derived affinity level with two electrons of parallel spin orientation ($S_z = 1$) in the NO $2\pi^*$ orbital.

number. As all electrons except the above-mentioned ones are spin paired, the two possible values are $S_z = 1$ (also abbreviated as ↑↑) and $S_z = 0$ (↑↓).

The energy changes of two states with $S_z = 1$ are plotted in Figs. 3 and 4 for the two impact parameters discussed above. Curve (*b*) represents the system which at not too close distances resembles an occupied He 2*s* orbital. Curve (*c*) corresponds at not too close distances to an empty 2*s* orbital and a doubly occupied NO $2\pi^*$ wave function. This electronic configuration corresponds to the occupation of the first affinity level of adsorbed NO in the presence of the positive ion He^+, i.e., the twofold population of the NO-derived $2\pi^*$ orbital with electrons of parallel spin orientation. At close distances curves (*b*) and (*c*) interchange their character, because curve crossing is forbidden. The lower-energy curve then acquires the character of the configuration He^+-NO^-. Though this electronic configuration is highly excited at large distances between the metastable helium atom and the target around the classical turning point of the noble-gas ion it turns out to be the electronic ground state of the system.

The reason for the stabilization of He^+-NO^- $(2\pi_x^* \uparrow 2\pi_y^* \uparrow)$/Pd(111) even below He^+-NO/Pd(111) lies in the strong bonding shift of the affinity level of NO through the electrostatic and quantum-mechanical interactions between the positive He^+ ion and the adsorbed NO molecule. All NO electrons are exposed to the unscreened core attraction from the positive He^+ ion, all NO-derived states experiencing bonding shifts. The first affinity level of adsorbed NO_a shifts even below the Fermi level and is populated through resonant electron charge transfer from the metal Fermi sea. This behavior is illustrated in Fig. 5(a), where the variations in the self-consistent one-electron energies of the lowest unoccupied NO_a $2\pi^*$-derived level and the highest occupied NO_a $2\pi^*$-derived level are plotted versus the He^+-Pd separation for impact geometry beside the NO molecule in the threefold hollow site of Pd(111). At a distance 1.5–2 Å between He^+ and the oxygen end of NO, the maximum of the spectral distribution of the lowest affinity level of adsorbed NO_a drops below the Fermi level. The lowest-lying affinity level $NO^-(2\pi_x^* \uparrow 2\pi_g^* \uparrow)$ is populated, as becomes obvious from the distance dependence of the electron occupation of the NO $2\pi_x^*$ level, which in the gas phase and in NO_a adsorbed at equilibrium on Pd(111) is unoccupied.

The behavior of the affinity level of NO in the interacting system is obviously not only a consequence of the strong electrostatic attraction provided by the positive helium ion He^+. At closer distances between He^+ and NO (the distance between He^+ and the oxygen end of NO ≤ 1.5 Å) the quantum-mechanical interactions, especially between the diffuse orbitals $2\pi^*$ of NO_a and 2*s* of helium, lead to splitting into bonding and antibonding combinations. The splitting provides an additional bonding shift of the bonding combination, which is mostly derived from the NO_a $2\pi^*$ affinity level. Of course, the quantum-mechanical interaction of He 2*s* and NO_a $2\pi^*$ is symmetry allowed for impact parameter $\alpha \neq 0$. For He^+ approaching the target along the NO molecular axis, the effect of the electrostatic field of He^+ is the only reason for the bonding shift of the NO_a affinity level below E_F, if the 2*p* orbitals of He are neglected as they are in our calculations.

