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Electron Spectroscopy of Surfaces by De-Excitation of Metastable Noble Gas Atoms [and Discussion]

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Electron spectroscopy of surfaces by de-excitation of metastable noble gas atoms

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Electronically excited, metastable noble gas atoms A^* (for example $He^* 2^1S$, excitation energy $E^* = 20.6$ eV) with thermal kinetic energy are very efficiently quenched upon collision with a surface S, i.e. $A^* + S \rightarrow A + S^+ + e^-$. De-excitation proceeds through two competing mechanisms: (i) Auger de-excitation (equivalent to Penning ionization), or (ii) resonance ionization followed by Auger neutralization. The energy distribution of the emitted electrons is governed by the overlap between the wavefunctions of the target and the unoccupied (ground-state) level of the impinging atoms. As a consequence, this technique is extremely sensitive to the density of valence electronic states of the outermost atomic layer. Results for clean and adsorbate-covered surfaces are presented in comparison with data recorded by ultraviolet photoelectron spectroscopy, to demonstrate the capabilities of this method.

1. INTRODUCTION

The properties of (occupied) valence electronic states at surfaces have been studied quite extensively and with great success by means of ultraviolet photoelectron spectroscopy (u.p.s.), by using either gas discharge lamps or synchrotron radiation as light sources. Owing to the finite mean free paths of the electrons in the solid, these spectra also contain information on the bulk (see, for example, Ertl & Küppers 1985). Neutral atoms with thermal kinetic energy (under 0.1 eV), on the other hand, do not penetrate into a solid but interact only with the outermost atomic layer, and therefore offer probes with extreme surface sensitivity. In this sense diffraction of ground-state He atoms can be successfully applied for structural determinations of single-crystal surfaces (Engel & Rieder 1982), and electronically excited (metastable) noble gas atoms may serve to provide information on the valence electronic properties of the surface without interference from bulk contributions. The mechanisms of de-excitation leading to electron emission (whose kinetic energy distribution is measured) are quite similar to those underlying ion neutralization spectroscopy (i.n.s.) as developed by Hagstrum (1978) several years ago, with the major difference that with the latter technique positive ions (for example He^+) are used as primary particles, whose incident kinetic energy will, however, never be below about 5 eV for experimental reasons.

Metastable de-excitation spectroscopy has been developed as a powerful surface technique in several laboratories during recent years (Munakata *et al.* 1978; Johnson & Delchar 1978; Conrad *et al.* 1979; Boiziau *et al.* 1980; Bozso *et al.* 1983). This paper will first give a short outline about the two principal de-excitation mechanisms, followed by a description of the apparatus and of a few selected examples demonstrating the capabilities of this method.

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2. De-excitation of metastable noble gas atoms at surfaces

The properties of various metastable noble gas atoms are listed in table 1. Optical transitions into the respective ground states are either forbidden by selection rules or by spin conservation. Collision of such a particle with a solid surface leads to very efficient (i.e. better than 99%, Conrad *et al.* (1982*a*, *b*) de-excitation into the ground state, whereby the excitation energy (20.6 eV for singlet He*) may be used to eject an electron:

$$A^* + S \rightarrow A + S^+ + e^-(\epsilon_{kin}).$$

De-excitation may occur by one of the following mechanisms, as illustrated in figure 1.

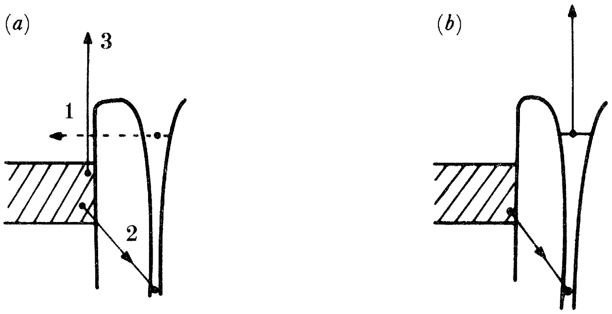

Figure 1. De-excitation mechanism of a metastable noble gas atom at a surface. (*a*) Two-stage resonance ionization (1) + Auger neutralization (2, 3) mechanism (r.i. + A.n.). (*b*) Auger de-excitation (A.d.) of Penning ionization.

