

## Projectile and target autoionization electron emission in 700-eV $\text{Ne}^+$ -Na/ $M$ ( $M = \text{Cr}, \text{Cu}, \text{Mo}, \text{and Pt}$ ) collisions

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We report on a systematic study of Ne-projectile and Na-target atom autoionization electron emission during 700-eV  $\text{Ne}^+$  ion bombardment of polycrystalline Cr, Cu, Mo, and Pt surfaces covered with an increasing amount of Na. We show that the collisionally excited  $\text{Ne } 2p^4(^1D)$  singlet core can be efficiently converted to a  $2p^4(^3P)$  triplet through an Auger rearrangement process involving a solid valence electron and that the conversion is highly localized at the excitation site and its rate is strongly dependent on local electronic properties. We found that the Na  $2p$  electron excitation essentially results from an  $L$ -shell vacancy transfer from the  $\text{Ne } 2p^4(^1D)$  at low Na coverages and from direct excitation in Na-Na symmetric collisions at high coverages. We demonstrate the great potential of the low-energy collisionally excited autoionization electron spectroscopy as a surface-analysis technique in alkali-metal adsorption studies.

### I. INTRODUCTION

Projectile or/and target autoionization electron emission during low-energy ion bombardment of solid surfaces has received much interest in recent years because it can provide a great wealth of information on ion-solid interactions regarding both inner-shell electron excitation and outer-shell charge transfer processes.<sup>1-10</sup> In the framework of the molecular-orbital (MO) curve-crossing model,<sup>2,3</sup> a transient molecule is formed during a close collision. When the minimal approach distance reaches a critical value, some MO's will suddenly lower their binding energies, leading to electron promotion into high-lying unfilled MO's. For collision partners with small and similar atomic numbers,  $2p$  excitation will occur in the lighter partner<sup>2,3</sup> and in some cases the  $L_{23}$ -shell hole(s) can also be transferred to the heavier partner when two atoms separate from each other.<sup>4-6</sup> Besides, secondary energetic encounters between target atoms can also give rise to core excitation.<sup>7,8</sup> Because of the extended nature of outer orbitals in a solid, the promoted electrons will merge into the valence band and the excited particle will leave the surface as an ion. The formation of autoionizing states is achieved by electron capture from the solid during its escape from the surface. Due to energy constraints in the resonant charge transfer processes, many autoionization transition lines are totally suppressed for clean metal targets with relatively large surface work functions and can be observed if the surface is adequately modified.<sup>9,10</sup>

In an early study, Zampieri and Baragiola<sup>11</sup> demonstrated that the sharp transition lines seen in electron spectra are due to deexcitation of scattered or sputtered atomic particles in vacuum and suggested the possibility of using the kinetic energies of detected electrons to monitor the surface work function changes directly. Unfortunately, most previous studies were conducted on clean samples and this technique was applied only in a few works on oxygen chemisorption.<sup>10,12</sup>

Recently, we have reported on a study of Ne autoionization electron emission for  $\text{Ne}^+$ -Na/Al and  $\text{Ne}^+$ -Na/Mo systems,<sup>13</sup> showing that the conversion of the  $\text{Ne } 2p^4(^1D)$  single core state into a  $2p^4(^3P)$  triplet is a well-localized process and that its rate strongly depends on the electronic properties at the target atomic sites. In this paper, we present a systematic investigation of Na adsorption on various polycrystalline transition-metal (Cr, Cu, Mo, and Pt) substrates using both projectile Ne and target Na autoionization electron spectroscopy. Our purpose is to gain a detailed insight into the peculiarities of ion-solid interactions regarding inner-shell vacancy sharing and configuration conversion processes and to obtain information on the overlayer growth morphology and work function variation. We demonstrate the great potential of low-energy collisionally excited autoionization electron spectroscopy as a surface analysis tool in studies of interface formation involving alkali-metal adsorption.

### II. EXPERIMENTAL

The experiments were performed in an ultrahigh-vacuum chamber with a base pressure of  $5 \times 10^{-10}$  Torr. The 700-eV  $\text{Ne}^+$  ion beam, produced in a differentially pumped ion source, was focused on the target samples with an incidence angle of  $70^\circ$  with respect to the surface normal and set to raster over a large area of  $4 \times 4 \text{ mm}^2$  to minimize the sputtering erosion effects. Polycrystalline Cr, Cu, Mo, and Pt samples were cleaned by long-time sputtering with 5-keV  $\text{Ne}^+$  ions. The emitted electrons were collected with a hemispherical analyzer, working with a constant energy resolution of 0.2 eV.

Na was evaporated from carefully outgassed commercial getters and during deposition the substrates were kept at room temperature. The Na overlayer was grown by sequential evaporation and in this paper the relative coverage will be expressed in terms of deposition time. Since the experimental conditions for alkali-metal evaporation

poration were different for each series of measurements and the sticking coefficient may change from one substrate to another, a comparison in relative deposition time between various systems bears no direct physical meaning. The samples were exposed to the ion beam only during data acquisition (typically 0.5–1 min) between two consecutive evaporations and no ion-bombardment-induced effects have been observed throughout the experiments.

