

## Unusual Metastable-Quenching Spectrum of K/Ni(111) and its Explanation by a New Quenching Mechanism

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We present helium metastable-quenching spectra of K/Ni(111) whose spectral features show unusual coverage dependence. These are explained by a mechanism in which the surface ionizes the incident singlet  $\text{He}^*$  and then neutralizes the ion to form a  $\text{He}^*$  triplet. These spectra reflect the fact that the local work function varies strongly along the surface.

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Since adsorbed alkali-metal atoms promote several major catalytic reactions there is great interest in their electronic properties. These can be profitably studied by using a relatively new surface science technique, metastable-quenching spectroscopy (MQS).<sup>1</sup> This exposes the surface to a thermal beam containing long-lived (metastable) excited atoms which cause electron ejection from the outermost orbitals of the surface. The MQ spectrum is the plot of the number of electrons ejected with a given kinetic energy and contains information concerning the electronic state of the surface. The advantage of the method is its surface specificity; under special circumstances additional information is provided by the fact that a metastable atom is a localized excitation source.

In this Letter we report several MQ spectra of a K/Ni(111) surface, obtained by using a  $\text{He}^*(2^1S)$  beam, whose spectral features depend in an unusual way on the potassium coverage  $\theta_K$ . We present a number of experiments which suggest that our observations can be explained by the assumption that, in a certain coverage range, the surface converts the singlet  $\text{He}^*$  into a triplet. We propose for this transformation a mechanism in which the incident singlet  $\text{He}^*$  is ionized by resonant charge transfer to the surface and the  $\text{He}^+$  ion thus formed is then resonantly neutralized to produce a triplet  $\text{He}^*$ . The latter is then quenched by the surface, through Penning ionization (PI), producing the unexpected features in the MQ spectrum.

The  $\text{He}^*$  MQ spectra of several K/Ni(111) surfaces having various potassium coverages are shown in Fig. 1. The apparatus<sup>1c</sup> and the method of potassium deposition<sup>2</sup> have been described previously. Since the MQ spectra are extremely sensitive to the presence of impurities, generated by the potassium source or present in the UHV system, we prepared each K-overlayer sample by deposition of K multilayers followed by heating which desorbed K (and the impurities) and achieved the desired submonolayer coverage. The sample was then cooled to 90 K and its MQ spectrum was immediately taken. Then the surface was heated again to higher temperature, to achieve lower  $\theta_K$ , recooled for taking a new MQ spectrum, etc. To avoid contamination the coverage was not measured during

this series of MQS measurements: It was calibrated separately, by repeating exactly the same heating pattern and taking the Auger spectra of the surface. The K/Ni peak-to-peak intensity ratio was previously<sup>3</sup> related to the coverage by Auger, thermal desorption, and LEED measurements.<sup>3</sup> Because of this procedure the coverage at which the MQ spectra were taken is not accurately known.

The number of peaks in Fig. 1 is larger than what is expected on the basis of known properties of the surface and the accepted quenching mechanisms.<sup>1</sup> Since  $\text{He}^*$  has two metastable states, a singlet  $\text{He}^*(2^1S)$  and a triplet  $\text{He}^*(2^3S)$ , it is reasonable to suspect that the

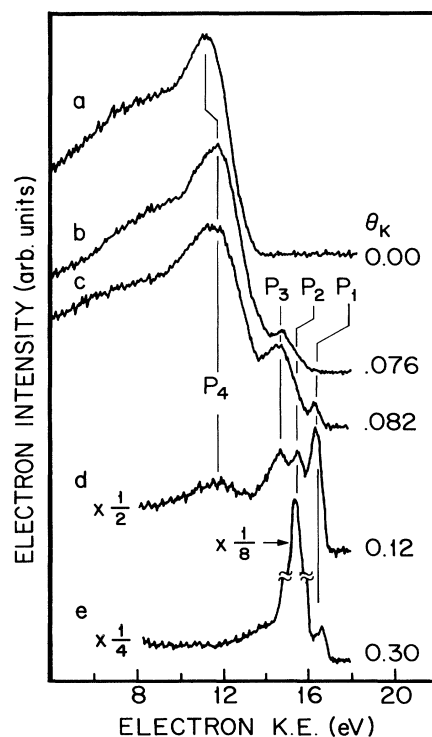


FIG. 1. The metastable-quenching spectra of a K/Ni(111) surface for various potassium coverages. The spectra were taken at a surface temperature of  $\sim 100$  K and a background pressure of  $\sim 10^{-10}$  Torr.