Table 1. Properties of ground state and metastable noble gas atoms

	energy/eV	ionization potential/eV	lifetime/s
He $^1S_0(1s^2)$	0.0	24.58	∞
$^3S_1(1s2s)$	19.82	4.77	4.2×10^3
$^1S_0(1s2s)$	20.62	3.97	2.0×10^{-2}
Ne $^1S_0(2p^6)$	0.0	21.56	∞
$^3P_2(2p^5 3s)$	16.62	4.95	24.4
Ar $^1S_0(3p^6)$	0.0	15.76	∞
$^3P_2(3p^5 4s)$	11.55	4.21	55.9

(i) Resonance ionization (r.i.) followed by Auger neutralization (A.n.) (figure 1*a*). The electron in the He 2s level first tunnels into a degenerate empty level of the solid (r.i.). The hole in the 1s level can then be filled by electron transition from the solid, whereby the energy released is used to eject a second valence electron from the target through an Auger process (A.n.).

(ii) Auger de-excitation (A.d.) (figure 1*b*). The He 1s hole is filled by electron transition from the surface and the electron in the 2s level is ejected via an Auger process.

If electron emission is caused by r.i. + A.n. *two* electrons from the target will determine the energy of the ejected electron, while with the A.d. process only *one* target electron is involved. Accordingly the resulting electron energy distributions will be quite different. Since the rate for r.i. is much faster than that for A.d., the r.i. + A.n. mechanism will dominate in all those cases where the excited 2s electron may tunnel into the solid. Accordingly this channel dominates with clean metal surfaces whose *local* work function exceeds the effective ionization potential of the 2s level in front of the surface (which is smaller than the gas-phase value due to polarization effects); and even with atomic ('small') adsorbates the r.i. process will not be efficiently suppressed. The spectra are, on the other hand, characteristic for the A.d. process if the local work function is low enough that the 2s level is located in the energy range of occupied states, if the 2s level falls into the band gap of a semi-conductor or insulator, or if tunnelling of the 2s electron is suppressed by the presence of a dense layer of a molecular adsorbate.

3. Apparatus

The experimental system that is in use in the author's laboratory (Conrad *et al.* 1982*a*, *b*) is shown schematically in figure 2. A beam of noble gas atoms is produced by a three-stage differentially pumped source. The atoms are excited by electron impact. Likewise, created ions and Rydberg atoms are removed by a high electric field. For He, the singlet: triplet ratio depends on the kinetic energy of the exciting electrons. At 240 eV more than 90% of the metastable atoms are in their singlet state, while at 40 eV about equal concentrations of singlet and triplet atoms are formed. A practically pure triplet beam can then be generated by optically quenching the singlet atoms by irradiation with light of wavelength 2.06 μm from a He discharge lamp, causing excitation into the ^1P state from where rapid fluorescent decay occurs. By chopping the beam and applying 'time of flight' techniques the metastable atoms can be separated from photons and from fast ground-state atoms. Under typical working conditions a flux of about 10^8 He* atoms per second of mean kinetic energy of 60 meV strikes the surface. Analysis of the electrons emitted from the sample is achieved by an electrostatic hemispherical analyser. In addition, the apparatus is equipped with a He discharge lamp for simultaneous u.p.s. measurements and with the standard techniques (l.e.e.d., Auger, mass spectrometer) for characterization of the surface.