An important point is that the affinity level of NO_a with the two $2\pi^*$ electrons having *antiparallel* spin orientations $NO_a^-(2\pi_x^* \uparrow 2\pi_x^* \downarrow)$ is not stabilized below the He^+-NO/Pd(111) curve until distances correspond to the classical turning for thermal energies (cf. Fig. 6). This is

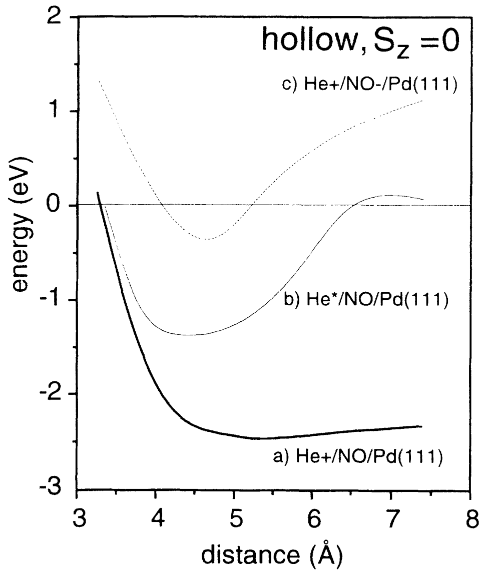

FIG. 6. The same as in Fig. 4 for $S_z=0$.

essential for understanding why the NO $2\pi^*$ feature is not visible in the $^3S_1$ He* spectrum (cf. Sec. IV).

C. Reaction channels and electronic transitions in $^1S_0$ He*-NO/Pd(111)

In this subsection we discuss the most likely pathway the system will follow if the He* projectile hits the NO-covered Pd(111) surface. The resonance ionization of a metastable He* atom in front of the Pd(111) surface with an adsorbed NO molecule has been discussed in our recent paper.[9]

In principle the Auger deexcitation (AD) to the helium ground state can occur at all distances. However, resonance processes such as RI and tunneling of an electron from the metal to an empty level below the Fermi level are known to be much faster than AD. As discussed in our previous paper, at large distances between the projectile and the Pd(111) surface the dominant reaction is the resonance ionization of He* via the unoccupied NO resonance states into the unoccupied part of the metal band symbolized by the following chemical equation:

$$\mathrm{He}_g^* + \mathrm{NO}_a \rightarrow \mathrm{He}_a^+ + \mathrm{NO}_a + e^- \ .$$

This means that RI of the impinging He* atom will occur at large distances with overwhelming probability. The transition to the ground state [curves (a) in Figs. 3 and 4] through He* resonance ionization occurs 35 times faster in proximity to NO compared to the clean Pd(111) surface at the same perpendicular distances from the palladium surface.[9] We therefore assume that we have a He^+ ion at distances where there is a noticeable probability for AD.

At smaller distances around 5 Å, an associative complex ion is formed which leads to a minimum in the potential curves (a) [cf. Figs. 3, 4, and 6]:

$$\mathrm{He}_g^+ + \mathrm{NO}_a \rightarrow (\mathrm{He}-\mathrm{NO})_a^+ \ .$$

In this region Auger neutralization to the He ground state can occur, as evidenced by a featureless background in the experimental spectra discussed in Sec. I [cf. Fig. 1(a)].

As demonstrated by our theoretical study, the electronic configuration He*-NO represents at all distances between the projectile and Pd(111) an excited state of the combined system, if we remember that the curves (b) and (c) interchange their character at close distances. However, at closer distances between He^+ and the target, beyond the minima in the potential-energy curves for He^+-NO/Pd(111) [curves (a) in Figs. 3 and 4] and very close to the classical turning point of the He^+ projectile, the electronic configuration abbreviated by He^+-NO^- becomes energetically more favorable than curve (a). This means that another resonantlike transition occurred in a state, which asymptotically corresponds to electron charge exchange between He* and NO:

$$\mathrm{He}_g^+ + \mathrm{NO}_a + e^- \rightarrow [\mathrm{He}^+ - \mathrm{NO}^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)]_a \ .$$

The resonant occupation of the NO_a-derived electron affinity level with the same spin orientations of the two $2\pi^*$ electrons at distances close to the classical turning point of the He^+ ion has very important consequences for Penning transitions in the system. Though the metastable He* atom has lost its $2s$ electron through resonance ionization, the complex adsorbate $(\mathrm{He}^+\text{-}\mathrm{NO}^-)_a$ has gained a substitute for the lost helium $2s$ electron, which can be ejected as a Penning electron.

