Theory of the resonance ionization of metastable helium on clean and NO-covered Pd(111) surfaces

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A theory of resonance ionization (RI) of metastable He* atoms in interaction with a clean and NO-covered Pd(111) surface is presented which is based on stationary scattering theory. The exact electron scattering states and the RI-inducing potential as well as the adsorption behavior of He* and NO on Pd(111) are obtained within the same self-consistent quantum-mechanical mean-field approach. The rate of He* $2s$ resonance ionization is nearly a factor 35 larger on the NO-covered Pd(111) surface compared to clean Pd(111) at the same perpendicular distance with respect to the first layer of Pd atoms. This is in contrast to earlier expectations that molecular species (NO, CO) adsorbed on transition-metal surfaces should play a shielding role with respect to the RI of metastable He* atoms. The enhanced rate of RI on NO/Pd(111) is due to the strong direct (electrostatic and quantum-mechanical) and indirect interactions (through the metal surface, including the interactions with the image potential) in the adsorption layer. The broadening of the diffuse unoccupied NO states through coupling to unoccupied metal band states leads to quasidegeneracy with the He* $2s$ state, which provides the necessary condition for a resonance process.

I. INTRODUCTION

An unresolved problem in the theory and experiment of adsorption is whether a localized spin magnetic moment on the gas particle is quenched upon adsorption. In the Newns-Anderson[1] theory of adsorption, which employs the model Hamiltonian of Anderson,[2] retaining the spin magnetic moment on the adsorbed particle is not possible even in the limit of weak chemisorption because of the spin-exchange scattering of the conduction electrons in the substrate surface (Kondo effect[3,4]). In the limit of strong chemisorption interaction, magnetic polarization of the adsorbed species cannot be expected anyhow. The two spin quenching mechanisms in the weak and in the strong chemisorption limit are of different physical nature. Spin exchange scattering is a slow process and experiments which probe the surface on a short time scale might therefore be able to detect a local moment on an adsorbate in the weak adsorption limit.

There exist very few experimental techniques permitting the selective measurement of the magnetic moment localized on the adsorbate. Besides a few spin-resolved ultraviolet-photoelectron (UP) and inverse-photoemission spectroscopic measurements, which render data averaged over several surface atomic layers, metastable-deexcitation (MD) spectroscopy [(MDS), also called Penning spectroscopy, or metastable-quenching spectroscopy] is a technique which permits spin resolution and high *surface* sensitivity and selectivity of the signal.

The elucidation of the deexcitation mechanism of metastable He* thermal atomic beams due to scattering from clean and adsorbate-covered metal surfaces is a matter of importance in view of the understanding of the MD spectra. This seems to be a resolved problem only in the case of He* interacting with clean transition-metal surfaces of high work function, where the resonance ionization (RI) of the $2s$ electron of the metastable projectile accompanied by Auger neutralization (AN) of He^+ and the emission of an electron from the metal surface is the adopted mechanism. The work by Dunning, Nordlander, and Walters[5] suggests that even in this case Auger deexcitation might compete with RI plus AN. A controversy exists even in the simple cases of He* deexcitation in front of alkali-metal surfaces (small work function) or alkali-metal-covered transition-metal surfaces.[6,7] In these cases complications due to the resonance ionization of the He* $2s$ electron can be excluded [because of the low work function ($\phi \leq 3.5$ eV) of the target] and Auger deexcitation (Penning transitions) is expected. Two different models have been proposed for understanding the kinetic-energy distribution of the emitted electrons.

(i) The quantum-mechanical calculation of Auger transition matrix elements by von Trentini and Doyen[6] shows that the kinetic-energy distribution of the emitted electrons reflects the shape of the partially filled $2s$ resonance of He* perturbed by the interaction with the target electron states.

(ii) Hemmen and Conrad[7] propose that in addition to the Penning transitions intra-atomic Auger deexcitation of the core-excited negative ion $He^{*-}(1s^1 2s^2)$ occurs.

The problem is much more complex in the case of the interaction of He* thermal beams with transition-metal surfaces covered with adsorbates, which do not lead to a large decrease of the work function. Considering the high work function of these targets ($\phi \geq 4$ eV) there is no physical argument against the involvement of the resonance ionization 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 and NO) has been suggested, i.e., the screening of the substrate surface by the adsorbate layer.[8-13] The screening of the interaction be-

tween 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. However, an important point has been missed. The interaction of He* with the adsorbed species can be rather strong (the 2s wave function of He* is rather diffuse and singly occupied, so that He* may resemble chemically 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*.

Gaining insight into the mechanism of He* deexcitation in front of adsorbate-covered metal surfaces is important if we want to understand the spectra obtained with the help of MDS. The unresolved questions concerning the interaction of metastable He* atomic beams with adsorbate-covered metal surfaces that need to be answered can be summarized as follows.

(i) Can the resonance ionization of He* be excluded so that Penning transitions occur?

(ii) If RI plus AN is the dominating mechanism, why are the observed MD spectra not similar to the spectra obtained with He$^+$ ion neutralization spectroscopy but rather resemble the UP spectra?

In this paper we approach the problem of the resonance ionization of He*$(1s^12s^1)$ in interaction with the clean and NO-covered Pd(111) surface. Within the present theory of resonance ionization of He* we establish that the rate of RI on the NO-covered Pd(111) surface is even higher than on the clean palladium surface, due to the mediatory role of adsorbed NO. This result raises the question of why Penning transitions are observed on NO/Pd(111). We will deal with a mechanism of the Penning transitions and the spin selection which operates when metastable He* interacts with NO chemisorbed on Pd(111) in a forthcoming paper,[14] where the resonance ionization of He* will be explicitly accounted for.

In the next section a scattering theoretical approach to resonance ionization of He* on clean and adsorbate-covered transition-metal surfaces is presented. In Sec. III a brief summary of the chemisorption model is presented which forms the framework for evaluating the RI rates. The results concerning the adsorption of the gas particles He* and NO on Pd(111) and their coadsorption are summarized in Sec. IV. The numerical results for the rates of RI in the systems He*/Pd(111) and He*+NO/Pd(111) are also presented in Sec. IV.

II. THEORY OF RESONANCE IONIZATION OF He* ON CLEAN AND ADSORBATE-COVERED TRANSITION-METAL SURFACES

The resonance ionization of the He* 2s electron into the continuum of unoccupied metal states (for metals of a high work function) is regarded as the decay of an unsta-

ble system prepared by a scattering event. The decay of the He*$(1s^12s^1)$ excited states into a positively charged He$^+(1s^1)$ ion is caused by broadening of the He* 2s state through interaction with the quasidegenerate unoccupied metal states, thus reducing the excited-state lifetime of He*$(1s^12s^1)$ in front of the metal surface.

