

Detection by Metastable Quenching Spectroscopy of Enhanced Back-Donation from a Ni(111) Surface to the $2\pi^*$ Orbital of Chemisorbed CO, Caused by Coadsorption of Potassium

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The influence of coadsorbed potassium atoms on the electronic structure of CO adsorbed on Ni(111) was studied by use of surface metastable quenching spectroscopy. An enhancement of electron emission from the partially filled $2\pi^*$ antibonding orbital of CO is observed, and the result is interpreted in terms of increased electron back-donation from the metal to the $2\pi^*$ orbital, caused by potassium atoms.

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Surface additives, such as alkali-metal atoms, are known to be promoters in the Fischer-Tropsch and the methanation reactions.¹ Since CO dissociation is believed to be² the first step in these reactions, an understanding of the interaction between CO and coadsorbed potassium is an important part in the clarification of the reaction mechanisms. Several investigations performed with single-crystal samples under UHV conditions have shown that the coadsorbed potassium atoms increase the strength of the CO surface bond and the dissociation probability of CO on Fe(110),³ Fe(100),⁴ Ni(100),⁵ and Ni(111).⁶ A large red shift of the CO stretch frequency to a value as low as 1400 cm^{-1} was also observed in a recent electron-energy-loss spectroscopy study of CO on K-covered Pt(111).⁷

The behavior of CO adsorbed on transition-metal surfaces has been rationalized by assuming that the binding is accompanied by a back-donation of electrons from the metal into the $2\pi^*$ antibonding orbital of the molecule.⁸ This should have important chemical consequences, since populating an antibonding orbital reduces the CO (or NO) bond strength, making the molecules more reactive. The promoting effects of alkali adsorbates are generally attributed to their ability to transfer electrons to the metal, which leads to enhanced "back-donation." Furthermore, electron-withdrawing additives, such as sulphur, act in an opposite manner, and strengthen the CO bond, thus becoming catalytic poisons.

A large number of observations support these ideas⁹ but there is no direct evidence that the presence of alkali atoms increases the electron population of the $2\pi^*$ orbital of CO. In this Letter we use metastable quenching spectroscopy (MQS)¹⁰ to provide such evidence. This consists of using a thermal beam of noble-gas atoms containing atoms excited to a long-lived (metastable) electronic state. In favorable cases, the metastable

atom A^* coming in contact with an adsorbed molecule B transfers its excitation energy to B , causing electron emission by Penning ionization ($A^* + B \rightarrow A + B^+ + e^-$). The MQ spectrum, consisting of the kinetic energy distribution of the emitted electrons, has peaks which contain information regarding the electron binding energies of the adsorbate. In particular, one of the peaks will correspond to emission from the $2\pi^*$ orbital filled by back-donation.

While the electron kinetic energy spectrum generated in an MQS experiment has the same information as an ultraviolet photoelectron spectrum (UPS) taken at a photon energy equal to the excitation energy of the metastable atom,¹⁰ the MQS has the advantage of a greater surface specificity. This is due to the fact that the metastable atom transfers energy through orbital overlap with the adsorbate, thus ionizing only the molecular orbitals protruding from the surface. Therefore, in MQS all primary electrons originate from the adsorbate, while in UPS most of them originate from the metal. Since the $2\pi^*$ orbital straddles the $3d$ bands of the Ni substrate, the surface specificity of MQS is essential for its detection;¹¹ in UPS the $3d$ emission from the Ni surface covers completely the photoemission from the $2\pi^*$ orbital.

The detailed description of the experimental system was given elsewhere.^{10c} Potassium was deposited on the Ni(111) sample at 300 K by heating a getter wire (SAES getter) impregnated with K. The absolute surface coverage was calibrated by using low-energy electron-diffraction, thermal-desorption, and Auger-electron-spectroscopy measurements.¹¹ A monolayer of K on Ni(111) was found to correspond to a surface density of $\sigma_K \approx 6.3 \times 10^{14}$ atoms/cm². This corresponds to a potassium coverage θ_K of 0.34 potassium atom per surface nickel atom.