### III. RESULTS AND DISCUSSION

In Figs. 1 and 2 we present four sets of Ne and Na autoionization electron spectra taken for 700-eV  $\text{Ne}^+$  bombardment of Cr, Cu, Mo, and Pt substrates covered with increasing amounts of Na. All the spectra have been corrected for the analyzer transmission factor and normalized to the same height to emphasize line-shape changes. To approximately correct the Doppler shifts, the energy scale has been adjusted in such a way that the position of peak II for the clean Al surface (work function 4.26 eV) coincides with 23.55 eV. The three main sharp lines, labeled Ne-I, Ne-II, and Na, are commonly attributed to the autoionization transitions from  $\text{Ne } 2p^4(^3P)3s^2$ ,  $\text{Ne } 2p^4(^1D)3s^2$ , and  $\text{Na } 2p^53s^2$ , respectively.<sup>14</sup> We point out that only Ne-Na and Na-Na encounters are relevant for our discussion on autoionization transitions since collisions involving the much heavier substrate metal atoms ( $M = \text{Cr, Cu, Mo, and Pt}$ ) cannot produce  $2p$  electron excitation in either Ne or Na.

We first note that the spectral lines in all systems shift toward lower energies upon Na deposition. As discussed in detail in Refs. 11 and 15, the kinetic energy of elec-

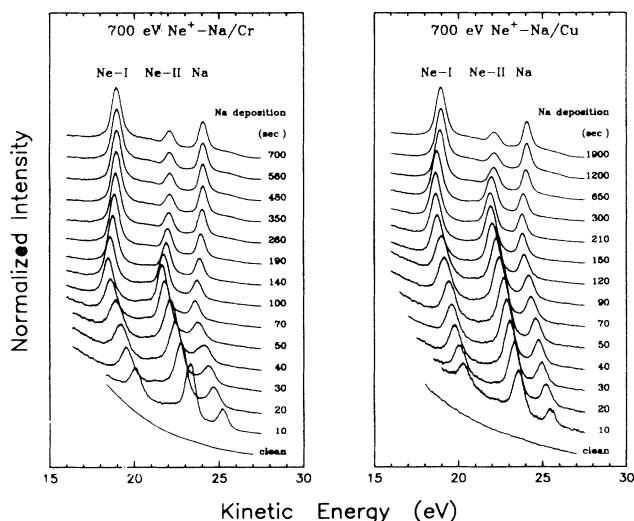


FIG. 1. Autoionization electron spectra for 700-eV  $\text{Ne}^+$  ion bombardment on polycrystalline Cr and Cu surfaces covered with increasing amounts of Na. All the spectra have been corrected for the analyzer transmission factor and normalized to the same height. Note that the Na deposition time, which gives only a relative measure of the Na coverage, is not comparable for different systems because of the different evaporation conditions.

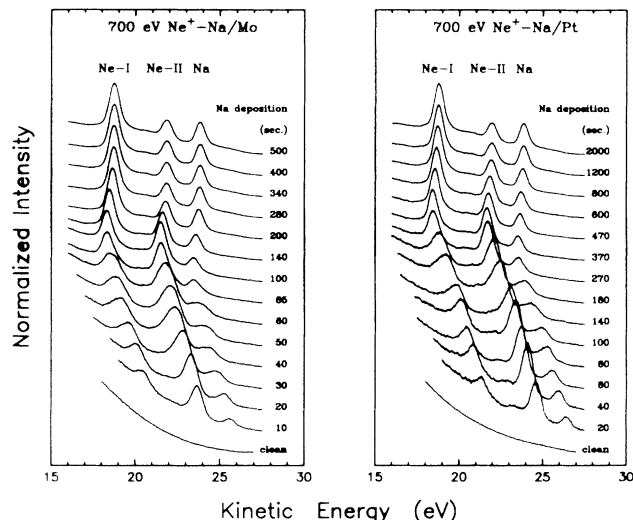


FIG. 2. Same as in Fig. 1 but for Mo and Pt substrates.

trons emitted in atomic particles in the vicinity of the surface and detected by the analyzer is strictly related to the electrostatic potential difference between the sample and analyzer; thus the shift of the sharp atomic peaks is a direct measure of the surface work function variation  $\Delta\Phi$ . The results plotted in the first panels of Figs. 3–6, where the starting energy positions of the atomic peaks for clean metal substrates were determined by extrapolation, show a qualitatively common behavior for all the systems. Initially,  $\Phi$  decreases with coverage, changes its slope at  $\Theta_1$ , reaches a minimum at  $\Theta_2$ , increases slowly thereafter, and finally levels off at  $\Theta_3$ . This is very similar to that reported in the literature for alkali-metal adsorption on single-crystal samples<sup>16–18</sup> and  $\Theta_2$  should roughly correspond to the coverage of half a monolayer.<sup>19,20</sup> We note that the final values of  $\Phi$  at Na saturation coverages are nearly the same for all the substrates, as listed in Table I, and very close to that of bulk Na [2.75 eV (Ref. 21)].