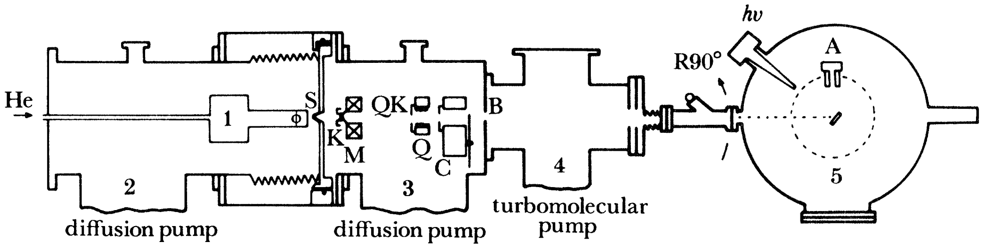

Figure 2. Experimental arrangement for metastable de-excitation spectroscopy. (1) Nozzle source. (2) Expansion chamber: S, skimmer. (3) Excitation chamber: K, cathode; M, magnet and accelerating grid; Q, quench lamp; QK, quench condenser; C, chopper. (4) Buffer chamber: B, beam-defining aperture. (5) Spectrometer chamber: A, electron energy analyser; *hν*, He gas discharge lamp for u.p.s.

4. Results

The left side of figure 3 shows typical spectra obtained from a clean and oxygen-covered Cu(110) surface by de-excitation of Ne* atoms (Sesselmann *et al.* 1983). Data recorded with other metastable noble gas atoms are qualitatively quite similar. In particular, it was observed