The formation of a negative NO ion does not occur with antiparallel spin orientation ($S_z=0$), as can be seen in Fig. 6.

III. THE AUGER DEEXCITATION TRANSITIONS IN He^+-NO/Pd(111)

The results described in Sec. II present the background for the mechanism of the Penning transitions from NO adsorbed on the Pd(111) surface we propose.

The point is that He* loses its $2s$ electron at large distances from the NO/Pd(111) target. Its resonance ionization occurs via the diffuse unoccupied NO-derived resonances in the unoccupied part of the metal band. Therefore, the conventional mechanism of the deexcitation of metastable He* as an Auger transition accompanied by the ejection of the $2s$ He* electron (cf. Refs. 1, 3, 5, and 18) as is schematically shown in Fig. 7 cannot work. The rates of the Penning transitions from the relatively contracted occupied NO-derived states into the He* $1s$ hole must be negligible at the remote He*-NO separations (due to the exponentially decreasing rate of Penning ionization with increasing distance) compared to the rate of resonance ionization from the diffuse He* $2s$ orbital via the diffuse unoccupied NO resonances.

The mechanism we propose takes into account the fast resonance ionization of He* at a large distance from the target, where the Penning ionization of NO must be the slower process. Figure 8(a) illustrates the quasiresonant transfer of the He* $2s$ electron into the unoccupied part of the palladium band via the diffuse broadened NO-derived unoccupied resonance states. For a closer dis-

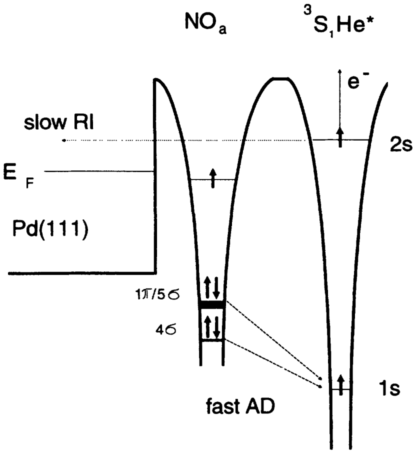

FIG. 7. The conventional mechanism of the Penning transitions in molecularly covered transition-metal surfaces via Auger deexcitation (AD) of the metastable helium atom, neglecting its resonance ionization (RI) (Refs. 1, 3, 5, and 18).

tance between He^+ and the target, the bonding shift of all NO-derived states through attraction by the unscreened He^+ ion core and the quantum-mechanical interference with the 2s wave function of helium is shown schematically in Fig. 8(b). At helium distance 3–4 Å from the palladium surface and 1–2 Å from the oxygen end of the adsorbed NO molecule, this interaction leads to a shift of the first NO affinity level below the Fermi level and hence to its quasiresonant occupation. The quasiresonant electron charge transfer from the metal Fermi sea into the broad NO $2\pi^*$ affinity level should be much faster than the ion neutralization of He^+ for at least two reasons. The 1s state of the helium positive ion is very contracted and lies below the lower edge of the metal band, and the projectile is farther from the metal surface than NO. Starting from large distances the lowest affinity level of NO_a becomes populated first via quasiresonant electron transfer from the metal surface; that is, the one which already has the additional $2\pi_x^*$ electron with spin orientation parallel to the electron occupying the NO $2\pi_y^*$ orbital in the gas phase and the adsorbed state. All remaining NO_a^- negative ionic states still lie above the Fermi level at this separation. Spin-conserving Auger transitions are possible in He^+-NO^- $(2\pi_x^*\uparrow 2\pi_y^*\uparrow)$/Pd(111) from the occupied NO-derived orbitals 4σ, 5σ, 1π, and $2\pi^*$ into the 1s hole of He^+, accompanied by the ejection of the electron in the highest occupied NO_a^- level [Fig. 8(c)].