Given that the outer-shell electron capture occurs at a few Å away from the surface and the autoionizing states have relatively long lifetimes of  $10^{-13}$  sec,<sup>22</sup> the distance at which the deexcitation takes place should be some 10 Å from the surface, and the electrostatic potential the emitted electrons experience should be an average of the underlying sample region. Thus the presence of adsorbates on the surface, which will modify the local vacuum level, can result in a broadening of the spectroscopic features. The full widths at half maximum (FWHM's) of peaks Ne-I, Ne-II, and Na are plotted in the second panels of Figs. 3–6 versus Na coverage  $\Theta$ . As can be seen, in all cases, the linewidths of the atomic peaks first increase, reaching their maximum values, then decrease, and finally level off for a large amount of Na deposition. This coverage dependence of the peak widths, similar for all three atomic features, reflects the increasing inhomogeneity of the local surface electrostatic potentials in the very initial stage of interface formation and the subsequent gradual evolution of the overlayer toward a more homogeneous Na film.

The presence of only one single component in all transition lines clearly indicates an essentially uniform distribution of the deposited Na atoms on the surface, without formation of large clusters or patches. We would like to stress that the rigid shift seen for all the atomic peaks upon Na deposition implies that these decays occur sufficiently far away from the surface so that the average electrostatic potential to be experienced is the same for electrons emitted in these atoms. The broadening of the transition lines, on the other hand, is a consequence of the nonflatness of the vacuum level over the surface and the variation of the FWHM can be somehow regarded as a measure of the amplitude of the modulation around the mean value of  $\Phi$ .

It is interesting to note that, for all systems, the initial fast drop of the average surface work function is accompanied by an increase of the widths of all the atomic transition lines and the subsequent slower reduction in  $\Phi$  corresponds to a simultaneous decrease of the FWHM. We

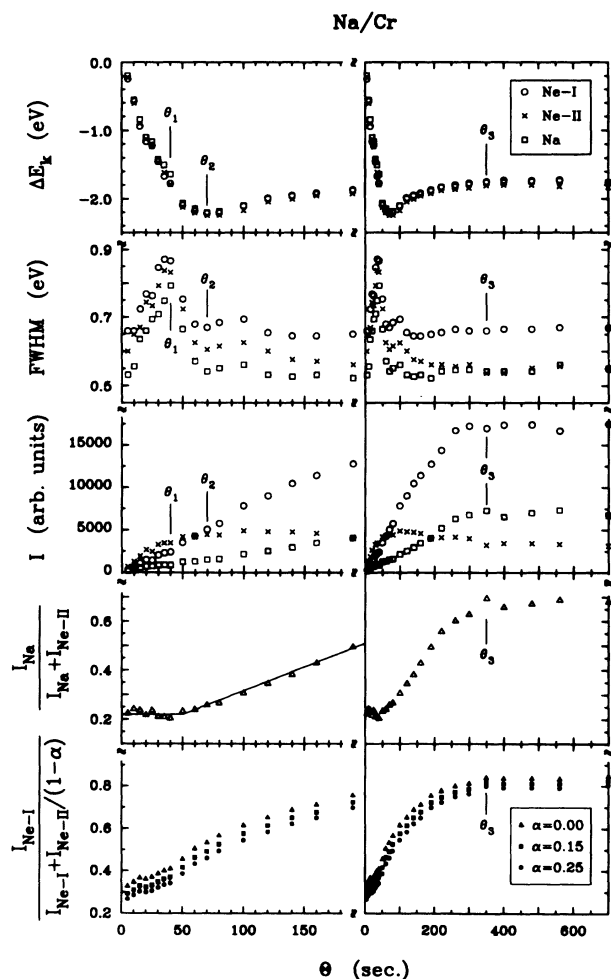


FIG. 3. Energy shift, linewidth, and intensity of Ne-I, Ne-II, and Na autoionization peaks shown in Fig. 1 versus Na coverage (expressed in deposition time) for Na/Cr. Also shown are the intensity ratios as a function of Na coverage, relevant for the discussion on inner-shell vacancy transfer from Ne  $2p^4(^1D)$  to Na and on Ne  $2p^4$  singlet to triplet conversion.