additional peaks might be due to the presence of a singlet-triplet mixture in the beam. To find out the singlet/triplet ratio in the He\* beam we installed a He lamp<sup>4</sup> inside the beam preparation chamber and used the 2.06- $\mu\text{m}$  resonance line to excite He\*( $2^1S$ ) to the  $2^1P$  state and thus remove most of the singlet from the beam. To find the singlet/triplet ratio in the beam we used the MQ spectrum of a Ni(111) surface saturated with CO.<sup>1c</sup> In Fig. 2 we show the spectra obtained with the quench lamp (QL) on and off. Turning the lamp on shifts the Penning peaks in the CO spectrum by 0.7 eV, which is (within the experimental error) equal to the difference between the singlet and the triplet excitation energy (which is 0.8 eV). This indicates that the singlet was efficiently removed by the lamp. The fact that turning on the lamp lowers the intensity by a factor of 10 means that the He\* beam has roughly 90% singlet content (the quenching yield is 1 for both singlet and triplet).

To show unambiguously that some peaks in the MQ spectra are generated by He\*( $2^3S$ ) we measured the spectrum of a K/Ni(111) surface with  $\theta_K=0.14$ , with the quench lamp on and off. We find (Fig. 3) that when the He\* beam contains the triplet only (i.e., QL on) the spectrum has two peaks ( $P_3$  and  $P_2$ ). The addition of singlet to the He\* beam (i.e., QL off) produces two new peaks, denoted  $P_4$  and  $P_1$ . This evidence that the multiple peaks are related to the presence of a singlet-triplet mixture is strengthened by the fact that the MQ spectra taken with Ar\* and Ne\*, for which the singlet-triplet splitting (0.1 eV) is much too small to cause multiple peaks, are identical with that given by the beam containing the triplet He\* only.

We can now proceed to assign the peaks present in Figs. 1 and 3. Curve *a* in Fig. 1 is the ion neutralization (IN)<sup>1,5</sup> spectrum of Ni(111).<sup>1a</sup> This is produced because the work function  $\phi_\infty=5.3$  eV exceeds the ionization potential of both He\*( $2^1S$ ) (3.9 eV) and He\*( $2^3S$ ) (4.7 eV) and He\* is resonantly ionized and

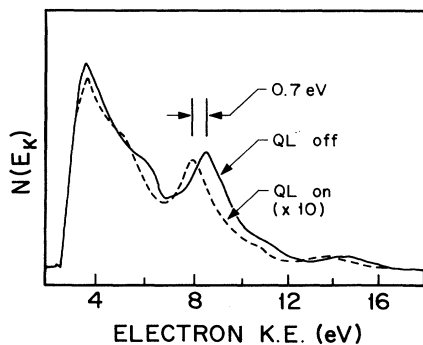


FIG. 2. The metastable-quenching spectra of CO/Ni(111) at saturation coverage, with the quench lamp (QL) on and off. Pressure and temperature as in Fig. 1. The intensity for the QL-on spectrum is multiplied by 10.

the He\* ion is subsequently Auger neutralized.<sup>1,5</sup> The measured signal gives the kinetic energy distribution of the Auger electrons. The addition of a very small amount of K (i.e.,  $\theta_K=0.076$ ) leads to spectrum *b*, Fig. 1. We assign the peak  $P_4$  to the IN spectrum of Ni sites because it appears at roughly the same energy as the IN Ni peak of curve *a*, Fig. 1. The peak  $P_3$  is assigned to the PI spectrum of the Ni  $3d$  orbitals generated by He\*( $2^3S$ ) because (a) the peak  $P_3$  is present in Fig. 3 when the quench lamp is on and the beam contains mostly triplet He\*, and (b) the kinetic energy of the  $P_3$  peak corresponds to Ni  $3d$  electrons ejected by the triplet He\*. We do not observe in spectrum *b* of Fig. 1 any signal that we can associate with potassium emission, in spite of the fact that MQS is very surface sensitive and that the presence of K changes the work function and the quenching mechanism. An increase in potassium coverage causes the gradual appearance of the new peaks  $P_1$  and  $P_2$ . We assume that  $P_1$  and  $P_2$  correspond to emission from the K  $4s$  orbitals generated by the singlet and the triplet He\*, respectively. We made this assignment because (a)  $P_1$  disappears when the singlet is removed from the beam (Fig. 3, QL on); (b) the  $P_1$ - $P_2$  splitting is the same as the singlet-triplet splitting in He\*; (c) these two peaks are the only ones present in the spectra taken at high potassium coverage (e.g., spectrum *e* in Fig. 1) and therefore must originate from potassium. The latter observation also supports the assignment of  $P_3$  and  $P_4$  to Ni emission.