Another problem should be elucidated. One might be inclined to think that resonance ionization of metastable He*, being the dominating reaction channel at larger separations between the projectile and NO/Pd(111), causes all differences between the singlet and triplet He* atomic beams to vanish. What is the reason, then, for the different experimental MD spectra observed with $^1S_0$ He* and $^3S_1$ He* as probing beams (Fig. 1). In Sec. IV we describe a spin-selection mechanism, operating in the system He*-NO/Pd(111).

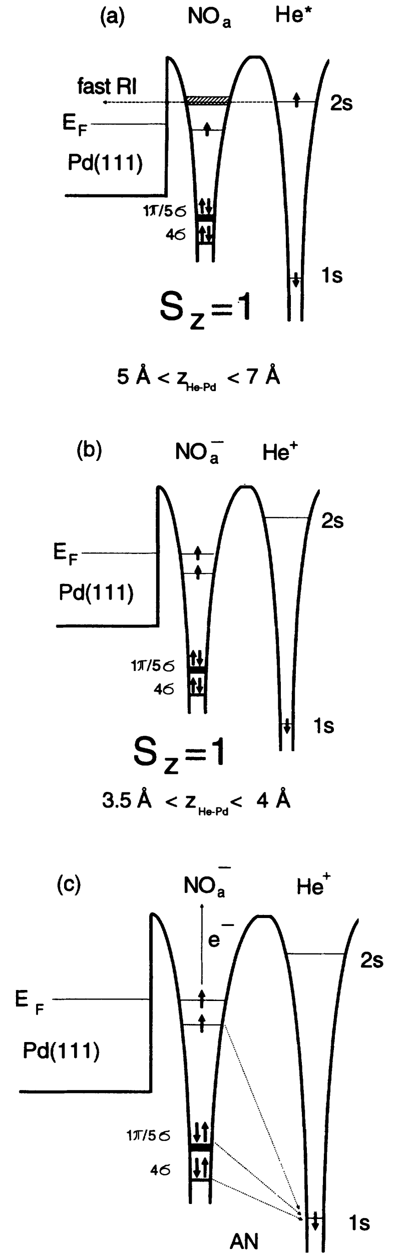

FIG. 8. (a) Schematic drawing of the resonance ionization of He* in front of the Pd(111) surface covered with adsorbed NO molecules in the unoccupied part of the metal band via the NO-induced unoccupied resonance states. This is the dominating reaction channel at distances 7 Å $> z_{\text{He-Pd}} >$ 5 Å between the helium projectile and the first atomic layer. (b) Schematic picture of the bonding shift of all NO-derived electron states through the electrostatic and quantum-mechanical interaction with He^+. At helium-palladium distance 3.5–4 Å, it leads to a drop of the lowest-lying affinity level of NO_a below the metal Fermi level. This is equivalent to a transition to the negative NO_a^- ion with both $2\pi^*$ electrons having the same spin orientation ($S_z=1$). (c) The spin-conserving Penning transitions occur as Auger neutralization (AN) in He^+-$NO^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)$/Pd(111) from the occupied NO-derived orbitals 4σ, 5σ, 1π, and $2\pi^*$ into the 1s hole of He^+, accompanied by the ejection of the electron in the highest occupied $2\pi^*$ level of NO_a^-.

IV. THE SPIN-SELECTION MECHANISM

The electron-spin orientation in the He*-NO/Pd(111) system is governed by quantum-mechanical and electrostatic interactions at remote distances between the target and the metastable helium atom before the He* atom has been resonantly ionized. Our scattering theoretical results of He* RI in interaction with NO adsorbed on the Pd(111) surface[9] give evidence that at distances larger than 8 Å between the metastable He* atom and the palladium surface the rate of RI is lower than 10^{13} sec^{-1}. Therefore, at $z > 8$ Å we can regard the system as still retaining the initial electron state before the resonance ionization of He* has become an efficient competing reaction pathway. However, the spin orientation in the system must occur at distances larger than 5 Å, since we know[9] that at that distance the survival probability of the metastable He* atom is reduced to e^{-}.