In order to be able to describe the decay process we adopt the following philosophy: At time $t=0$ the He* atom is at a certain distance in front of the metal surface where it interacts strongly with the neighboring substrate atoms. Franck-Condon factors due to the nuclear motion are not treated (cf. Ref. 15 for a discussion of the influence of the nuclear motion). Considering only the He* with the adjacent metal atoms would give rise to a local complex (surface molecule) with its own set of eigenstates which are expanded in a local basis set containing the He*2s orbital. This surface molecule is then coupled to the rest of the solid surface and this coupling gives rise to the decay of the 2s electron into the continuum of metal states. We now assume that the decomposition of the 2s electron over the eigenstates of the isolated surface molecule is a fast process which we consider to occur instantaneously. The decay of these localized surface molecule eigenstates into the bulk metal is a slower process and determines the rate of the decay of the He*2s electron into the metal continuum according to the probability with which the 2s electron can be found in each of the eigenstates of the surface molecule. The decay of the eigenstates of the surface molecule into the metal continuum is treated using stationary scattering theory as proposed by Böhm.[16] An electron in the surface molecule eigenstates has a certain probability P of tunneling into unoccupied target states far away from the scattering center:

$$P = \sum_f \left| \left\langle f \left| E_{SM} - i\frac{\Gamma}{2} + \right\rangle \right| \right|^2 . \tag{1}$$

$|E_{SM}-i(\Gamma/2)+\rangle$ is a resonance state which evolves from the unperturbed eigenstate of the surface molecule $|E_{SM}\rangle$ in interaction with the continuum states of the metal.[16] It has to be chosen "as if it was prepared before the decay interaction as the initial state which at time $t=0$, under the influence of the interaction, has acquired a Breit-Wigner energy distribution."[16] E_{SM} is the center of this energy distribution and Γ indicates its width. $|E_{SM}-i(\Gamma/2)+\rangle$ can in fact be considered as a generalized eigenvector of the Hamiltonian of the whole system H with the eigenvalue $E_{SM}-i(\Gamma/2)$.[16]

$|f\rangle$ is the state of the electron in the interior of the substrate far from the adsorption center, i.e., it does not experience the potential due to the interaction between the target surface and the He* particle V_{TA} but is rather an eigenstate of the target Hamiltonian H_T:

$$H_T|f\rangle = E_f|f\rangle . \tag{2}$$

The sum in Eq. (1) runs over all unoccupied target states on the energy shell.

The rate of resonance ionization of the state $|E_{SM}\rangle$ equals the time derivative of the probability for tunneling into the final states $|f\rangle$:

$$R_{SM} = \sum_f \frac{d}{dt} \left| \left\langle f \left| E_{SM} - i\frac{\Gamma}{2} + \right\rangle \right| ^2 \right. .$$ (3)

According to Lippman's generalization[17] of Ehrenfest's theorem[18] the rate can be written in the form

$$R_{SM} = 2\pi \sum_f \left| \left\langle f \left| V_{TA} \left| E_{SM} - i\frac{\Gamma}{2} + \right\rangle \right| ^2 \delta(E_f - E_{SM}) \right. \right. .$$ (4)

The sum runs again over all unoccupied target states $|f\rangle$ on the energy shell, unperturbed by the interaction V_{TA} between the target and He*. We should emphasize that this expression for R_{SM} is a formally *exact* result for an idealized decay process. It reduces to an expression analogous to Fermi's golden rule, if the generalized vector $|E_{SM} - i(\Gamma/2)+\rangle$, which is a Breit-Wigner weighted superposition of exact scattering states, is replaced by the orbital state $|2s\rangle$, which does not include the interaction between the target and the projectile. It is only in this limit of first-order perturbation theory that one obtains the result[16]

$$R_{SM} = \Gamma .$$ (5)

The total decay rate of the He*2s is then obtained by multiplying the decay rate of the surface molecule eigenstates by the modulus squared of the coefficient with which the 2s basis wave function enters in the linear expansion of $|E_{SM}\rangle$:

$$R_{2s} = \sum_{SM} R_{SM} |C_{2s}^{SM}|^2 .$$ (6)

The formalism described requires the expansion of the eigenstates of the surface molecule in terms of the exact scattering eigenvectors of the total Hamiltonian. In time-independent scattering theory an exact scattering state $|k+\rangle$ is derived from the nonperturbed stationary state $|k\rangle$ by applying the wave operator Ω^+:

$$|k+\rangle = \Omega^+ |k\rangle .$$ (7)

$|k\rangle$ is an eigenstate of the unperturbed Hamiltonian H_0:

$$H_0 = H - V_{TA} .$$ (8)

The wave operators $\Omega^\pm$ needed for the evaluation of the exact scattering state $|k+\rangle$ are defined with the help of the Green's operators $G^\pm$ of the interacting system:

$$\Omega^\pm = 1 + G^\pm V_{TA} ,$$ (9)

$$G^\pm(E) = \lim_{\epsilon \to 0} (E \pm i\epsilon - H)^{-1} .$$ (10)

In order to construct the decaying states $|E_{SM} - i(\Gamma/2)+\rangle$ as a superposition of exact scattering states $|k+\rangle$ we therefore need the total chemisorption Hamiltonian H, the exact Green's operators $G^\pm(E)$ related to H and the interaction potential between the metastable He* and the target V_{TA} and their matrix elements in a basis set, comprising the eigenstates of the noninteracting projectile and the target.

In the next section the major features of the model Hamiltonian, used for the solution of the problem, are briefly summarized. The same chemisorption Hamiltonian is used to study the adsorption of the separate adsorbates He*, He$^+$, NO on Pd(111), and all competing channels of the chemisorption interaction between Pd(111) and the combined adsorbate, which asymptotically represents a metastable He* atom and a neutral NO molecule. Once the chemisorption Hamiltonian is defined and solved, it is a straightforward procedure to extract the matrix elements of the operator V_{TA} (employing the self-consistent potentials which induce the resonance ionization of the He*2s electron) and to calculate the matrix elements of the exact Green's operators $G^\pm(E)$. The reader who is interested in the results about the rates of RI of He* alone can find them in Sec. IV C.

III. THE ADSORPTION MODEL

The model Hamiltonian has been described and extensively used for the study of different phenomena at the interface between the gas phase and metal surfaces.[19−25,6,38] The model Hamiltonian is formulated in a basis-set description which means that the one-electron eigenfunctions are linear combinations of basis orbitals. The Hamiltonian contains a complete set of one- and two-electron matrix elements. The basis orbitals describe the separate partners [gas phase He* and NO and the clean Pd(111) surface] and are taken from first-principle calculations [see Refs. 6 and 19 for a summary of the wave functions and some parameters of the Pd(111) surface, He*, and NO used in the calculations]. All overlap integrals between the basis orbitals are calculated numerically exactly. The one- and two-electron matrix elements of the Hamiltonian between basis functions on the gas particles and the metal surface are calculated from the overlap integrals by employing relationships of semiempirical character.[25] The Hamiltonian is solved in an effective self-consistent mean-field approximation. Formally the calculation proceeds as in the Hartree-Fock approximation; however, the electrons do not react on the naked external potential provided by the adparticles but on the total screened potential which contains the induced potential changes caused by the response of the metal surface (e.g., image screening).