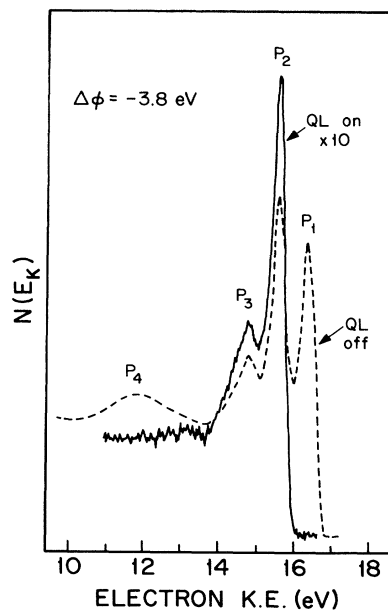


FIG. 3. The metastable-quenching spectra of K/Ni(111) at  $\theta_K=0.14$ , with the quench lamp (QL) on and off. The temperature and the pressure are as in Fig. 1. The intensity of the QL-on spectrum is multiplied by 10.

While the simultaneous presence of the singlet and the triplet in the  $\text{He}^*$  beam can explain the existence of four peaks in the MQ spectrum, it does not explain why the addition of singlet atoms to the beam causes an eightfold increase in the intensity of the peak  $P_2$  (associated with the triplet). Nor does it explain why in the QL-off spectrum the  $P_2$  peak (generated by the triplet) has a higher intensity than the  $P_1$  peak (generated by the singlet) even though the singlet concentration in the incident beam is 90%. Furthermore, it is not clear why the character of the spectra changes very substantially with  $\theta_K$  (see Fig. 1) while the singlet/triplet ratio in the incident beam is the same for all coverages.

These observations can be reasonably explained by the assumption of the existence of a new quenching mechanism which works in parallel with the ones already documented<sup>1</sup> in the literature: The singlet  $\text{He}^*$  is resonantly ionized by electron transfer to the surface to form  $\text{He}^+$ ; this is resonantly neutralized by electron transfer from the surface to form triplet  $\text{He}^*$ ; the triplet is then Penning ionized by the surface. These newly formed triplet atoms are responsible for the excess triplet emission observed in our measurements. The change of the spectrum with potassium coverage reflects the fact that different quenching mechanisms take place at different surface sites; a change in coverage varies the proportion in which different sites are present, and hence the relative yields of different quenching mechanisms, which in turn affects the shape of the MQ spectra.

We can understand the processes invoked here in terms of the following functions: the energies  $I^1(\mathbf{r})$  and  $I^3(\mathbf{r})$  required to ionize the singlet and the triplet  $\text{He}^*$ , respectively, when the atom is located at  $\mathbf{r}$ ; and the energy  $\phi(\mathbf{r})$  gained by taking an electron of zero kinetic energy located at  $\mathbf{r}$  and placing it at the Fermi level. In the language of the one-electron theory  $I^1(\mathbf{r})$  and  $I^3(\mathbf{r})$  specify the location of the singlet and the triplet levels below the local vacuum level.  $\phi(\mathbf{r})$  gives the position of the local vacuum level with respect to the Fermi level (which is the same throughout the sample and is equal to the detector Fermi level). One could call  $\phi(\mathbf{r})$  the local work function. Since adsorbed potassium is partly ionized we expect strong electric fields<sup>6</sup> along the surface and therefore the electron local vacuum level is different at different surface sites.

This is relevant to the present study because energy conservation and the Pauli principle impose constraints on the processes of interest here, which can be expressed in terms of  $\phi(\mathbf{r})$ ,  $I^1(\mathbf{r})$ , and  $I^3(\mathbf{r})$ .  $\text{He}^*(2^1S)$  [or  $\text{He}^*(2^3S)$ ] can be resonantly ionized when they are at the point  $\mathbf{r}$  only if  $I^1(\mathbf{r}) \leq \phi(\mathbf{r})$  [or  $I^3(\mathbf{r}) \leq \phi(\mathbf{r})$ ], since these conditions assure that the singlet (or triplet) levels resonate with empty metal states.