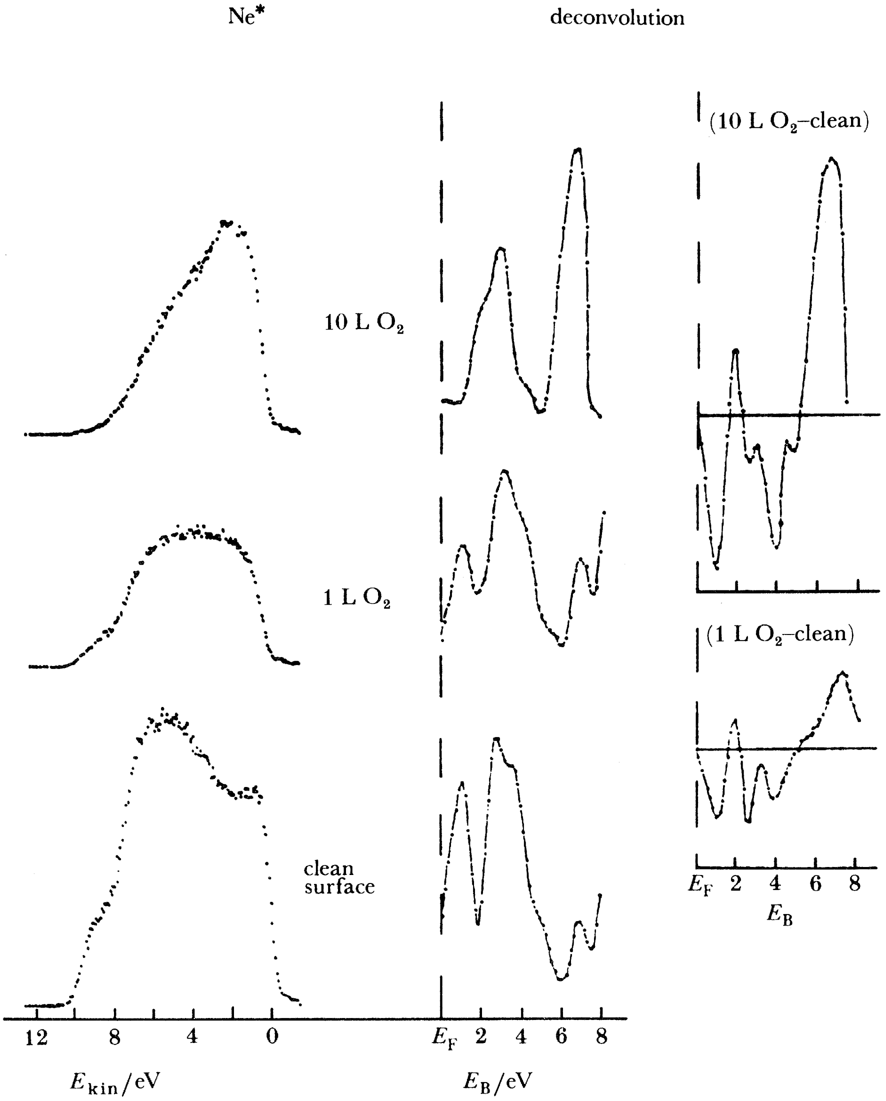

FIGURE 3. The left side shows kinetic energy distributions of electrons emitted from clean and oxygen-covered Cu(100) surfaces by de-excitation of Ne* atoms. The right side shows deconvoluted spectra representing the weighted surface densities of states. The binding energy (E_B) is with respect to the Fermi level E_F.

that identical spectra are produced by singlet and triplet He*, which underlines the occurrence of Auger neutralization in this case. So far this mechanism has been found to be operative with all clean metal surfaces (where the work function exceeds the effective ionization potential of the metastable atom so that r.i. rapidly takes place).

The energy distribution $P(\zeta)$ of the emitted electrons is, in this case, correlated with the electronic surface density of states (s.d.o.s.), $N(\zeta)$, through

$$P(\zeta) \sim \int_{-\zeta}^{+\zeta} [H_1\, N(\zeta+\epsilon)]\,[H_2\, N(\zeta-\epsilon)]\,\mathrm{d}\epsilon, \tag{1}$$

where H_1 and H_2 are the (*a priori* unknown) matrix elements for the two transitions involving electrons of the target (Hagstrum 1978). H_1 will be determined by the overlap of the hole state at the noble gas ion and the corresponding tail of the wavefunction of the solid, and H_2 by the overlap of the second target state with the wavefunction of an outgoing electron. H_1 and H_2 will consequently differ from each other. Their evaluation would require detailed theoretical treatment, which has recently been formed for the first time for appropriate model systems (Trentini & Doyen 1985). As a first (although somewhat questionable) approximation (Hagstrum & Becker 1971), (1) is replaced by

$$P(\zeta) \sim \int_{-\zeta}^{\zeta} U(\zeta+\epsilon)\, U(\zeta-\epsilon)\, \mathrm{d}\epsilon, \tag{2}$$

where $U(\zeta)$ is the 'effective' transition density, i.e. the s.d.o.s. weighted by an average matrix element. $U(\zeta)$ will thus reflect the s.d.o.s. as 'seen' from a particle approaching the surface, be it a metastable atom as used here as a probe or a molecule interacting chemically. $U(\zeta)$ can be extracted from $P(\zeta)$ by mathematical deconvolution of the experimental spectra, or qualitatively even by evaluating the first derivative, $U(\zeta) \approx \mathrm{d}P(\zeta)/\mathrm{d}\zeta$.

The deconvoluted data of figure 3 are reproduced at the right of this figure, whereby the energy scale is referred to the Fermi level E_F. With the clean Cu(110) surface a pronounced peak centred at -1 eV is attributed to surface states above the d-band (ranging from about -2 to -6 eV), which had been previously identified in u.p.s. measurements as a weak feature (owing to masking by bulk emission) (Heimann *et al.* 1979). Adsorption of atomic oxygen causes rapid suppression of these surface states while new structures at -2 and -7 eV, which are derived from coupling of the O 2p states to the surface, grow up. A weak maximum at -7 eV is already apparent in the data from the 'clean' surface and has to be attributed to spurious amounts of oxygen that are already present, which are below the detection limit of other techniques (such as Auger spectroscopy), and this underlines the extreme surface sensitivity of this method.