The interaction between the adparticles and the metal surface involves short-range and long-range effects. The short-range effects are calculated within the region overlapped by the adparticle wave functions and include electron-electron interactions and potentials due to the adparticle cores. The long-range interactions due to image screening effects are included statically by renormalizing the values of the Coulomb repulsion integrals and the core energies on the adparticles. Other interactions accounted for explicitly in the model Hamiltonian are interactions with the dipole layer and the core-core repulsion. For more details, concerning the adsorption of single adsorption species, we refer the reader to previous publications.[6,19,20,21,24,25]

The Pd(111) metal surface is semi-infinite. The sp electrons are described in the effective one-electron model of Sommerfeld. A discretization of the metal sp band is performed, permitting a reduction of the dimensions of the Hartree-Fock matrices involved. The d electrons of pal-

ladium are explicitly introduced by means of localized wave functions[26] centered at the lattice sites. The d band is centered at 1.3 eV below the Fermi level.

The theoretical treatment of the NO molecule and the metastable He* atom is as outlined in Refs. 19 and 6. The electronic structure of the adparticles is described by a basis set of *ab initio* wave functions found in the literature.[27,6] In the present study the basis set of valence molecular orbitals describing the gas phase NO molecule (4σ, 5σ, 1π, and 2π) has been extended by a diffuse 6σ wave function, which has been orthogonalized to the remaining σ-type molecular orbitals. The He* atom has the electronic configuration $^1S_0(1s^1 2s^1)$. Only the $2s$ electron is explicitly treated in the calculations, the $1s$ electron and the hole in the $1s$ orbital are neglected because they are too contracted to be of any significance for the adsorption interaction. The electronic interaction of He* should therefore be rather similar to the interaction of a Li atom with an adsorbed NO molecule.

The coadsorption of He* and NO is described within the same Hamiltonian, used for the description of the adsorption of the single adsorbates, making use of the *transferability* of the adcore potentials acting on metal electrons and metal-adsorbate overlap charges. The simultaneous adsorption of two adspecies in close proximity to one another implies to consider the interactions between the coadsorbing particles. In addition to the direct interactions in the adsorbate layer, which are of electrostatic and quantum-mechanical nature, the indirect interactions mediated through the substrate are accounted for as well.

The interaction energy E(He*-NO/Pd) of the metastable helium atom with the NO/Pd(111) surface complex equals the difference between the energy of interaction of the gas phase complex He*-NO with the metal surface E^{tot} and the adsorption energy of NO alone on Pd(111)$-E^{ad}_{NO/Pd}$:

$$= E^{tot} - E^{ad}_{NO/Pd} \tag{11}$$

$$= E^{el\,stat} + E^{quant} + E^{ad}_{He^*-NO} - E^{ad}_{NO/Pd} \tag{12}$$

$$= E^{el\,stat} + E^{quant} + E^{loc}_{He^*-NO} + E^{im} - E^{ad}_{NO/Pd} . \tag{13}$$

In Eq. (12) E^{tot} is split up into a purely electrostatic part $E^{el\,stat}$, which describes the classical interaction between the unperturbed charge distributions of He* and NO in the gas phase, a contribution due to the quantum-mechanical mixing of their wave functions E^{quant}, and the energy of interaction between the complex He*-NO and the metal substrate $E^{ad}_{He^*-NO}$. In Eq. (13) the energy of interaction between the complex He*-NO and the metal substrate $E^{ad}_{He^*-NO}$ has been expressed as the sum of a local term $E^{loc}_{He^*-NO}$ and the interaction of the adsorbed NO molecule with the helium image E^{im}. Near the surface the adparticle cores and the electrons induce images in the metal and the interaction with these images has to be included. The self-interaction of the NO molecule and the metastable He* atom with their own images are accounted for as described earlier.[21] The cross image interactions of one adparticle with the image of the other is

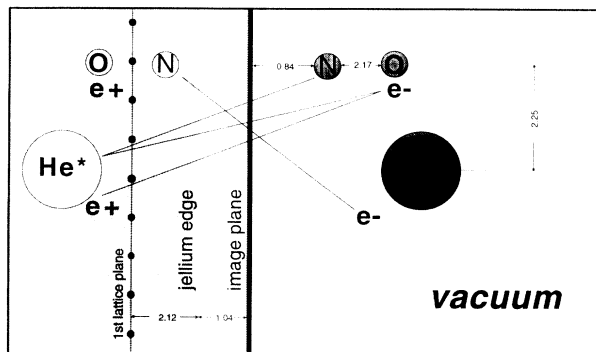FIG. 1. Cross image interactions for He*-NO/Pd(111). NO is adsorbed at equilibrium on top of a palladium atom in the Pd(111) surface. The molecular axis of NO is parallel to the surface normal; its N end is closer to the metal surface; the distance between N and the underlying Pd atom equals 4 bohrs. The N-O interatomic distance is left unperturbed upon adsorption on Pd(111) and equals the gas phase value of 2.174 bohrs.

an additional interaction we have to deal with in the case of coadsorption of two gas particles (see Fig. 1 for the description of the cross image interactions in the He*-NO/Pd system). For the calculation of all interaction terms involving charge images the position of the image plane is chosen to agree with the results of Appelbaum and Hamann[28] as it is described in Ref. 21.

IV. RESULTS

The collision between a metastable He* atom of thermal energy with a clean and NO-covered Pd(111) surface involves many competing reaction channels. With the clean palladium surface these can be, e.g., elastic scattering of He*, trapping, and resonance ionization. The scattering of He* from the molecularly covered surface provides even more reaction channels because of possible involvement of both adspecies. In analogy to the gas phase[29] we can expect Penning ionization of adsorbed NO on Pd(111), which is accompanied by the ejection of an electron:

$$He^*_{(g)} + NO_{(a)} \rightarrow He_{(g)} + NO^+_{(a)} + e^- , \tag{14}$$
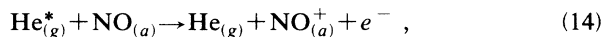
where the subscript (g) means gas phase species and (a) an adsorbed particle. In addition to Penning ionization there are other competing reaction channels, e.g., associative ionization, where the associative complex ion is trapped in an adsorption potential well:

$$He^*_{(g)} + NO_{(a)} \rightarrow (He-NO)^+_{(a)} + e^- . \tag{15}$$
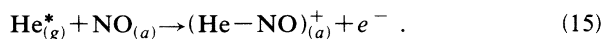
The formation of excited intermediate states

$$He^*_{(g)} + NO_{(a)} \rightarrow (He-NO)^*_{(a)} \tag{16}$$
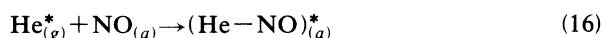
may be regarded as a first step, yielding various chemisorbed products via a number of channels.