$\text{He}^*(2^1S)$  [or  $\text{He}^*(2^3S)$ ] are quenched by Penning ionization if  $I^1(\mathbf{r}) > \phi(\mathbf{r})$  [or  $I^3(\mathbf{r}) > \phi(\mathbf{r})$ ] since the levels resonate with filled states. The  $\text{He}^+$  ion can be resonantly neutralized to  $\text{He}^*(2^1S)$  [or  $\text{He}^*(2^3S)$ ] if  $I^1(\mathbf{r}) > \phi(\mathbf{r})$  [or  $I^3(\mathbf{r}) > \phi(\mathbf{r})$ ] since the empty singlet (or triplet) level resonates with filled metal states. If  $I^1(\mathbf{r})$  and  $I^3(\mathbf{r})$  are less than  $\phi(\mathbf{r})$ ,  $\text{He}^+$  is Auger neutralized producing an ion neutralization spectrum.

With these in mind we can now examine the data.  $\text{He}^*(2^1S)$  is ionized by the Ni(111) surface and because  $\phi(\mathbf{r}) > I^3(\mathbf{r})$  no neutralization of the newly formed  $\text{He}^+$  to  $\text{He}^*(2^3S)$  is observed; the spectrum is IN. At very low K coverage the interpretation of the data is slightly ambiguous in the sense that the small triplet peak  $P_3$  might originate from the  $\text{He}^*(2^3S)$  initially present in the beam, while the IN spectrum  $P_4$  might be due to the ionization of the  $\text{He}^*(2^1S)$ ; or we might assume that some triplet was formed by the new mechanism proposed here. The ambiguity disappears for the higher coverages used to obtain spectra *c* and *d* in Fig. 1 and the spectra in Fig. 3. The large excess of triplet-generated signal can only be explained by a mechanism in which the surface transforms the incident  $\text{He}^*$  singlet into triplet  $\text{He}^*$ . This can happen if the particle goes successively through the positions  $\mathbf{r}$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$  and  $I^1(\mathbf{r}_1) < \phi(\mathbf{r})$ , so that  $\text{He}^*(2^1S) \rightarrow \text{He}^+$  takes place; then  $I^3(\mathbf{r}_2) > \phi(\mathbf{r}_2)$ , so that  $\text{He}^+ \rightarrow \text{He}^*(2^3S)$ ; and finally,  $I^3(\mathbf{r}_3) > I^1(\mathbf{r}_3)$  and Penning ionization of the triplet occurs. This mechanism is strongly supported by Hagstrum's important observation<sup>7</sup> that a  $\text{He}^+$  beam colliding with a potassium-covered surface produces  $\text{He}^*(2^3S)$ . The presence of Ni 3*d* and K 4*s* emission by triplet quenching indicates that  $\mathbf{r}_3$  could be either a site at which the Ni 3*d* orbitals contribute substantially to the outermost surface orbitals (the only ones accessible to Penning ionization), or one at which the K 4*s* orbitals make a major contribution. We refer to these as Ni and K sites, respectively. Note that the simultaneous presence of  $P_4$  and  $P_3$  shows that the sequence mentioned above is not the only one possible. At some surface sites  $\phi(\mathbf{r})$  is such that  $\text{He}^* \rightarrow \text{He}^+$ , which produces the Ni INS peak  $P_4$ .

Finally, spectrum *e* of Fig. 1 belongs to a surface having high K coverage and the disappearance of  $P_4$  and  $P_3$  indicates that the Ni sites are no longer accessible to the metastables; however, the singlet to triplet conversion is still substantial since the triplet emission exceeds the singlet one (in Fig. 3) even though the beam contains 90% singlet and the quenching has unit efficiency.

The mechanism proposed here seems to describe reasonably well the complex experimental observations which we have presented. Thus, the local nature of the metastable-atom probe allows the inhomogenei-

ty of the local work function  $\phi(\mathbf{r})$  at the surface to manifest itself in observable MQ spectral features, and suggests that the function  $\phi(\mathbf{r})$  has a rather interesting behavior which in principle could be tested by electronic structure calculations. Besides their conceptual importance, such observations might aid our understanding of the catalytic activity of activated surfaces, since the local work function may be related<sup>8</sup> to reactivity in all cases in which the reagents exchange charge with the surface.

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