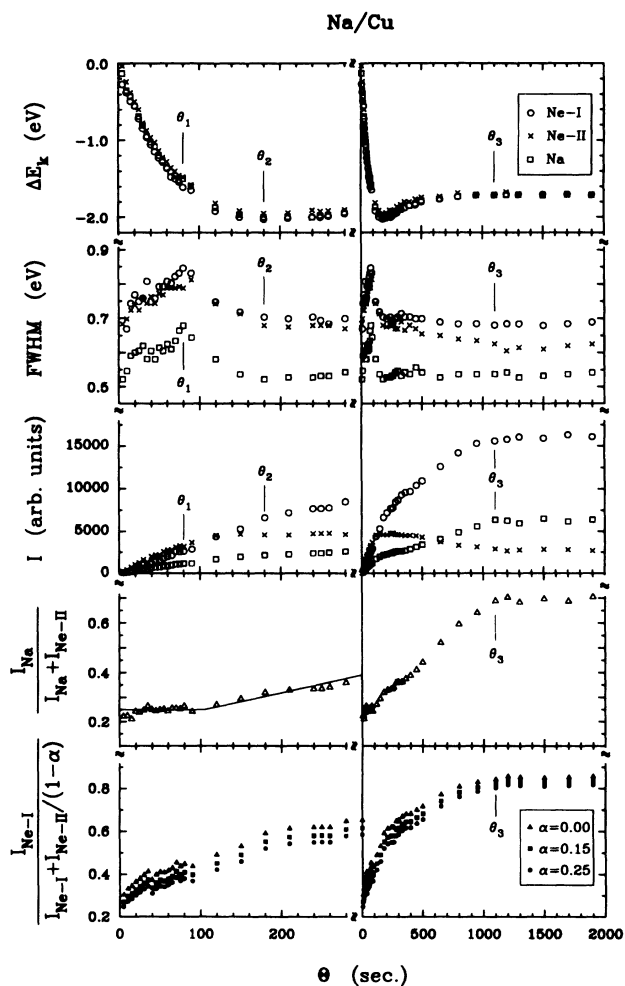


FIG. 4. Same as Fig. 3 but for Na/Cu.

notice that at the same  $\Theta_1$  the work function variation undergoes a change in its slope and the peak widths reach their maximum values, that at the same  $\Theta_2$   $\Phi$  reaches its minimum and the decrease in the FWHM slows down, and that at the very same saturation coverage  $\Theta_3$  all of them start to level off. These observations confirm that the variation of the average surface work function is strongly correlated to the evolution of the peak widths.

For  $\Theta < \Theta_1$ , the deposited Na atoms are well spread over the surface and a charge transfer from the Na adatoms to the substrate or a polarization of the Na  $3s$  electron toward the substrate occurs, resulting in the formation of surface dipoles.<sup>23-26</sup> In this coverage range, the large difference between the local electrostatic potentials at the adsorbate Na and substrate metal sites causes a broadening of the transition lines, and the inhomogeneity of the surface potentials is expected to be roughly proportional to the adatom density. As more surface area is covered by Na ( $\Theta_1 < \Theta < \Theta_2$ ), the electrons emitted from the excited Ne<sup>\*\*</sup> and Na<sup>\*</sup> atoms experience an increasingly uniform potential determined essentially by that at the Na sites, giving rise to a narrowing of the spectral lines. At the coverage  $\Theta_2$  (corresponding to the minimum value of  $\Phi$ ), the surface is already quite homo-

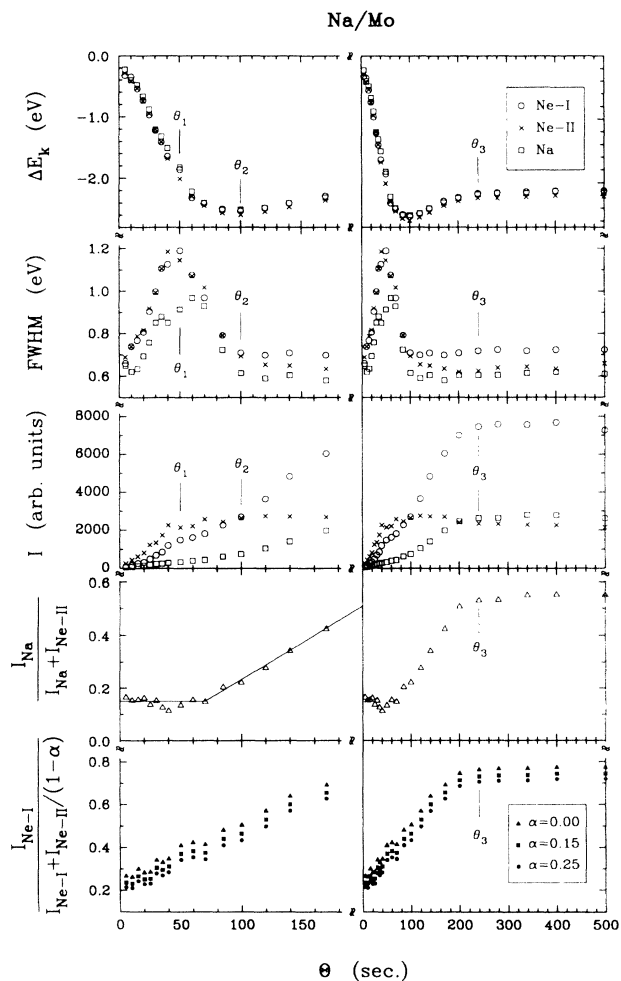


FIG. 5. Same as Fig. 3 but for Na/Mo.