In the present study we are interested in the resonance ionization of metastable He* on clean and NO-covered Pd(111). Therefore, we shall consider two reaction channels only: the interactions of He* and He$^+$ with Pd(111)

and NO/Pd(111):

$$He_{(g)}^* + T \rightarrow (He_{(a)}^* - T) , \tag{17}$$

$$He_{(g)}^* + T \rightarrow (He_{(a)}^+ - T) + e^- , \tag{18}$$
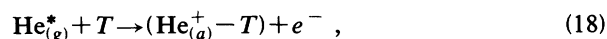
where T is an abridged notation for the targets Pd(111) and NO/Pd(111).

In a forthcoming paper[14] we intend to deal with the mechanism of Penning ionization of the target NO/Pd(111). Some of the remaining reaction channels, which are relevant for the process, will be considered there as well. Here we will concentrate on NO adsorption complexes and He* impact geometries, which are interesting for the Penning spectroscopy. Penning transitions in NO/Pd(111) have been observed from a Pd(111) surface saturated with adsorbed NO at 140 and 300 K.[13] There is evidence from high-resolution electron-energy-loss spectroscopy experiments[31,32] that in the saturated NO adsorption layer at 300 K two-thirds of the molecules are adsorbed at on-top sites and one-third at bridge sites. Hence the adsorption site for the NO molecule we choose is above a Pd atom and not in the bridge position, which emerges as the favored equilibrium adsorption form at low NO coverages both in experiment[31,32] and in our theory.[19]

Two impact geometries of the metastable He* atom are chosen relative to the equilibrium NO/Pd(111) adsorption complex: right on top of the NO molecule and in the threefold hollow site of the hexagonal Pd(111) surface layer in close proximity to the adsorbed NO molecule.

In the next section the results concerning the adsorption of the simple adspecies are briefly described, followed by the results about the interaction of the He* projectile with the NO molecule adsorbed on Pd(111) at equilibrium position on top of a metal atom.

A. Interaction of He*, He+, and NO with Pd(111)

The motivation for describing the adsorption of the single adspecies is twofold. There is no experimental study, with the exception of the Penning spectroscopy of NO/Pd(111),[13] providing any information on the interaction of metastable noble-gas beams of thermal energy with NO covered metal surfaces. Hence the comparison of the theoretical results with experimental data concerning the single adspecies is the only criterion we can use. Furthermore, the three adsorbates are of interest insofar as their bonding to Pd(111) has different physical and chemical nature.

The energy changes, relative to infinite separation from the metal surface, for He*($^1S_0$), He+, and NO adsorption are plotted in Fig. 2 versus the distance to the first layer of Pd(111) measured along the surface normal. The adsorption sites in the hexagonal fcc(111) face are indicated for each particle in Fig. 3. They are chosen in view of the study of the Penning transitions in NO/Pd(111) at saturation coverage.[14] NO approaches the metal surface with its nitrogen end closer to a Pd atom. The molecular axis is oriented perpendicular to the metal surface and the N-O bond length is set equal to the gas phase value. The adsorption distances and binding energies at equilibrium are collected in Table I and they are compared to experi-
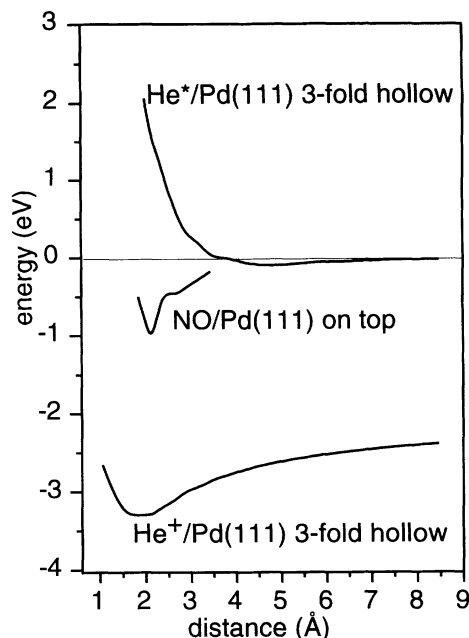

FIG. 2. Variation of the energy (in eV) of the three adsorption complexes between He*($^1S_0$), He+, NO, and Pd(111) versus the perpendicular distance to the first metal layer. He*($^1S_0$) and He+ approach the surface above a threefold hollow site; NO is adsorbed on top of a Pd atom with the nitrogen atom closer to it; the molecular axis is perpendicular to the geometric surface.

mental data where possible.

There is no experimental data to our knowledge concerning the adsorption energy of the positive ion He+. The theoretical value of 2.8 eV for the binding energy of He+ on a Cu(110) surface obtained within a similar formalism[35] lies in the same range as the present data for
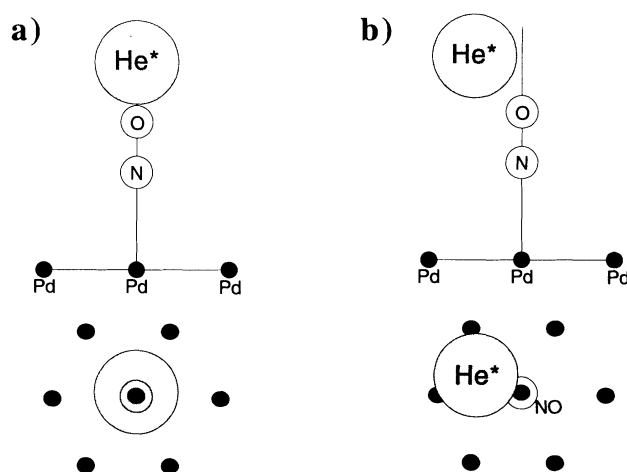

FIG. 3. Side and top views of the two impact geometries of He* relative to the target, which represents a NO molecule adsorbed at equilibrium position on top of a metal atom in the Pd(111) face with its N end closer to the underlying metal atom. (a) Impact geometry of He* on top of NO. (b) He* approaching the target in the threefold hollow site of the hexagonal Pd(111) face in close proximity to the adsorbed NO molecule.

TABLE I. Binding energies E_{ad} (eV) at the equilibrium distances z_{eq} (Å) for the adsorption of He*($^1S_0$), He$^+$, and NO on Pd(111). ω (meV) is the energy of the lowest vibration of the NO molecule against the Pd(111) surface.