While analysis of A.n. spectra requires proper data handling the interpretation of A.d. spectra is much more straightforward and indeed very similar to that for u.p.s. If E_B is the binding energy of the target electron (with respect to the Fermi level), the kinetic energy of the emitted electron is given by

$$E_\mathrm{kin} = E^* - E_\mathrm{B} - \varphi, \tag{3}$$

where E^* is the effective excitation energy of the metastable atom and φ is the work function. The corresponding relation for u.p.s. reads

$$E_\mathrm{kin} = h\nu - E_\mathrm{B} - \varphi. \tag{4}$$

The spectral features of both techniques are therefore displaced from each other on the E_kin scale by $h\nu - E^*$ and transformation onto the E_B scale is straightforward. These conclusions are confirmed by the results for CO adsorbed on Pd(111), as shown in figure 4 (Sesselmann *et al.* 1984). The u.p.s. data exhibit strong emission from the d-band between $E_\mathrm{B} = 0$ and 5 eV, and additional features at 8 and 11 eV, which are attributed to the CO-derived $5\sigma/1\pi$ and 4σ levels, respectively. The $\mathrm{He}^{*1}\mathrm{S}$ and $^3\mathrm{S}$ spectra, on the other hand, show essentially only the last two peaks (on a continuously increasing background of secondary electrons), since the valence states of the metal are then shielded. There is, however, also some emission in the energy range below the Fermi level, which had also been observed for CO/Ni(111) (Bozso *et al.* 1983) and was attributed to states created by coupling of the empty $2\pi^*$ level to metallic d-states.

This 'back-donation' effect manifests itself indirectly also in a lowering of the C–O stretch frequency. The intensity of this emission increases in the presence of coadsorbed potassium (enhanced 'back-donation') (Lee *et al.* 1983) and is practically absent with CO/Cu(110) (Sesselman *et al.* 1984), where the d→π* coupling and hence the strength of the adsorption bond is much weaker. This example demonstrates nicely the power of m.d.s.: spectral features characteristic for the surface bond of an adsorbate that are totally masked in u.p.s. by bulk contributions may become clearly evident with this technique.

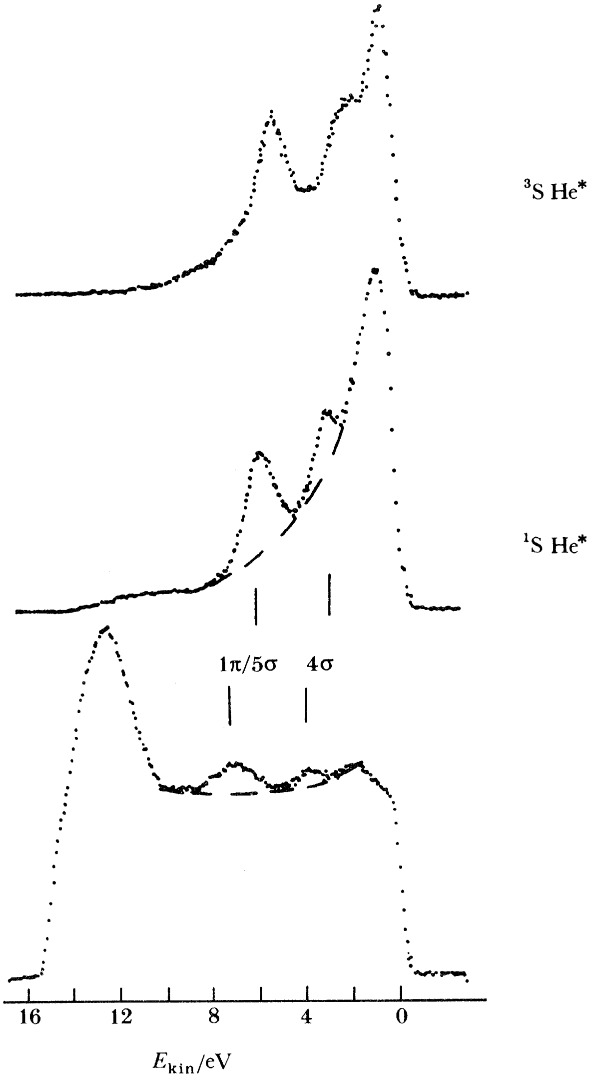

FIGURE 4. Ultraviolet photoelectron spectroscopy data ($h\nu = 21.2$ eV) and ^{1}S as well as ^{3}S He* spectra from a Pd(111) surface saturated with adsorbed CO at 140 K.