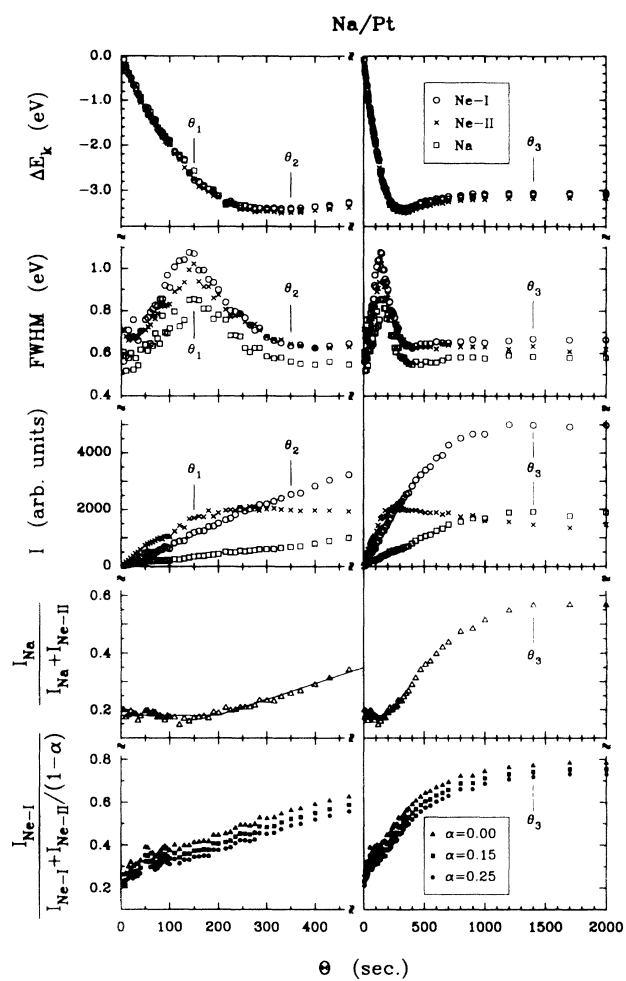


FIG. 6. Same as Fig. 3 but for Na/Pt.

geneous from an electrostatic potential point of view. Thereafter, the depolarization or the weakening of the Na-substrate covalent bonds causes a back increase of the surface work function and at the saturation coverage  $\Theta_3$  all the measurable parameters become constant.

The differences in the FWHM of the Ne-I, Ne-II, and Na peaks for Na-saturated surfaces are mainly due to the differences in the Doppler effects of the scattered Ne\*\* or sputtered Na\* particles. In a recent angle-resolved study of Ne<sup>+</sup> ion bombardment of clean Mg, Lacombe *et al.*<sup>27</sup>

showed a substantial difference in the spatial distribution of the Ne\*\* in the singlet and triplet states. As we will discuss below in detail, the ejected excited Na atoms are mainly produced by the Na-Na symmetric collisions; thus their mean velocity is expected to be significantly lower than that of the scattered Ne\*\* projectiles. It should also be noted that the differences in the FWHM values of the three atomic features do exist in the whole coverage range. This would suggest that the lifetime and Doppler broadening play an important role in determining the

TABLE I. Some values of autoionization electron emission for 700-eV Ne<sup>+</sup>-Na/metal.

Substrate	$\Phi$ (eV)	Clean surface <sup>a</sup>					Na-saturated surface					
		FWHM (eV)			$\rho_0$	$\lambda$	$\Phi$ (eV)	FWHM (eV)			$\rho_{\text{sat}}$	$\lambda_{\text{sat}}$
		Ne-I	Ne-II	Na				Ne-I	Ne-II	Na		
Cu	4.53	0.63	0.65	0.50	0.24	0.30	2.81	0.69	0.63	0.54	0.69	0.86
Cr	4.57	0.62	0.57	0.50	0.18	0.31	2.79	0.67	0.55	0.55	0.68	0.85
Mo	4.72	0.60	0.60	0.53	0.22	0.24	2.59	0.72	0.65	0.62	0.55	0.77
Pt	5.73	0.56	0.61	0.50	0.18	0.30	2.65	0.66	0.62	0.58	0.57	0.78

<sup>a</sup>Values obtained by extrapolation.

overall linewidth of each transition peak, though these contributions are not responsible for the observed behavior versus Na coverage.

As the Na adatom density increases, the Ne-Na collision events and the consequent Ne excitation events should increase accordingly. In the third panels of Figs. 3–6 are plotted the intensities of peaks Ne-I, Ne-II, and Na as a function of the Na coverage. These intensities have been evaluated by calculating the peak areas after background subtraction and have been normalized to the total beam current. It can be noticed that, for all systems, the intensities of the Ne triplet and Na peaks increase steadily toward their saturation values, whereas that of the Ne singlet peak changes its rate at  $\Theta_1$ , decreases slightly at  $\Theta_2$ , and approaches the final value at  $\Theta_3$ .