The MQS measurements were carried out by

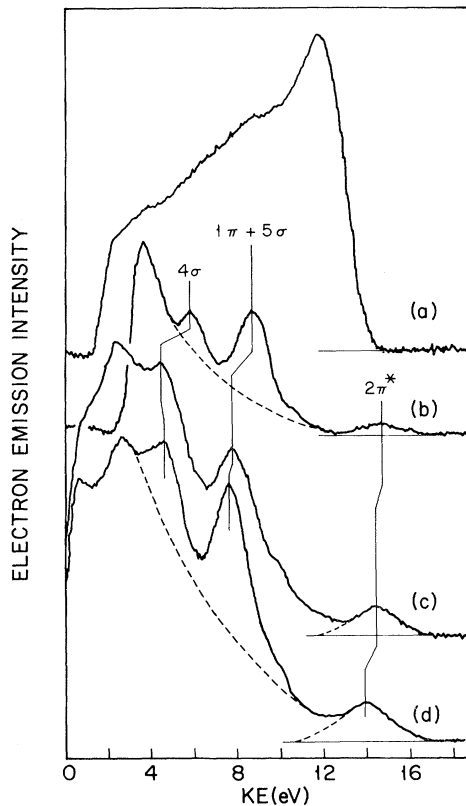


FIG. 1. $\text{He}^*(2^1S)$ quenching spectra taken at 90 K. The electron current is plotted vs electron kinetic energy. Curve *a*, clean Ni(111); curve *b*, 3.2 L CO on Ni(111); curve *c*, 1.2 L CO on K-covered ($\theta_K = 0.11$) Ni(111); curve *d*, 3.2 L CO on K-covered ($\theta_K = 0.11$) Ni(111). The peak assignments are given in Table I. The Fermi level is at 16.9 eV.

using a $\text{He}^*(2^1S)$ beam produced by passing a He supersonic beam through a Penning discharge. The He^* beam incidence was normal to the surface. The electrons emitted from the surface were energy analyzed with a four-grid retarding-field analyzer. The energy resolution in the present work is estimated to be better than 0.5 eV.

In Fig. 1, curve *a* represents the MQ spectrum of a clean Ni(111) surface. This is the result of the resonant ionization of He^* by the surface, followed by the Auger neutralization of the ion.^{10c} The other curves represent the Penning-ionization spectra for various surfaces covered with CO: curve *b*, a Ni(111) surface exposed to 3.2 L CO [1 langmuir (L): the surface has been exposed for 1 sec to CO gas whose pressure is 10^{-6} Torr]; curve *c*, a K/Ni(111) surface with $\theta_K = 0.11$ potassium atom per surface nickel atom, exposed to 1.2 L CO; and curve *d*, the same K/Ni(111) surface exposed to 3.2 L CO. The peak energies in the Penning-ionization spectrum are essential-

TABLE I. Electron binding energies of CO/Ni(111) and (CO + K)/Ni(111) with respect to the Fermi level of the sample.

Orbitals	CO ^a	(CO + K) ^b	(CO + K) ^c
4σ (CO)	10.9	12.4	12
$(1\pi + 5\sigma)$ (CO)	8.0	8.7	9.1
$2\pi^*$ (CO)	2.1	2.5	3
K ^d	...	0.3	0.3

^aCO exposure 3.2 L.

^b $\theta_K = 0.11$ and CO exposure 1.2 L.

^c $\theta_K = 0.11$ and CO exposure 3.2 L.

^dPotassium emission was measured in Ref. 12.

ly the same as would be obtained from an ultraviolet photoelectron spectrum at a photon energy of 20.6 eV, which is the internal energy of the excited 2^1S He^* atom. The assignment of the peaks and the resulting electron binding energies are presented in Table I.