The interactions between He* and NO_a adsorbed on Pd(111) at large distances depend especially upon the spin orientation of the electrons in the subsystem composed of the $2s$ electron of He* (spin $s_{2s} = \frac{1}{2}$) and the unpaired $2\pi^*$ electron of adsorbed NO (spin $s_{2\pi^*} = \frac{1}{2}$). The parallel spin orientation of the two electrons yields a triplet ($S_z = 1$), the antiparallel gives rise to a singlet component ($S_z = 0$). We remind the reader that the notations $S_z = 0$ and 1 refer to the combined spin of the two unpaired electrons in the $2\pi^*$ orbital of NO_a and He* $2s$, and not to the total electron spin of the metastable helium atom. The energy changes for $S_z = 0$ and $= 1$ (Figs. 4 and 6) at large separations between He* and Pd(111) that we are interested in ($6 \text{ Å} < z_{\text{He-Pd}} < 7$ Å) are slightly different. There is a small activation barrier for He* penetration closer to the target for the antiparallel spin orientation ($S_z = 0$) $E_{\text{act}} \approx 0.1$ eV (Fig. 6). In a metastable helium atomic beam of thermal energy ($E_{\text{kin}} \approx 0.025$ eV), the activation barrier would lead to reflection of the He* atoms, if their $2s$ electron has antiparallel spin orientation relative to the $2\pi^*$ electron of adsorbed NO_a.

The origin of the activation barrier is the electron-electron repulsion between He* and NO_a. Due to NO-Pd chemisorption interaction, charge will flow from the metal into the molecule. This results for large distances in a repulsive interaction with He*. Although this repulsion is of quasiclassical electrostatic character, it is induced by the quantum-mechanical interaction between the NO molecule and the metal surface. The potential barrier vanishes, however, for the parallel spin orientation of He*-$2s$ and NO-$2\pi^*$ electrons (Fig. 4). The reason is the stabilization due to mixing in with the electron state arising through electron charge exchange between the two adsorbates, i.e., $\text{He}^+\text{-NO}^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)$. At He*-Pd distances smaller than 7 Å the two electronic configurations yield a triplet, $\text{He}^*(2s\uparrow)\text{-NO}(2\pi^*\uparrow)$ and $\text{He}^+\text{-NO}^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)$, and become nearly degenerate because of the image stabilization of the latter. The electron transfer between He* and NO_a at $6 < z_{\text{He-Pd}} < 7$ Å resembles near-resonant charge exchange between the two adsorbates. At $6 < z_{\text{He-Pd}} < 7$ Å the two electronic configurations $\text{He}^*(2s\uparrow)\text{-NO}(2\pi^*\uparrow)/\text{Pd}(111)$ and $\text{He}^+\text{-NO}^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)/\text{Pd}(111)$ can hardly be distinguished. The metastable He* atom is already on the way to resonance ionization of its $2s$ electron through near-resonant charge transfer into the empty NO_a orbitals.

The potential barrier for penetration of He* closer to the target does not vanish for the antiparallel spin orientation of the He* $2s$ and NO_a $2\pi^*$ electrons ($S_z = 0$) (Fig. 6). The reason is that the respective state having a singlet component, arising through electron charge exchange $\text{He}^+\text{-NO}^-(2\pi_x^*\uparrow 2\pi_y^*\downarrow)$, lies too high in energy due to the electron-electron repulsion in the $2\pi^*$ orbitals of NO. The two electronic configurations having a singlet component ($S_z = 0$), namely $\text{He}^*(2s\uparrow)\text{-NO}(2\pi^*\downarrow)/\text{Pd}(111)$ and $\text{He}^+\text{-NO}^-(2\pi_x^*\uparrow 2\pi_y^*\downarrow)/\text{Pd}(111)$, are not quasidegenerate, therefore their interaction does not lead to the reduction of the activation barrier at $6 \text{ Å} < z_{\text{He-Pd}} < 7$ Å, as it is the case with the states belonging to the triplet ($S_z = 1$).