According to the MO model, during a close collision between a Ne and a Na atom, the electrons in the  $4f\sigma$  MO (correlated to Ne  $2p$ ) will be promoted to the high-lying unfilled MO's, leading to the creation of a Ne  $2p^4(^1D)$  singlet core.<sup>2,3</sup> Olsen *et al.*<sup>14</sup> observed a relatively large Na  $2p$  electron excitation cross section in gas-phase  $\text{Na}^+$ -Ne collisions and determined its efficiency to be  $\sim 0.4$  for  $\text{Na}^+$  impact energy of 6 keV. They attributed it to the  $2p$  core vacancy sharing with Ne  $2p^4(^1D)$  during the separation of the two colliding partners. We note that the probability of such a  $2p$  hole resonance transfer from the screened Ne  $2p^4(^3P)$  triplet to Na is expected to be much smaller than that from the screened Ne  $2p^4(^1D)$  singlet, since the energy deficit is much larger for the former process ( $> 5$  eV) than for the latter one (2 eV). Unlike the gas-phase binary single collisions, Na  $2p$  electron excitation, however, can be produced also in secondary encounters between the target Na-Na atoms, both because the energy transfer in the primary Ne-Na collision can be quite substantial due to their very similar atomic masses and because the threshold energy for the Na  $2p$  excitation in symmetric collisions is expected to be only around 300 eV.<sup>28</sup> To better distinguish these two contributions, in the fourth panels of Figs. 3–6 are shown the intensity ratios between the Na line and the sum of the Na and Ne-II peaks,  $\rho = I_{\text{Na}} / (I_{\text{Na}} + I_{\text{Ne-II}})$ , versus the Na coverage. The very similar  $3s$  binding energies of  $\text{Na}^*2p^53s^2$  and  $\text{Ne}^{**}2p^4(^1D)3s^2$  exclude any substantial difference in their outer-shell electron capture probabilities, causing this ratio to be correlated only to the inner-shell process.

As can be seen, for all systems studied,  $\rho$  remains constant  $\rho = \rho_0$  for a small amount of Na deposition and starts to increase linearly at some coverages between  $\Theta_1$  and  $\Theta_2$  and finally reaches its saturation value  $\rho_{\text{sat}}$  at  $\Theta_3$ . Initially, the Na adatoms are well spread over the surface and their mean distance is large enough so that virtually all the Na excitations are produced by the Ne  $2p$  vacancy transfers whose probability should be independent of  $\Theta$ . It is important to underline that in ion-solid collisions the probabilities of the projectile backscattering and target atom ejection in vacuum depend on the experimental geometry and their determination can be complicated by possible recoiling from the substrate atoms. Therefore  $\rho$  should not be considered as a direct measure of the Ne-

Na  $L$ -shell vacancy-sharing probability.

As the Na adatom density becomes larger, the possibility of a Na recoil to collide with another Na atom increases, so that the contribution of Na-Na encounters to the Na excitation increases accordingly. This mechanism should become dominant for high Na coverage, both because of its low threshold energy and because of its square proportionality to the Na density instead of a linear dependence as for the Ne-Na collisions. We mention that, due to the progressive decrease of the Na sticking coefficient at large  $\Theta$ , the amount of deposited Na atoms is not directly proportional to the exposure time; thus the apparent linear increase of  $\rho$  seen in Figs. 3–6 bears no direct physical meaning. The difference in the final saturation values  $\rho_{\text{sat}}$  for various systems (see Table I) is an indication of the different density or/and thickness of the Na overlayers grown at room temperature on these substrates.

In the framework of the MO model, the Ne  $2p^4(^3P)$  triplet configuration cannot be directly produced in a Ne-Na collision unless there is an initial vacancy present in the  $3d\pi$  MO (correlated to Ne  $2p$ ) in the transiently formed molecule.<sup>14</sup> When approaching the surface, most  $\text{Ne}^+$  ions are neutralized to the  $2p^6$  ground state through an Auger capture (AC) or a resonance neutralization to  $2p^53s$  followed by Auger deexcitation (AD). The initial  $2p$  vacancy in an eventually surviving  $\text{Ne}^+$  or neutralized  $\text{Ne}^0 2p^53s$  can be located in either  $3d\pi$  or  $4f\sigma$  MO's. However, in the former case the  $3d\pi$  hole can again be transferred to  $4f\sigma$  through an AD or be filled via AC during the evolution of this Ne-Na molecule. The probability of the presence of a  $3d\pi$  hole is thus expected to be very small. The nearly identical  $3s$  binding energies of both the singlet and triplet configurations make unlikely any sizable difference in their probability of formation due to differences in outer-shell electron captures.