	He* threefold hollow	He$^+$ threefold hollow	NO on top
z_{eq} (Å)	4.8	1.9	2.1
E_{ad} (eV)	0.08	3.27	0.94
Expt.		2.8	0.9
Ref.		30	31,32
ω (meV)			53
Expt.			35–39,60
Ref.			31,32

He$^+$/Pd(111). Experiments on Auger deexcitation rates in the gas phase gave evidence that metastable triplet He* and lithium have similar binding energies with other gas phase particles.[36] Therefore at this place we compare their adsorption energies. The adsorption of NO on Pd(111) has been investigated in detail recently.[19] The theoretical and experimental data concerning the binding energies of the equilibrium adsorption complexes and the electron-hole excitation spectra compare nicely.

The ground state of the system, which asymptotically represents a metastable He* atom and Pd(111), is adsorption in the form of the positive ion He$^+$. (The study of He* adsorption is performed by keeping the 2s basis orbital of He* occupied and calculating the self-consistent energy changes under this restriction. This procedure yields a highly excited state of the adsorption system.) As it will become clear from the results in Sec. IV C, the rate of He*2s resonance ionization is high even at large distances, resulting in transition to the ionic state in thermal beams at distances as large as 6–7 Å from the Pd(111) surface.

An interesting issue is the nature of the bonding of He* and He$^+$ to Pd(111). The analysis of the binding energy is performed with the help of partitioning the one-particle electron population into quasiclassical and interference contributions in the spirit of the analysis of the nature of the chemical bond performed by Ruedenberg.[37] The procedure has been described[24] and extensively used. It allows the partitioning of the adsorption energy into quasiclassical electrostatic contributions and contributions due to the quantum-mechanical interference of the wave functions. A further splitting of the energy components into local contributions and long-range part due to the image interactions is also performed, as it has been detailed in our earlier papers.[24,38] Without going into details the analysis of the energy of the adsorption bond shows that for He$^+$-Pd(111) the charge transfer and the electrostatic interactions in the system with quasiclassical charge distribution provide an energy gain of 3.8 eV, which is reduced by 0.5 eV through destructive interference of the wave functions, leading to 3.3-eV binding energy of the equilibrium adsorption complex. This type of chemisorption bonding resembles very much that of Li on Cu(110),[25] for example, and differs from the bonding of He* and NO with the palladium surface. The driving force for He* and NO adsorption is the constructive quantum-mechanical interference of the wave functions

of the gas particles and the metal surface, whereas the electrostatic interactions of the quasiclassical charge distributions are repulsive for both adsorbates. The interference stabilization of the NO 5σ state and d-metal states represents the major contribution to the stabilization of the adsorption complex NO/Pd(111).

B. Interaction of He* and He$^+$ with NO/Pd(111)

It is our conviction that understanding the Penning spectra of the Pd(111) surface saturated with NO implies an understanding of the interactions of the metastable noble-gas atomic beam with the target. With this aim in view we present the results of the quantum-mechanical model, described in Sec. III, concerning the interaction of He* with NO/Pd(111) and of He$^+$ with NO/Pd(111). In terms of the reaction channels described in the introduction to this section we will deal with the adsorption of the excited intermediate state of the coadsorbates (He-NO)* and the associative resonantly ionized state (He-NO)$^+$ on Pd(111). Interactions between the projectile and the target lead to mixing in of different asymptotic states of the system, so that the interacting states do not correspond to the asymptotic incoming states. We are in the position to calculate excited electronic states in order to follow the energy changes in a selected asymptotic electron configuration as a function of the internuclear distance. The transitions between different asymptotic states in the He*-NO/Pd(111) system are, of course, very important for the Penning processes.

Two limiting impact geometries of He* are chosen with respect to the NO molecule adsorbed at equilibrium on top of a Pd atom. They are shown in Fig. 3. The He* projectile approaches the target on top of the NO molecule [Fig. 3(a)] or on the side of it above the threefold hollow site of the hexagonal (111) face of palladium [Fig. 3(b)].

The energy changes in the systems He*-NO/Pd(111) and He$^+$-NO/Pd(111) are plotted versus the separation between the noble-gas atom and the first layer of the (111) face of palladium in Figs. 4 and 5 for the two impact geometries of Figs. 3(a) and 3(b). The two closely lying potential-energy curves in both plots refer to different values of the total spin component S_z of the subsystem composed of the 2s electron of He* (spin $s_{2s} = \frac{1}{2}$) and the unpaired 2π electron of NO (spin $s_{2\pi} = \frac{1}{2}$). The parallel orientation of the two electrons yields a triplet ($S_z = 1$)
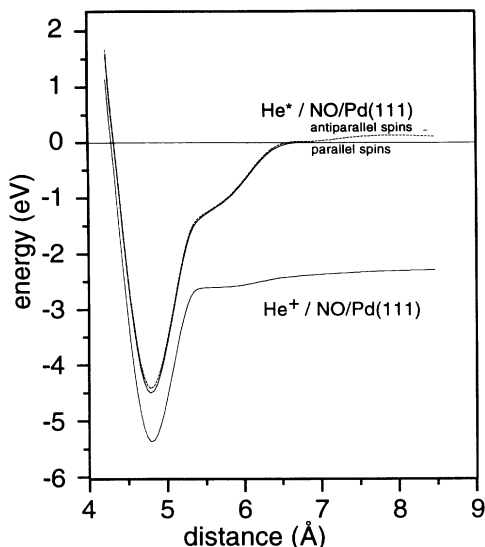
FIG. 4. Energy changes in the systems He^*-NO/Pd(111) and He^+-NO/Pd(111) versus the perpendicular distance between He^*(He^+) and the first atomic layer in the (111) face of palladium. NO is adsorbed at equilibrium on top of a Pd atom with the N end down; He^*(He^+) approaches the target on top of the oxygen end of NO [as in Fig. 3(a)]. The zero of the energy scale has been chosen to be the system He^*-NO/Pd(111) at infinite distance of He^* from the target.

and the antiparallel one gives rise to a singlet component ($S_z = 0$).