The way the spin-selection mechanism operates is the following. Even after the resonance ionization of the $2s$ electron of He* the electron in the He $1s$ orbital retains the information about whether it originates from triplet $^3S_1$ He* or singlet $^1S_0$ He* atomic beams through its spin orientation relative to the spin orientation of the single $2\pi^*$ electron in the adsorbed NO molecule. The metastable He* atoms with antiparallel spin orientation of their $2s$ electrons with respect to NO_a $2\pi^*$ are reflected; those

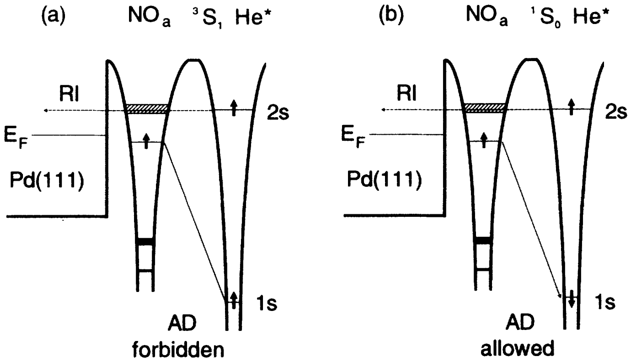

FIG. 9. Schematic drawing of the spin-selection mechanism operating in the deexcitation of metastable singlet and triplet He* interacting with NO/Pd(111). Only metastable He* atoms with the $2s$ electron having a spin orientation parallel to that of the single NO_a $2\pi^*$ electron approach the target. Even though the penetrating He* atom loses its $2s$ electron via resonance ionization, the electron in the helium $1s$ orbital retains the information whether it originates from triplet $^3S_1$ or singlet $^1S_0$ He* atomic beams. (a) The single electron in the $1s$ orbital of the helium projectile has its spin oriented *parallel* to that of the NO_a $2\pi^*$ electron if the metastable atomic beam before RI consists of triplet $^3S_1$ He*. The transition of the electron from NO_a $2\pi^*$ into the $1s$ hole of He^+ is therefore forbidden for $^3S_1$ He*. (b) The single electron in the $1s$ orbital of the helium projectile has its spin oriented *antiparallel* to that of NO_a $2\pi^*$ if the metastable atomic beam before RI consists of singlet $^1S_0$ He*. The Auger transition of the NO_a-$2\pi^*$ electron into the $1s$ hole of He^+ is allowed for $^1S_0$ He*.

metastable helium atoms which can approach the target have spin orientation parallel to the electrons in He* 2*s* and NO_a $2\pi^*$. In a triplet helium atomic beam the spin orientation of the 1*s* electron is, therefore, parallel to that of NO_a $2\pi^*$ [Fig. 9(a)], in a singlet helium atomic beam it has the antiparallel spin orientation [Fig. 9(b)]. Therefore, the Auger transition of an electron from NO_a $2\pi^*$-derived orbitals into the 1*s* hole of He^+ can occur only with singlet He* beams [Fig. 9(b)], as has been observed experimentally. For this explanation it is essential that only the He^+-NO^- complex with $S_z=1$ become stabilized below the He^+-NO configuration (cf. Figs. 4 and 6). If the He^+-NO^- complex with $S_z=0$ (antiparallel spins) is accessible, then the NO $2\pi^*$ feature should be visible in the $^3S_1$ He* spectrum as well, in spite of the spin-selection mechanism described.

V. SUMMARY AND CONCLUSIONS

Attempting to understand the Penning transitions in molecularly covered transition metal surfaces within a consistent model, we proposed a mechanism for the deexcitation of a metastable helium atom on a Pd(111) surface which has a NO molecule adsorbed in the equilibrium geometry.

The interactions (quantum-mechanical and electrostatic) between the target and the projectile are accounted for in a self-consistent way, proving to be very important for the understanding of the Penning processes in a molecularly covered Pd(111) surface. Contrary to earlier approaches toward the same problem,[1] the various reaction channels for the system and the transitions between different electronic configurations have been treated systematically.

