

Evidence for Paramagnetism of NO Molecules Chemisorbed on Transition-Metal Surfaces

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Metastable-atom deexcitation spectroscopy using singlet ($^1S\text{ He}^*$) as well as triplet ($^3S\text{ He}^*$, $^3P\text{ Ne}^*$, $^3P\text{ Ar}^*$) species reveals that NO chemisorbed on Pd(111) or Pt(111) surfaces remains paramagnetic (on a time scale $> 10^{-13}$ sec) with its 2π level close to the Fermi level. The $1\pi-5\sigma$ and 4σ metastable-atom deexcitation spectroscopy peaks show characteristic multiplet splittings which are, however, considerably smaller than with free NO. No paramagnetic properties are found for NO adsorbed on Cu(110) which is attributed to a stronger coupling between the 2π level and the metal.

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Free NO is paramagnetic with an unpaired electron in the 2π valence orbital. As a consequence the 1π , 5σ , and 4σ photoelectron peaks exhibit pronounced multiplet splittings by 2.8, 1.8, and 1.6 eV, respectively.¹ So far it has been unclear if this molecule preserves its open-shell character upon chemisorption at metal surfaces. The results of theoretical treatments are conflicting,² and clear experimental evidence has so far been missing. The present paper will demonstrate that for NO adsorbed on Pd and Pt surfaces the paramagnetism is indeed partially preserved, while this is not the case with a Cu surface.

The experimental evidence is based on electron spectra obtained by metastable noble-gas deexcitation spectroscopy.³ The deexcitation of the metastable atoms is based on an Auger transition which conserves the electron spin.⁴ If the adsorbed molecule is paramagnetic (spin $\neq 0$), electron states with different spins are not energetically degenerate and, as will be shown, metastable deexcitation spectroscopy (MDS) will yield different results with singlet and triplet metastable atoms. The electronic properties of surfaces are probed by this technique within about 10^{-13} sec,⁵ and hence any conclusions have to be referred to this time scale. In particular, MDS probes selectively the occupied electron states of adsorbed molecules in the energy range close to the Fermi energy (E_F) [where with ultraviolet photoelectron spectroscopy (UPS) the high electron density of states of the underlying metal surface dominates⁶], which is of relevance for the magnetic properties of adsorbed molecules. NO adsorbed on a Ni(111) surface has been studied before with MDS^{7,8}—however, without information on the magnetic nature of the chemisorbed NO molecules. The conclusions of the present work will be based on comparison of spectra with singlet ($^1S\text{ He}^*$) and tri-

plet ($^3S\text{ He}^*$, $^3P\text{ Ne}^*$, $^3P\text{ Ar}^*$) atoms recorded under identical experimental conditions.

The experimental system has been described previously.⁹ Adsorption of NO on Pd(111), Pt(111), and Cu(110) surfaces was investigated at either 140 or 300 K substrate temperature. On Pd(111) and Pt(111), NO adsorbs molecularly under these conditions, and the LEED, TDS, and $\Delta\phi$ data were in accordance with results published in the literature.¹⁰⁻¹⁴ On Cu(110), partial dissociation takes place even at 140 K, but molecularly adsorbed species are formed at higher coverages.^{15,16} Special care was taken to avoid the formation of small amounts of N_2O .¹⁷ MDS and UPS ($h\nu = 21.2$ eV) data were recorded with a resolution of 0.3 eV.

Figure 1 shows UP and MD ($^1S\text{ He}^*$) spectra from a Pd(111) surface saturated with adsorbed NO at 140 K, exhibiting maxima characteristic for emission from the $1\pi-5\sigma$ and 4σ levels as indicated. The FWHM of these peaks in the UP spectrum is consistent with Ref. 10 and, apparently, much larger than in the MD spectrum. The most obvious difference between the spectra is the high emission intensity from the metal valence-band electronic states with the UPS which is absent with MDS. In the latter a small emission peak (marked by an arrow) is seen which is ascribed^{7,8} to the NO 2π state. Contributions due to electron emission by the small amount ($\leq 1\%$) of photons in the metastable atom beam can be neglected as was checked separately. Similar spectra are observed for the Pt and Cu surfaces. In the latter case the 2π emission is, however, absent and a small peak at $E_B = 6$ eV is observed due to small amounts of adsorbed oxygen from partial NO dissociation. At 300 K the intensities of the NO-derived peaks are somewhat lower because of the lower coverages.