The procedure used to establish the kinetic energy scale and derive the binding energy is briefly described below. The graphs in Fig. 1 represent the kinetic energy of the emitted electrons given by the energy analyzer. The fact that the curves *a* and *b* start at kinetic energies higher than zero indicates that the work function ϕ_d of the detector is smaller than the work function ϕ_s of the sample; in particular $\phi_s - \phi_d = 1.5$ eV, for curve *a* [clean Ni(111)] and $\phi_s - \phi_d = 2.7$ eV for curve *b* [3.2 L CO on Ni(111)]. Using $\phi_s = 5.3$ eV for clean Ni(111) and $\phi_s = 6.3$ eV for 3.2 L CO on Ni(111), we obtain $\phi_d = 3.8$ and 3.6 eV, respectively. Since the analyzer grids are fully contaminated with all the adsorbates used previously in the chamber, we assume that ϕ_d is unchanged during the full set of experiments. Doing the same measurements within days shows no drift in the measured electron kinetic energy, and hence no change in ϕ_d . The slight differences between the two values of ϕ_d obtained above is caused by the imperfect energy resolution and the uncertainty in the precise location of the low-energy cutoff on the graphs. We take, therefore, the average value $\phi_d = 3.7$ eV. Using this value we can now compute the binding energy E_{BF} (with respect to the Fermi level of the sample), corresponding to a given electron kinetic energy E_k , from $E_{BF} = (20.6 \text{ eV}) - E_k - (3.7 \text{ eV})$. This formula and the peak kinetic energies taken from Fig. 1 lead to the binding energies shown in Table I. The value for potassium is from our unpublished work.¹²

Before concentrating on the main observations of this article we make several remarks. The $2\pi^*$ orbital overlaps with the $3d$ band of the Ni surface. In an UPS experiment the $3d$ emission will completely cover the $2\pi^*$ peak. The fact that no $3d$ emission is present in the Penning spectrum, because of the surface specificity of the excited-atom probe, permits the $2\pi^*$ detection. The growth of the peaks with CO exposure confirms that the peaks are associated with the CO orbitals.

The presence of potassium on the surface causes several spectral changes which need to be emphasized and explained: (a) The CO Penning emission in the presence of K [Fig. 1(d)] is more intense than in its absence [Fig. 1(b)] even though thermal-desorption experiments⁶ show that at equal exposures the CO uptake of the clean and potassium-covered surfaces is the same. (b) The relative intensity of the $2\pi^*$ emission increases with respect to the 4σ and $1\pi + 5\sigma$ peaks.

The overall enhancement of the CO Penning spectrum by potassium is explained by the following observation¹³: A 2^1S He* atom approaching the surface can be ionized by electron transfer to the surface or it can be quenched by the Penning ionization of CO. Normally both these processes take place with finite probability and compete for He* atoms. Conditions favorable to resonant ionization weaken the Penning emission and *vice versa*. The presence of potassium on the surface lowers the work function to the extent that the excited electron of the He* 2^1S atom resonates with filled states of the surface. As a result, He* ionization becomes extremely improbable and almost all the metastable atoms are quenched by Penning ionization. As a result, the intensities of all the CO peaks in the Penning spectrum of CO on K/Ni(111) are increased.

The enhancement of the $2\pi^*$ peak intensity is, however, larger than that of the other CO peaks, as can be seen qualitatively from Fig. 1. To see this more clearly, we need a method of removing the underlying broad secondary electron emission. To do this subtraction, we used the measured secondary electron emission due to a 150-eV electron beam. This is the lowest energy at which our electron gun gives enough electron current to carry out the measurement. This choice should not affect the results since the low-energy distribution part of the secondary emission is not affected by the incident electron energy.¹⁴ The result of the subtraction is given in Fig. 2. The $2\pi^*$ -peak enhancement (as meas-

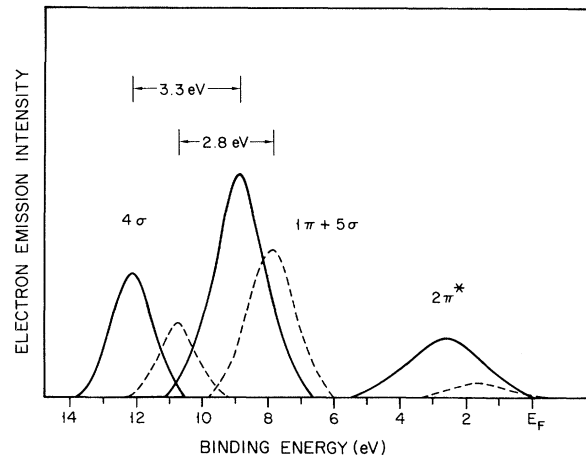


FIG. 2. Comparison of the 4σ , $1\pi + 5\sigma$, and $2\pi^*$ CO peak intensities after subtraction of the background contribution by the secondary electrons. 3.2-L CO exposure at 90° K on Ni(111) (dashed line) and on K-covered ($\theta_K=0.11$) Ni(111) (solid line).