The scattering theory of resonance ionization of He* on clean and NO-covered Pd(111) surfaces,[9] which relies on the chemisorption model for the calculation of the self-consistent transition-inducing potentials and the scattering wave functions of the initial and final states, gives evidence that the resonance ionization of He* on NO/Pd(111) is the dominant reaction channel. The dominance of RI, accompanied by ion neutralization of the positive helium ions, provides a structureless background of the features due to the Penning ionization of NO, which have been observed in MD experiments on NO/Pd(111) as well. Despite the RI of metastable He*, "Penning"-like ionization of NO_a can occur via a different mechanism. Close to the classical turning point of the positive ion He^+, a competing reaction channel brings the adsorbate He^+-NO via resonant electron charge transfer into a state of lower energy: He^+-$NO^-(2\pi_x^*\uparrow 2\pi_y^*\uparrow)$, which corresponds to the occupation of the lowest NO_a-derived affinity level. For the Penning transitions this is equivalent to replacing the He* 2*s* electron by the additional electron in the NO_a-derived $2\pi^*$ affinity level, which lies close below the Fermi level. Electrons from NO-derived orbitals tunnel into the 1*s* hole of He^+, transferring the released energy to the additional electron in NO_a^-, which is then emitted and detected. Hereby a spin-selection mechanism operates, permitting the detection of NO majority-spin electrons by deexcitation of singlet $^1S_0$, He*, and of minority-spin electrons by deexcitation of triplet $^3S_1$ He*. Spin selection occurs at large distance between the target and the projectile before He* is resonantly ionized. A low activation barrier of 0.1 eV for the penetration of the He* atom with an antiparallel spin orientation of its 2*s* electron relative to the singlet $2\pi^*$ electron of NO_a would cause its reflection back into the gas phase. The metastable helium atoms, which penetrate closer to the target, have spin orientation parallel to the He* 2*s* and NO_a $2\pi^*$ electrons. The spin orientation of the 2*s* electron of He* fixes the spin orientation of its 1*s* electron relative to the spin orientation of the single electron in the NO_a-derived $2\pi^*$ orbital. Hence even after the resonance ionization of the metastable atom its 1*s* electron retains information about whether it originates from singlet or triplet He*. The spin-selection rules following from the present theory allow electron transition from NO_a $2\pi^*$ into the 1*s* hole of He^+ only in the case of singlet $^1S_0$ He*. Therefore, the $2\pi^*$ electron of NO_a, which can be regarded as an unpaired electron on the time scale of the resonance processes involved in the proposed mechanism, can be detected in the MD spectrum using singlet $^1S_0$ He* atomic beams alone. This theoretical result is corroborated by metastable deexcitation experiments with NO/Pd(111).

We can make a tentative generalization about the consequences of the proposed He* deexcitation mechanism on other molecular adsorbates on transition-metal surfaces. The Penning transitions in CO at saturation coverage on transition-metal surfaces should occur along the same lines. Empty CO-derived $2\pi^*$ bands have been detected in the energy range 1–4 eV above the Fermi level of many transition-metal surfaces by means of inverse-photoemission experiments.[19] The lowest CO_a $2\pi^*$ state can easily be bond shifted below the Fermi level through the electrostatic effect of the He^+ ion and by their quantum-mechanical interaction, thus leading to the negative ion CO_a^-. The Penning ionization of CO_a^- will be accompanied by the emission of the electron in the $2\pi^*$ orbital, which will substitute the missing 2*s* electron of He^+, exactly as with NO/Pd(111).

There remains the question of why in the experiment different effective deexcitation energies are observed for $^1S_0$ He* and $^3S_1$ He*. As we investigated only $^1S_0$ He*, we cannot give a quantitative answer. However, it is clear that $^3S_1$ He* will quantitatively lead to different potential-energy curves, although the qualitative aspects should remain the same. This implies then that deexcitation energies and deexcitation distances will be different. We can also safely argue that the deexcitation energy will be smaller in the case of $^3S_1$ He, because the 2*s* energy level lies deeper and therefore will interact more strongly with the NO $2\pi^*$ level, leading to more attractive total energies in the initial state. It should be noted that in the experiment the difference in the deexcitation energies between singlet and triplet helium by no means always coincides with the gas phase value of 0.8 eV.[18]

An interesting issue remains concerning the deexcitation of metastable atoms at metal surfaces which are saturated with atomic adsorbates like oxygen and hydrogen. No Penning transitions have been observed in these cases. Why does the above mechanism of He* deexcitation not work for atomically covered transition-metal surfaces? The resonance ionization of He* is followed by ion neutralization, giving rise to a rather structureless spectrum. We envisage two possible reasons.