Compared to the adsorption of He^* on clean Pd(111) the interaction with the NO-covered Pd(111) surface is much stronger as it is obvious from Figs. 2, 4, and 5. The interactions in the adsorption layer lead to very stable coadsorption with equilibrium binding energies varying from 1.5 to nearly 4.5 eV as He^* approaches NO laterally. The antiparallel spin orientation of the electrons
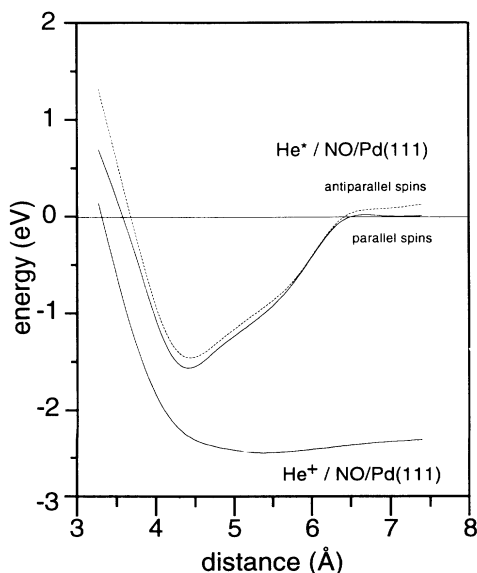
$He^*(2s)$ and $NO(2\pi)$, which remains unpaired in the adsorption complex,[19] is slightly repulsive at large distances. For thermal He^* beams this may present a potential barrier against penetrating closer to the target. Due to the NO-Pd(111) chemisorption interaction electron charge flows into the diffuse unoccupied NO-derived orbitals. This results for large distances between He^* and the target in a repulsive interaction. The repulsion vanishes for the parallel spin orientation ($S_z = 1$).

Both the potential barrier for the $S_z = 0$ configuration and the formation of a strong chemical bond between He^* and NO/Pd(111) have very important consequences for the Penning processes in NO/Pd(111). In this place we only point out that the interactions in the adlayer are very strong; therefore they should not be ignored in trying to elucidate the mechanism of Penning transitions.

The ground state of the system corresponds to the asymptotic electron configuration of a positive ion He^+ interacting with NO/Pd(111). Resonance ionization of the He^* $2s$ electron into unoccupied target states is responsible for the transition He^*-NO/Pd(111)$\rightarrow He^+$-NO/Pd(111), which occurs even at large distances from the target, as it will be shown in Sec. IV C. The binding energy of He^+ to NO/Pd(111) varies as a function of the impact geometry: the bond is stronger, compared to the chemisorption bond with the clean Pd(111) surface, for impact on top of NO and less strong for the other impact geometry.

The nature of the interactions can be analyzed using Eq. (13), which allows the partitioning of the binding energy of He^*(He^+) with NO/Pd(111) into electrostatic contributions, contributions due to the interaction of NO with the image of He^*(He^+) in the metal surface and a rest. The rest includes the direct quantum-mechanical interactions between He^*(He^+) and NO in the gas phase and the short-range quantum-mechanical interactions be-

FIG. 5. The same for impact of He^*(He^+) in a threefold hollow position of Pd(111) as shown in Fig. 3(b).
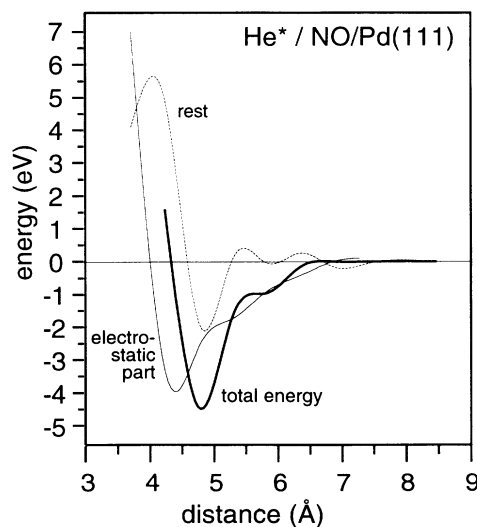

FIG. 6. Energy changes (heavy solid curve) upon He^* approaching the NO/Pd(111) target and its components: electrostatic contributions (thin solid curve) and contributions due to the quantum-mechanical interactions (dotted curve). The impact geometry of He^* is on top of NO as in Fig. 3(a).
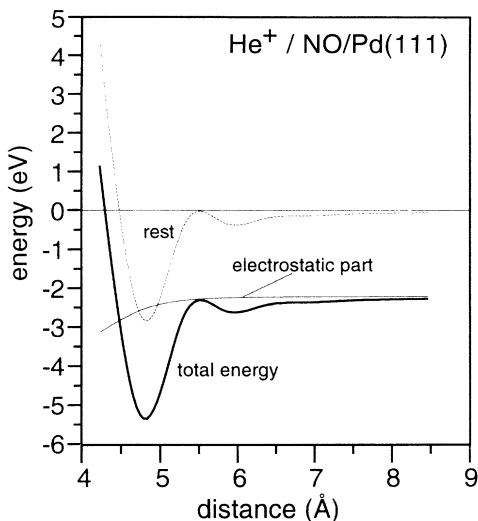
FIG. 7. The same for He^+-NO/Pd(111).

tween $He^*(He^+)$-NO and the Pd(111) surface. The sum of all electrostatic terms including the energy of NO interaction with the image of $He^*(He^+)$ and the energy gain due to electron charge transfer in the case of He^+ resonance ionization has been plotted in Figs. 6 and 7 as thin solid curves for varying $He^*(He^+)$-Pd(111) distances. The sum of the quantum-mechanical contributions ("rest") has been plotted with dotted curves. At larger distances between $He^*(He^+)$ and the target the electrostatic attraction is responsible for the energy lowering. At closer distances the quantum-mechanical interactions start playing a role and they are especially important between the minimum and the classical turning point of He^* where the Penning transitions are expected to occur. The strong fields provided by each adparticle and its image and the quantum-mechanical interactions in the adsorption systems have very important consequences both for the rate of resonance ionization of He^* and the mechanism of Penning ionization of NO adsorbed on Pd(111).

In the next section we present the theoretical results for the rates of He^* resonance ionization on the clean and NO-covered Pd(111) surface.

C. He* resonance ionization

As it was pointed out in the preceding sections, the wave functions and the matrix elements of the potential operator, inducing the resonance ionization of He^*, are calculated self-consistently within the same Hamiltonian, which is used for the study of the adsorption and coadsorption of He^* and NO on Pd(111). Therefore, the results concerning the RI rates are consistent with the whole adsorption behavior of the systems we study, allowing us to understand the trends in the rates of resonance ionization in terms of the interactions in the adsorption systems.

The rate of RI is evaluated using Eqs. (4) and (6). The logarithm of the rate of He^*2s RI is plotted versus the separation between the projectile and the first layer of

palladium atoms in Fig. 8. Curve (a) refers to He^* interacting with the clean palladium surface and curves (b) refer to He^* interacting with the NO-covered Pd(111) surface for the two impact geometries shown in Figs. 3(a) and 3(b).

The most important result is that the rate of He^*2s RI is nearly a factor 35 larger on the NO-covered palladium surface compared to clean Pd(111). This is in contrast with the expectation that the "shielding" of the metal surface by molecular adspecies should reduce the probability for He^*2s RI.[8–13] As it can be seen from the plots in Fig. 8, R_{RI} on the clean Pd surface has more or less the same value as the rate of helium resonance ionization on the NO-covered surface at a 2.4-Å larger distance from the target [the oxygen end of the NO molecule adsorbed on Pd(111) lies 3.3 Å above the geometrical surface]. Therefore, the argument based on shielding of the metal surface by NO cannot be correct. To the contrary the adsorbed NO molecule serves as a mediator, extending the metal wave functions into the vacuum by nearly 2.5 Å and mediating the resonance ionization of He^*2s into unoccupied metal states at larger distances than it occurs on the clean Pd(111) surface.