ured by the relative areas under the peaks) is a factor of about 4.26, whereas the enhancement factors for the 4σ and $1\pi + 5\sigma$ peaks are 2 and 1.6, respectively. Although this analysis is crude, as a result of the uncertainty involved in the background estimation, a more pronounced enhancement of electron emission is clearly seen for the $2\pi^*$ peak.

We end this discussion of results with several remarks. (a) The addition of potassium causes shifts in the Penning-ionization peak positions. These are best seen in Fig. 2, in which we plot the electron binding energy with respect to the Fermi level. The peak shifts are caused by molecular changes induced by the presence of potassium. Large shifts have also been observed by UPS for CO on K/Fe(110)^{3a} and on K/Pt(111).^{3b} (b) The absence of any electron emission from K is due to the fact that CO absorption on K/Ni(111) screens the potassium from interaction with the metastable atoms.¹³ Removal of CO by desorption results in the appearance of a K peak at high electron kinetic energy.¹³ (c) The dependence of the $2\pi^*$ emission enhancement on potassium coverage is very weak.¹³ About the same amount of enhanced $2\pi^*$ emission is seen in the coverage range $0.05 \leq \theta_K \leq 0.24$. At higher K coverages the CO uptake by the Ni(111) surface is strongly diminished and this depresses the CO Penning spectrum. (d) The existence of the $2\pi^*$ orbital of chemisorbed CO has been observed by other groups: Young and Gomer¹⁵ by field emission; Koel, Peebles, and White¹⁶ by elec-

tron energy loss; Himpfel and Fauster¹⁷ by inverse photoemission spectroscopy; and Loubriel *et al.*¹⁸ by observing a satellite in the x-ray photoemission spectrum. The position of the $2\pi^*$ orbital in these measurements varies, since they are measuring different quantities. In Penning and field emission it is a $\text{CO} \rightarrow \text{CO}^+$ transition, in electron energy loss a $\text{CO} \rightarrow \text{CO}^*$ transition, in inverse photoemission a $(\text{CO}^-)^* \rightarrow \text{CO}^-$ transition, etc. Furthermore some methods detect the filled part of the orbital^{15, 16} and some the empty one.^{17, 18} All methods that measure the filled part are in agreement in placing the $2\pi^*$ orbital at $\sim 1-2$ eV below the Fermi level; the others place it above. As pointed out, since different quantities are being measured, these numerical disagreements do not imply that any of these works are erroneous.

In conclusion, being highly surface sensitive, MQS allows us to detect subtle changes in the electronic structure of chemisorbed CO on Ni(111), caused by coadsorbed potassium atoms. The results presented here clearly show that potassium enhances the electron emission from the valence orbitals of CO by closing the resonant-ionization-Auger-neutralization channel of deexcitation. The $2\pi^*$ antibonding orbital is further enhanced with respect to the 4σ and $1\pi + 5\sigma$ peaks, and we interpret this observation to be *direct* evidence that potassium enhances electron "back-donation" to the $2\pi^*$ orbital of CO. This is due to the fact that potassium increases the surface electron density by transferring electrons to the surface. The present results are consistent with the observations that coadsorbed potassium atoms increase the binding energy and the dissociation probability of CO on Ni(111)⁶ and on other single-crystal surfaces,³⁻⁵ and decrease the CO stretch frequency.⁷ They are generally consistent with the idea that K is capable of strongly influencing the properties of chemisorbed CO molecules by transfer of electrons to the metal. This could well be a "long-range" interaction through the metal. However, we cannot rule out the possibility of a direct, chemical interaction between K and CO. The enormous downwards shift of the CO stretching frequency⁷ caused by the presence of potassium and the large shifts in the electron binding energies reported here could suggest some complex formation.

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