The oxidation of a Si(111) surface represents an example in which the de-excitation mechanism switches from A.n. to A.d. (Hess *et al.* 1985). With a clean Si(111) (7 × 7) surface the spectra obtained with ^{1}S and ^{3}S He* are identical and quite different from the u.p.s. data indicating de-excitation by the A.n. mechanism. When the metastable atom approaches the surface the level of its 2s electron is shifted across the band gap into the range of the conduction band and as a consequence resonance ionization (followed by A.n.) occurs. Upon oxidation in 1000 l of O_2 at 700 K, a thin overlayer of SiO_2 is formed, whose band gap is much larger so that r.i. is suppressed and de-excitation occurs via A.d. The spectrum now exhibits the same features as the corresponding u.p.s. results. However, at intermediate states of oxidation an additional peak (not seen with u.p.s.) shows up, which is attributed to a surface state predicted by a band-structure calculation obviously characteristic for the SiO_2–vacuum interface.

An interesting effect was recently observed independently with thin films of evaporated alkali metals by both the Santa Barbara (Lee *et al.* 1985) and the Munich group (Woratscheck *et al.* 1985). The kinetic energy distributions caused by de-excitation of ^1S and ^3S He* were found to be identical, i.e. not displaced with respect to each other by the difference of the excitation energies (*ca.* 0.8 eV). Nevertheless the spectra are caused by A.d., as becomes particularly evident by comparing the results for Cs with the corresponding u.p.s. data. The explanation of this effect is that upon approaching the surface singlet He* is rapidly transformed into triplet He*, from where Auger de-excitation occurs. This conclusion is nicely confirmed by earlier observations (Hagstrum 1979), whereafter a He^+ ion colliding with a K surface is neutralized into ^3S He*, a process that is then followed by A.d. giving rise to the same kind of spectra as if the (neutral) metastable atoms had been used.

5. CONCLUSIONS

Electron emission from solids caused by de-excitation of metastable noble gas atoms is governed by the overlap between occupied valence states and the hole in the ground state of the impinging particle, which renders this technique extremely surface-sensitive. The low kinetic energy (*ca.* 0.1 eV) and small particle flux (*ca.* $10^8\ s^{-1}$) are additional advantages. De-excitation may proceed through two different mechanisms (r.i.+A.n. or A.d.). If A.d. dominates the resulting spectra may be directly compared with u.p.s. data and provide direct information on the electronic density of states of the outermost layer of the solid without superposition of bulk contributions.

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Discussion

J. T. YATES, JR (*Department of Chemistry, University of Pittsburgh, Pennsylvania, U.S.A.*). The fact that the Penning ionization phenomenon for adsorbed species depends so strongly upon overlap of the He(1s) orbital with adsorbate orbitals could suggest that surface Penning spectroscopy would be very useful in determining molecular orientations at surfaces. Could Professor Ertl comment on progress in his laboratory in this particular direction?

G. ERTL. There was some hope of obtaining information on the molecular geometry of adsorbed particles from angular resolved measurements. It transpired, however, that the angular distributions are essentially governed by the accessible impact parameters of the impinging metastable atoms, which in turn are determined by the configuration of the adsorbed particles with respect to each other, so that the effect of molecular orientation is largely masked (Conrad *et. al.* 1982*b*). In my opinion more direct methods like a.r.u.p.s. (angular resolved ultraviolet photoelectron spectroscopy) or e.s.d.i.a.d. (electron stimulated desorption of ions angular distribution) are superior in this aspect.

N. SHEPPARD (*School of Chemical Sciences, University of East Anglia, U.K.*). In Professor Ertl's comparison of the spectra obtained by using different metastable noble gas atoms, I noticed that the spectrum obtained with argon was notably different from that obtained with helium and neon. Why is this so?

G. ERTL. The excitation energy of metastable Ar is considerably smaller than that of He and Ne (see table 1) which displaces the spectra on the kinetic energy scale. The de-excitation mechanisms are identical.