We can estimate the survival probability $1-P(z_0)$ of the $2s$ electron of the projectile at distance z_0 from the NO-covered palladium surface assuming a classical trajectory for He^* and a classical constant velocity v of the projectile corresponding to metastable helium beams of thermal energy (27 meV). $P(z_0)$ is the probability for resonance ionization at distance z_0, defined as the integrated resonance ionization probability up to infinity:

$$P(z_0) = \int_{z_0}^{+\infty} \frac{R_{RI}(z)}{v}[1 - P(z)]dz \ . \tag{19}$$

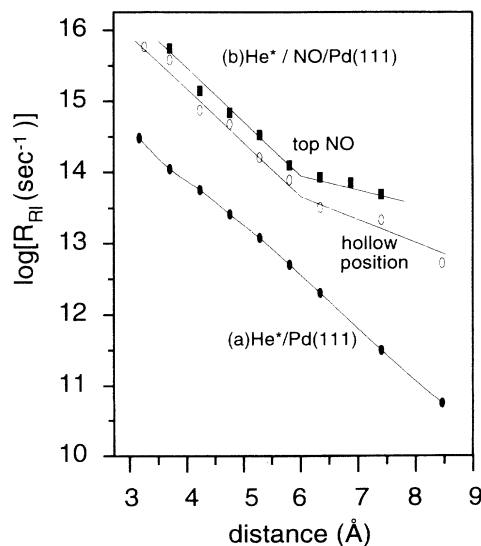Assuming an exponential distance dependence for both

FIG. 8. Logarithm ($\log_{10}$) of the rate of He^* $2s$ resonance ionization (in sec^{-1}) as a function of the perpendicular distance between He^* and the first layer of Pd(111). (a) He^* on a clean Pd(111) surface. (b) He^* approaching the target NO/Pd(111) in the two impact geometries which are displayed in Figs. 3(a) and 3(b).

R_{RI} and $P(z)$, which is justified by the plots in Fig. 8, we get the result that at a distance of 5.5 Å from the NO-covered Pd(111) surface only a part $1/e$ of the metastable He* atoms survives.

This discussion would have been useless if the ionization energy of the electron in the He* 2s-derived state would be larger than the sample work function due to strong bonding shifts. This is, however, not the case as it is demonstrated by the plots in Fig. 9. The He* 2s resonance lies above the Fermi level at all distances of interest. Neither the image interactions nor the electrostatic and quantum-mechanical interactions in the system can lead to a bonding shift of the 2s-derived level below E_F. The interaction with the target states at distances larger than 5 Å does not broaden the 2s resonance enough and it does not acquire a large weight in the occupied part of the target electron states.

Therefore, in the case of a metastable He* atom interacting with the NO-covered Pd(111) surface resonance ionization of He*(2s) does occur and its rate is nearly 35 times larger than on the clean Pd(111) surface. There is strong experimental evidence supporting this theoretical result from MDS of a Pd(111) surface saturated with adsorbed NO at 140 K.[13] The NO-derived 1π-5σ and 4σ MDS features are superimposed on an intense background due to the resonance ionization of He*.

The understanding of the enhanced rate of metastable helium resonance ionization in the vicinity of adsorbed NO lies in the strong interactions between the target and the projectile. The interactions of He*(2s) with the diffuse unoccupied NO-derived states (2π and 6σ) is especially important in this respect. We can make use of a simple perturbation theory argument to demonstrate in a qualitative way the effect of the diffuse orbitals of NO. The complete theory is based on the evaluation of the ex-

FIG. 9. (a) Distance dependence of the energetic position of the He* 2s-derived state (eV) in the system He*-NO/Pd(111) with parallel spin orientation of the unpaired electrons in the He* 2s and NO 2π orbitals. The position of the Pd(111) Fermi level is indicated with a thin solid line. The energetic position of He* 2s due to image interactions alone is also displayed. (b) Rate of the He* 2s resonance ionization (eV).

act wave functions and transition matrix elements, only the argument which we use for pedagogical reasons is derived from perturbation theory. At large distance between He* and the clean Pd(111) surface the rate of RI is proportional to the transition matrix element

$$\left\langle k|V_{TA}|E_{SM}-i\frac{\Gamma}{2}+\right\rangle \approx \langle k|\psi_{2s}\rangle V^{eff} ,$$

which has been set equal to the product of an effective potential V^{eff} times the overlap integral between the unoccupied target wave functions $|k\rangle$ and the nonperturbed wave function of the 2s electron on He* $|\psi_{2s}\rangle$. The interaction between NO and Pd(111) leads to broadening of the NO-derived affinity levels and their strong mixing with the empty metal band states. Using just the NO 2π component, for the sake of simplicity, we can write the transition matrix element for He*(2s) resonance ionization on the NO-covered Pd(111) surface in the following way:

$$\left\langle k|V_{TA}|E_{EM}-i\frac{\Gamma}{2}+\right\rangle$$
$$\approx \langle (k+\langle k|\psi_{2\pi}\rangle\psi_{2\pi})|V_{TA}|\psi_{2s}\rangle$$
$$\approx \langle k|\psi_{2s}\rangle V^{eff}+\langle k|\psi_{2\pi}\rangle\langle\psi_{2\pi}|V_{TA}|\psi_{2s}\rangle . \qquad (20)$$

The second term in Eq. (20) represents the change in the rate of He* RI due to the adsorbed NO molecule. Both the overlap of the diffuse unoccupied NO states with the unoccupied metal states (e.g., $\langle k|\psi_{2\pi}\rangle$) and their interaction matrix elements with He* $|\psi_{2s}\rangle$ (e.g., $\langle\psi_{2\pi}|V_{TA}|\psi_{2s}\rangle$) have large values, inferring an enhanced RI rate of He* on the NO-covered metal surface. Of course, this argument might be of no consequence for the rate of RI if the adsorbed molecule behaves as an insulating particle. However, this is not the case with either NO or CO adsorbed on transition-metal surfaces. NO- and CO-derived resonances have been identified above the Fermi level with the help of inverse photoemission spectroscopy,[39] their broadening being due to strong interactions with the unoccupied metal band states. The quasidegeneracy of the He* $|\psi_{2s}\rangle$ state with NO-derived unoccupied electron states and their finite lifetime in the unoccupied metal band provide favorable conditions for a resonance process.