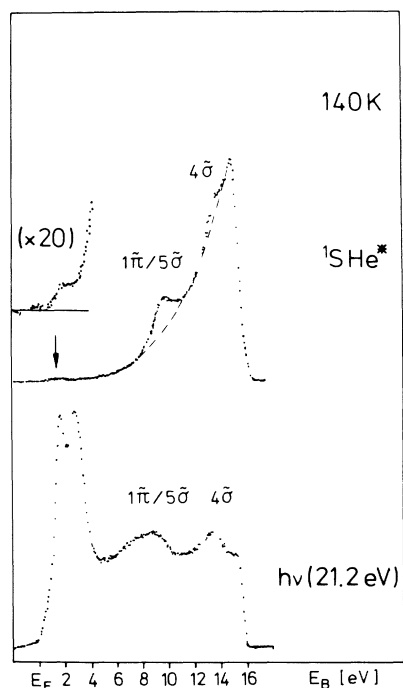


FIG. 1. MDS ($^1S \text{He}^*$) and UPS data for NO adsorbed on Pd(111) at 140 K up to saturation.

Figure 2 shows the emission onset at E_F of the singlet ($^1S \text{He}^*$) and triplet ($^3S \text{He}^*$, $^3P \text{Ne}^*$, $^3P \text{Ar}^*$) MD spectra on an enlarged scale, together with the difference spectra, $^1S \text{He}^* - ^3S \text{He}^*$. For Pd and Pt the singlet spectra exhibit a distinct emission peak which is absent with all triplet spectra. This spin-dependent emission feature is also observed at 300 K although with somewhat lower intensity. For Cu such an effect is not observed. The occupied part of the 2π level of adsorbed NO is located just below E_F , and the unoccupied part above E_F , as observed by inverse photoemission spectroscopy.¹⁸ The spin-dependent emission, therefore, has to be ascribed to the 2π level of the adsorbed NO molecule. The low 2π intensity in the MD spectra has two reasons. First, for gaseous NO the cross section for electron emission from the 2π level is much lower than from the 1π , 5σ , and 4σ levels.¹⁹ Second, the 2π charge density is mainly localized at the N atom.²⁰ Since NO adsorbs with the N atom towards the surface, the 2π orbital is geometrically shielded.

Interpretation of the pronounced difference of 2π -emission intensity between singlet and triplet MDS will start with the (tentative) assumption that the spin of the 2π electron as "seen" by this technique (i.e., on the time scale indicated of $\sim 10^{-13}$ sec) is unpaired. We then consider a three-electron system consisting of the 2π electron (spin $s_{\text{NO}} = \frac{1}{2}$) plus He^* (with $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$ being the spins of the $1s$ and $2s$ electrons, respectively). Following standard theory²¹ the total spin $S = \frac{1}{2}$

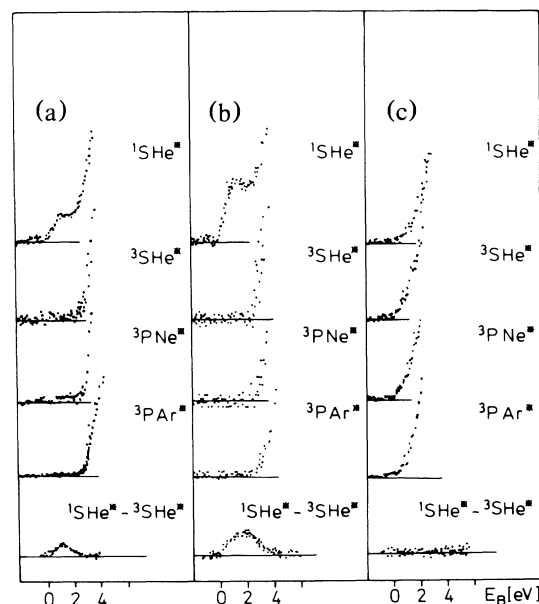


FIG. 2. MD spectra in the energy range close to E_F taken with different metastable noble-gas atoms from (a) Pd(111), (b) Pt(111), and (c) Cu(110) surfaces saturated with adsorbed NO at 140 K.

or $\frac{3}{2}$ can be constructed from three different basis sets:

(a) Basis I: $|S, S_{\text{He}}\rangle$. In addition to S , the spin S_{He} of the subsystem composed of s_1 and s_2 is specified, with $S_{\text{He}} = 0$ for singlet and $S_{\text{He}} = 1$ for triplet He^* , which is obviously appropriate for characterizing the initial situation.

(b) Basis II: $|S, S_V\rangle$. Here the spin of the subsystem composed of s_2 and s_{NO} is specified, i.e., $S_V = 0$ if the spins of the 2π and $2s$ electrons are antiparallel, and $S_V = 1$ if they are parallel.