(i) The two potential-energy curves for He^+-A and He^+-A^- do not cross. (A denotes an atomic adsorbate.) This supposition has to be confirmed by calculations.

(ii) The negative ions of oxygen O^- and hydrogen H^- lie embedded in the electron spillover in front of the metal surface and are very diffuse. Hence the Auger transitions are of very low rate and cannot be observed experimentally.

These proposals should be verified within a similar approach to the one we describe in the present work.

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[1] W. Sesselmann, B. Woratschek, J. Küppers, G. Doyen, G. Ertl, H. Haberland, and H. Morgner, Phys. Rev. Lett. **60**, 1434 (1988).

[2] F. Bozso, J. T. Yates, Jr., J. Arias, H. Metiu, and R. M. Martin, J. Chem. Phys. **78**, 428 (1983).

[3] W. Sesselmann, B. Woratschek, G. Ertl, J. Küppers, and H. Haberland, Surf. Sci. **146**, 17 (1984).

[4] H. Conrad, G. Ertl, J. Küppers, and S. W. Wang, Phys. Rev. Lett. **42**, 1082 (1979); H. Conrad, G. Ertl, J. Küppers, W. Sesselmann, and H. Haberland, Surf. Sci. **121**, 161 (1982).

[5] F. Bozso, J. Arias, J. T. Yates, Jr., R. M. Martin, and H. Metiu, Chem. Phys. Lett. **94**, 243 (1983).

[6] D. Drakova and G. Doyen, Surf. Sci. **226**, 263 (1990).

[7] D. Drakova and G. Doyen (unpublished).

[8] G. Doyen and D. Drakova, in *Quantum Chemistry Approaches to Chemisorption and Heterogeneous Catalysis*, edited by F. Ruette (Kluwer, Dordrecht, 1992), p. 139.

[9] G. Doyen and D. Drakova, Phys. Rev. B **49**, 13 787 (1994).

[10] G. Doyen and G. Ertl, Surf. Sci. **69**, 157 (1977).

[11] D. Drakova, G. Doyen, and F. von Trentini, Phys. Rev. B **32**, 6399 (1985).

[12] R. Hübner, D. Drakova, and G. Doyen, J. Electron. Spectrosc. Relat. Phenom. **44**, 333 (1987).

[13] N. Crisa, G. Doyen, and D. Drakova, J. Electron. Spectrosc. Relat. Phenom. **45**, 227 (1987).

[14] D. Drakova, G. Doyen, and R. Hübner, J. Chem. Phys. **89**, 1725 (1988).

[15] D. T. Wickham, B. A. Banse, and B. E. Koel, Surf. Sci. **243**, 83 (1991).

[16] M. Bertolo, K. Jacobi, S. Nettesheim, M. Wolf, and E. Hasselbrink, Vacuum **41**, 76 (1990).

[17] M. Bertolo and K. Jacobi, Surf. Sci. **226**, 207 (1990).

[18] W. Sesselmann, Ph. D. Thesis, LMU München, 1983.

[19] C. S. Feigerle, A. Seiler, J. L. Peña, R. C. Celotta, and D. T. Pierce, Phys. Rev. Lett. **56**, 2207 (1986); H.-J. Freund, J. Rogozik, V. Dose, and M. Neumann, Surf. Sci. **175**, 651 (1986); N. Memmel, G. Rangelov, E. Bertel, V. Dose, K. Kometer, and N. Rösch, Phys. Rev. Lett. **63**, 1884 (1989); N. Memmel, G. Rangelov, E. Bertel, and V. Dose, Vacuum **41**, 729 (1990).