The effect of adsorbates on the lifetime broadening of hydrogen levels has recently been studied by Nordlander and Lang using the complex scaling technique.[40] The authors find similar strong energy shifts and broadening of atomic levels near chemisorbed impurities due to induced long-range electrostatic fields as the effects established in our theory. Using the same technique for the study of tunneling rates for RI of metastable He*($^3S_2$) in front of a jellium surface Dunning, Nordlander, and Walters[5] reported RI rates and survival probabilities of the same order of magnitude as the data due to the present theory at comparable He* substrate separations.

V. CONCLUSIONS

The scattering theory of resonance ionization of metastable He* on molecularly covered transition-metal sur-
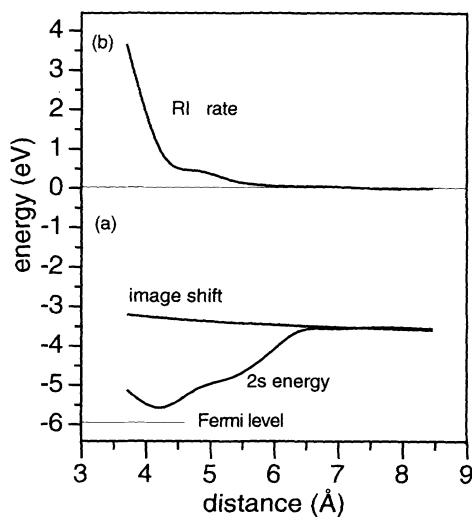
faces presented in this paper throws light on a long-lasting discussion in this field. Within this theory the exact transition matrix elements for resonance ionization have been evaluated with the help of the exact scattering electron states and transition potentials. They have been self-consistently calculated with the help of a quantum-mechanical mean-field type of adsorption theory. The adsorption theory has been further sophisticated to treat the coadsorption of metastable He* atom and another molecular adsorbate. The interactions in the adsorption layer, which have been accounted for explicitly, comprise the direct electrostatic and quantum-mechanical interactions and the indirect interactions through the metal surface. The effect of the cross images is included as well.

The theoretical evidence is that the rate of resonance ionization of He* on the NO-covered Pd(111) surface is nearly 35 times *larger* than on the clean metal surface. This is in contrast with earlier *ad hoc* expectations that molecularly adsorbed species shield the surface of the transition metal from the interaction with metastable atomic beam, causing a shift of the classical turning points further away in the vacuum region. We demonstrate that adsorbed NO *does not screen* the palladium surface for He* within a consistent quantum-mechanical treatment of He* and NO coadsorption and the scattering theory of He* resonance ionization, which is based on the self-consistent transition-inducing potentials and scattering wave functions. To the contrary NO-derived resonance states above the Fermi level mediate the resonance ionization of He*(2s) even at further distances from the metal surface compared to clean Pd(111).

The cause for the enhanced rate of He* resonance ionization on NO-covered Pd(111) lies in the strong interactions between the two adsorbates and between NO and the metal surface. Both the direct and indirect interactions through the metal surface are responsible for the large transition matrix elements. The interaction between NO and the palladium surface causes the broadening of the diffuse unoccupied NO states into resonances due to mixing with unoccupied metal band states. The result is their quasidegeneracy with the He* 2s state, which provides the condition for a resonance process. Hence the shielding argument cannot be correct, because the NO molecules are not insulating. They rather "extend" the empty metal states further away in the vacuum region, mediating the resonance ionization of He* at larger distances than it occurs on the clean palladium surface.

On transition-metal surfaces we expect an enhanced rate of metastable He* resonance ionization in the case of all molecular adsorbates which support unoccupied adsorbate-induced resonances between the Fermi level and the vacuum level. This raises the following question: If the He* projectile loses its 2s electron due to interactions with the molecularly covered transition metal surface, how can Penning ionization of the adsorbed molecules occur? The Penning transitions can lead to distinct adsorbate-derived spectral features only, if they are accompanied by the ejection of an electron from a state localized near the He*. The present state of our knowledge implies that this should be the 2s electron of He*. However, the results of the present theory of resonance ionization demonstrate that the 2s electron on He* is lost. We will search for a solution of this dilemma proposing a mechanism of the Penning transitions in molecularly covered transition-metal surfaces in a future communication.

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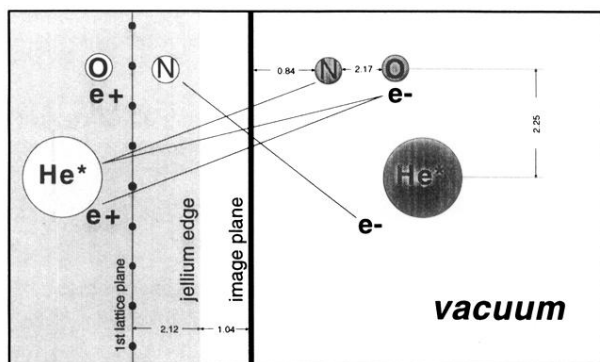[40]P. Nordlander and N. D. Lang, Phys. Rev. B **44**, 13 681 (1991).

FIG. 1. Cross image interactions for He*-NO/Pd(111). NO is adsorbed at equilibrium on top of a palladium atom in the Pd(111) surface. The molecular axis of NO is parallel to the surface normal; its N end is closer to the metal surface; the distance between N and the underlying Pd atom equals 4 bohrs. The N-O interatomic distance is left unperturbed upon adsorption on Pd(111) and equals the gas phase value of 2.174 bohrs.
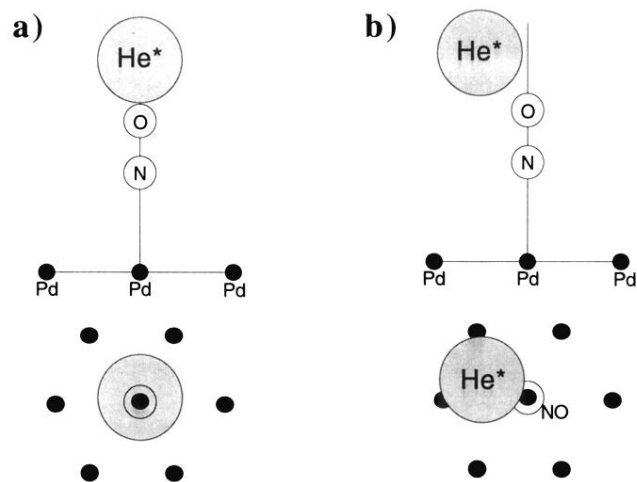
FIG. 3. Side and top views of the two impact geometries of He* relative to the target, which represents a NO molecule adsorbed at equilibrium position on top of a metal atom in the Pd(111) face with its N end closer to the underlying metal atom. (a) Impact geometry of He* on top of NO. (b) He* approaching the target in the threefold hollow site of the hexagonal Pd(111) face in close proximity to the adsorbed NO molecule.