(c) Basis III: $|S, S_I\rangle$. S_I is the spin of the subsystem composed of s_1 and s_{NO} . Auger deexcitation by transition of the 2π electron the $1s$ hole is obviously only permitted if $S_I = 0$.

Transformation between these basis sets is governed by Racah coefficients. The squares of the calculated matrix elements which determine the relative transition probabilities between the different spin systems are indicated in Fig. 3.

Next it will be shown that $S_V = 0$ states will not be subject to Auger deexcitation *if the NO molecule is chemisorbed on a metal surface*: The 2π - and $2s$ -electron-electron repulsion will raise the energies of both $S_V = 0$ and $S_V = 1$ configurations. On the other hand, chemical bond formation by hybridization between the 2π and $2s$ orbitals will cause a lowering in energy. However, the 2π -level energy is affected differently for $S_V = 0$ and $S_V = 1$. For $S_V = 1$, the 2π and $2s$ electrons exhibit the same spin orientation and therefore their orbital

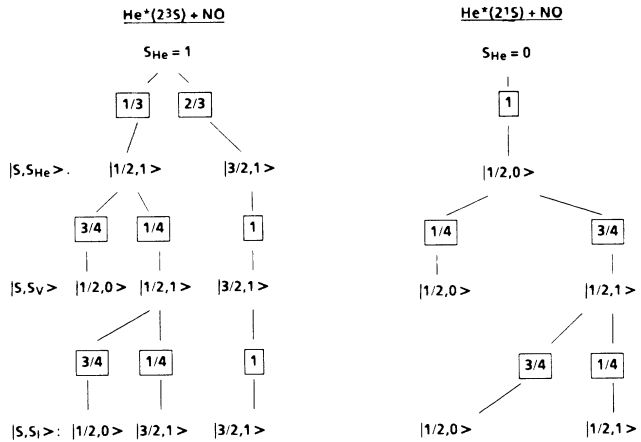
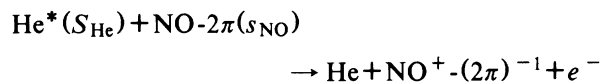


FIG. 3. Transformation scheme between the different basis sets for representation of the three-electron spin system. The numbers in boxes denote the relative probabilities for reaching the respective state as given by the squares of the Racah coefficients. With triplet He* the final $|\frac{1}{2}, 0\rangle$ state is reached with relative probability $\frac{1}{3} \times \frac{1}{4} \times \frac{3}{4} = \frac{1}{16}$; with singlet He* this is $1 \times \frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$.

functions may hybridize. For $S_V=0$, the occupied 2π orbital hybridizes with the empty $2s$ orbital which is well above E_F in energy. Model calculations in the framework of a Hamiltonian described by Drakova, Doyen, and von Trentini²² reveal that for $S_V=1$ the two energy contributions nearly compensate each other, while for $S_V=0$ the 2π level is shifted above E_F so that it will be ionized before Auger deexcitation may occur. This energy splitting of the 2π level between the $S_V=1$ and $S_V=0$ configurations will be further enhanced by the Coulomb-exchange interaction. Contributions to the total energy (such as the energy difference of the doublet-quartet potential curves which is derived from gas-phase experiments²⁰ to be <50 meV) are much smaller. The effect of quenching of the $S_V=0$ configuration for Auger deexcitation is of course restricted to NO coupled to a metal surface where the 2π electron is lost to the solid as soon as its level is pushed above E_F .

Now we return to the different representations of the spin systems: Description of the process



can be performed by a projection from basis I to basis II, and then from basis II to basis III, whereby all configurations with $S_V=0$ will not lead to Auger deexcitation. The resulting branching scheme is reproduced in Fig. 3. It shows that the relative probabilities for Auger deexcitation of the 2π level by singlet and triplet He* exhibit a ratio of 9:1. This result is in qualitative agreement with the experimental observation, according to which the intensity of the 2π emission with triplet He* is