In a gas-phase  $\text{Na}^+$ -Ne collision experiment Olsen *et al.*<sup>14</sup> reported the observation of a very small Ne triplet line and pointed out that the probability of  $^1D$ - $^3P$  core rearrangement is only a few percent. In an early study, Zampieri, Maier, and Baragiola<sup>15</sup> observed a large and very similar Ne triplet-to-singlet intensity ratio when bombarding an Al surface with either  $\text{Ne}^+$  ions or  $\text{Ne}^0$  neutrals. This led them to conclude that the Ne  $2p^4$  triplet core production cannot be attributed mainly to the survival of the  $\text{Ne}^+$  projectile ions before undergoing a hard collision with a target atom and suggested a great enhancement of the core singlet-to-triplet conversion at metal surfaces. In a recent paper<sup>13</sup> we proposed an Auger rearrangement (AR) mechanism for the singlet-to-triplet conversion in which a solid valence electron drops into the empty  $4f\sigma$  and a  $3d\pi$  electron with opposite spin is simultaneously excited to above the Fermi level  $E_F$ . This AR is different from the normal Auger deexcitation because the decay is not to the ground state, the excited electron itself belongs to the same inner orbital, and it requires the two electrons involved to have opposite spins. The electrons that can participate in the AR process should lie within a small energy range below  $E_F$  of width  $\Delta = 3.2$  eV, the energy separation between the atomic singlet and triplet configurations. Thus the con-

version probability should be dependent on the electrons in the interval  $E_F$  and  $E_F - \Delta$  available for the transition. For Na/metal systems these electrons are mainly those of Na 3s character; therefore, the conversion rate in these cases should yield unique information regarding the 3s electron distribution around the Na adsorbate site.

In the lowest panels of Figs. 3–6 are shown the triplet fractions of Ne  $2p^4 3s^2$  autoionization states,  $\lambda = I_{\text{Ne-I}} / (I_{\text{Ne-I}} + I_{\text{Ne-II}})$ . As can be seen, in all cases,  $\lambda$  steadily increases with the amount of deposited Na and approaches a constant value at the respective saturation coverages  $\Theta_3$ . Surprisingly, there does not seem to exist any clear correlation between the triplet fraction and all other quantities which depend somehow on the properties that are averaged over a more or less extended surface region, such as work function variation, peak widths, and the absolute peak intensities. This behavior, instead, would suggest a dependence of the measured  $\lambda$  on the local electronic properties.

In fact, for Auger rearrangement to occur, the  $3d\pi^4$  MO must lie below the  $3d\pi^3 4f\sigma^1$  MO. In gas-phase Ne-Na collisions, this occurs for internuclear distances larger than 1–1.5 Å, where they cross.<sup>14</sup> Since the surface electron density decays exponentially with distance into vacuum, the Auger rearrangement will most probably take place very close to this crossing point where the collision partners are still in a coupled molecular state. This conclusion about the local character of the conversion mechanism is further supported by the observation that the triplet fraction in Ne<sup>+</sup>-Si and Ne<sup>+</sup>-Al collisions is independent of the Cs adatom coverage even though a large variation of  $\Phi$  has been reported.<sup>29</sup>

It should be pointed out that, because of the possible L-shell vacancy sharing between the Ne and Na atoms during their separation, the triplet fraction  $\lambda$  in the detected Ne  $2p^4 3s^2$  autoionization peaks is an overestimate of the real singlet-to-triplet conversion rate. Given that the potential-energy curves of the intervening  $3d\sigma^2$  and  $3d\sigma^1 4f\sigma^1$  MO's calculated by Olsen *et al.*<sup>14</sup> are highly divergent at small internuclear distances  $R$  and become parallel only at  $R$  much larger than that at which the  $3d\pi^4$  and  $3d\pi^3 4f\sigma^1$  MO's cross over, the resonance vacancy transfer could occur only in those molecules which have survived the Auger rearrangement process. Thus, by denoting the vacancy-sharing probability with  $\alpha$ , the total Ne singlet core having survived the AR is  $I_{\text{Ne-II}} / (1 - \alpha)$  and the true singlet-to-triplet conversion rate  $\eta$  should be evaluated as

$$\eta = \frac{I_{\text{Ne-I}}}{I_{\text{Ne-I}} + I_{\text{Ne-II}} / (1 - \alpha)} = \frac{1 - \alpha}{1 - \alpha\lambda} \lambda.$$

The  $\eta$  so calculated are also plotted in Figs. 3–6 for two selected values of  $\alpha = 0.15$  and  $\alpha = 0.25$  (note the curves with  $\alpha = 0$  are the experimentally determined triplet fraction  $\lambda$ ).