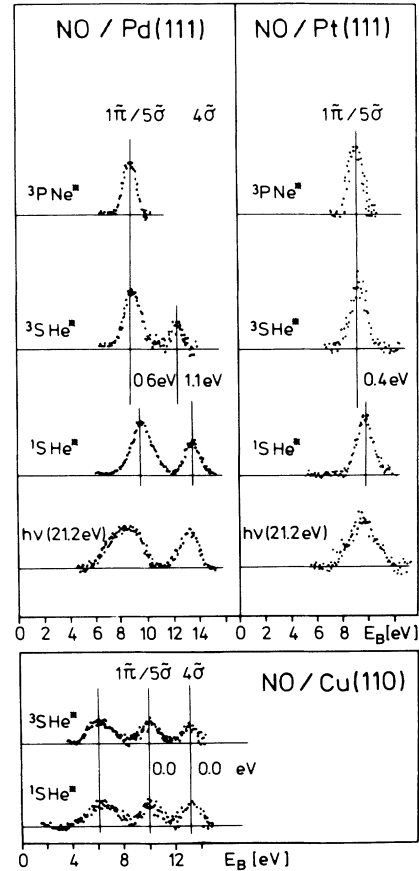


FIG. 4. The relevant parts of the MD and UP spectra (after background subtraction and our accounting for the differences in excitation energies). For NO/Pt, the 4σ emission is very close to the electron emission cutoff in the experimental spectra and therefore not shown.

at least 1 order of magnitude lower than that with the singlet species. Since the whole argumentation is based on the assumption of a nonvanishing spin of the 2π level, this conclusion is considered as evidence of the paramagnetic state of the adsorbate.

Explanation of the spectral features observed with ionization of the fully occupied valence levels is performed along similar lines. Resonance ionization of the 2π level from the $S_V=0$ configuration will cause a pronounced increase of the binding energies of the remaining levels so that these are no longer energetically accessible for Auger deexcitation. That means that in the $S_V=0$ state ionization of the 5σ , 1π , and 4σ levels is suppressed as well. Inspection of the effect of the $|S, S_I\rangle$ basis now yields that from an $S_I=0$ state only NO^+ singlet states can be populated, while $S_I=1$ states lead to the formation of NO^+ triplet states. The probabilities for the formation of singlet and triplet final states from either 2^3S or 2^1S He* can be determined in a straightforward manner: Triplet He* favors NO^+ triplet over singlet by

11:1, while singlet He^* yields a 3:1 preference of NO^+ singlet. Therefore, the electron emission from the $5\bar{\sigma}$, $1\bar{\pi}$, and $4\bar{\sigma}$ levels should reflect the multiplet splitting between the triplet and singlet final states, i.e., the corresponding peaks should appear at lower binding energies in the $^3S \text{He}^*$ than in the $^1S \text{He}^*$ spectra, as is indeed observed (Fig. 4).

The multiplet splitting of a saturated NO adlayer on Pd(111) results to be 0.6 eV for the $1\bar{\pi}$ - $5\bar{\sigma}$ orbitals and 1.1 eV for the $4\bar{\sigma}$ orbital. For Pt(111) the $1\bar{\pi}$ - $5\bar{\sigma}$ splitting at saturation coverage is found to be about 0.4 eV. Since UPS is not discriminating with respect to the spin, the $1\bar{\pi}$ - $5\bar{\sigma}$ and $4\bar{\sigma}$ peaks consist of contributions from both multiplet states and are considerably broader than with the MDS data. For Ne and Ar triplets the same argumentation holds as for $^3S \text{He}^*$ atoms. Figures 2 and 4 exhibit indeed analogous features for all three triplet metastable atom species. The results presented demonstrate that NO adsorbed on Pd(111) and Pt(111) surfaces preserves its paramagnetic character. However, the multiplet splitting is considerably smaller than for the free molecule, and it is further reduced if the surface is covered by NO at 300 K. In the latter case the coverage is smaller and the adsorption energy increased. This is obviously associated with a stronger coupling of the 2π orbital to the solid.

In contrast to the findings with Pd and Pt, the MD spectra from NO adsorbed on Cu(110) exhibit no spin-dependent $2\bar{\pi}$ emission and consequently also no multiplet splitting. It has to be concluded that in this case the coupling of the 2π level to the solid is strong enough to destroy the open-shell character. This difference from Pd and Pt manifests itself by additional effects: NO adsorption causes on Pd and Pt the work function to decrease while it increases on Cu. Adsorbed NO exhibits a strong tendency for dissociation on Cu but not on Pd or Pt.

Recent ESR experiments with NO adsorbed on Pt(111) failed to detect a sharp signal characteristic for well-localized magnetic moments.²³ The authors estimated that in case there should exist a paramagnetic surface species its relaxation rate due to exchange interaction with metal electrons would exceed $2 \times 10^9 \text{ sec}^{-1}$. MDS, on the other hand, probes the $2\bar{\pi}$ level of adsorbed NO on a much shorter time scale of the order of $\approx 10^{-13} \text{ sec}$.⁵ It can therefore be concluded that the spin-relaxation rate of NO chemisorbed on Pt(111) is in the range between 10^9 and 10^{13} sec^{-1} .

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