The nonconstancy of  $\eta$  even in the very low coverage range would suggest a continuous evolution of the local electronic properties at the target Na atom site, in particular, a continuous variation either of the 3s electron polarization or of the charge transfer from the Na adatom

to the substrate. A further support to this conclusion comes from the nonmonotonic behavior of the Ne  $2p^4$  singlet-to-triplet conversion rate for Na adsorbed on Mg, Al, and Si surfaces, where collision between Ne and substrate atoms can also produce Ne excitation.<sup>29</sup> This is in agreement with the observation by Woratschek *et al.*<sup>30</sup> of K 4s state occupation even in the very initial stage of K adsorption on Cu(110), and with the coverage dependence of the Na 2p core-level binding energy reported by Shi *et al.*<sup>20</sup> for Na/Cu(111) and Na/Ni(111), and is also consistent with the results of Lindgren, Svendsen, and Wallden<sup>31</sup> regarding the continuous decrease of the dynamic dipole charge in an electron energy-loss study of Na/Cu(111). Wimmer *et al.*<sup>25</sup> and Ishida<sup>26</sup> proposed that the alkali-metal adatom is essentially neutral in all coverages and its valence electron is only polarized toward the substrate without a real charge transfer. This is confirmed by Citrin and co-workers<sup>32,33</sup> in recent photoemission studies in which only very little change in the binding energy of the surface component of the substrate W 4f emission was observed for Na, K, and Cs adsorption on W(110). Ishida<sup>26</sup> further suggested the coverage dependence of the adatom polarization due to the hybridization of adatom and substrate orbitals even at low  $\Theta$ . Though our results for the conversion rate cannot provide a clear distinction between a continuous charge transfer and a continuous variation of 3s electron polarization, the steady increase of  $\eta$  through the whole coverage range definitely excludes an abrupt overlayer metallization, as proposed in some alkali-metal adsorption studies.<sup>23,24</sup>

The saturation values of the experimentally determined Ne  $2p^4$  triplet fraction  $\lambda_{\text{sat}}$  are slightly different for the four systems investigated. From Table I we can see that a larger  $\lambda_{\text{sat}}$  value corresponds to a larger  $\rho_{\text{sat}}$ , i.e., a greater amount of deposited Na. This, on one hand, confirms that the Na overlayer grown at room temperature on metal substrates is only one or a few monolayer thick; on the other, it suggests that a slight charge transfer or 3s electron polarization still exists even at Na saturation coverages, at least for Mo and Pt substrates.

#### IV. CONCLUSIONS

In conclusion, we have presented a detailed study on the autoionization electron emission from both backscattered Ne projectiles and sputtered Na target atoms for Na adsorption on four different transition-metal substrates (Cr, Cu, Mo, and Pt). We have demonstrated the great potential of low-energy collisionally excited autoionization spectroscopy in studies of interface formation with alkali-metal overlayers. The main results can be summarized as follows.

(1) The change of the kinetic energies of the detected autoionization electrons can be used to measure directly the average surface work function variation  $\Delta\Phi$ . The absence of two distinct components in each transition line and the rigid shift of all the peaks indicate a uniform growth of the Na overlayer without the formation of large clusters or patches.

(2) The peak-width evolution can also provide direct

information on the surface morphology. The presence of adsorbates on the surface and the consequent inhomogeneity of the local electrostatic potentials can cause a broadening of the spectroscopic features. In the case of Na adsorption on transition-metal substrates, the behavior of the FWHM of all the atomic peaks is strictly correlated to that of  $\Delta\Phi$  and indicates that at the coverage corresponding to the work function minimum the surface is already uniform from an electrostatic point of view.

(3) The absolute intensities of the autoionization peaks, in general, depend on both the inner-shell excitation and outer-shell electron capture processes. However, the nearly identical 3s binding energies of  $\text{Ne}^{**}2p^4(^1D)3s^2$ ,  $\text{Ne}^{**}2p^4(^3P)3s^2$ , and  $\text{Na}^*2p^53s^2$  states makes their intensity ratio independent of the neutralization mechanism, yielding unique information on the inner-shell processes. The constancy of  $\rho = I_{\text{Na}} / (I_{\text{Ne-II}} + I_{\text{Na}})$  at low coverages further confirms the uniform Na distribution on the surface. The subsequent increase of  $\rho$  suggests the increasing contribution of the Na-Na symmetric collision to the Na excitation, and the difference in the final saturation values for various systems studied indicates the difference in the overlayer density or/and thickness at saturation coverages.

(4) An intense transition line from the  $\text{Ne } 2p^4(^3P)3s^2$  triplet configuration has been observed and its formation is attributed to the conversion of a collisionally produced  $2p^4(^1D)$  singlet core at metal surfaces through an Auger rearrangement mechanism involving solid valence electrons. The singlet-to-triplet conversion rate is found to increase steadily with the Na coverage and no clear correlation with such averaged physical quantities as work function change, peak widths, and absolute intensities has been observed. This conversion process is well localized at the excitation site and depends on the local electronic properties. The steady increase of  $\eta$  even in the very initial stage of interface formation suggests a continuous variation of the 3s polarization toward the substrate or a continuous charge transfer from the Na adatoms to the substrate without an abrupt metallization of the overlayer.

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