Surface analysis by electron spectroscopy at high pressures

C. J. Powell

National Bureau of Standards, Washington, D.C. 20234

(Received 12 September 1977; accepted 16 November 1977)

Surface analyses are now made by techniques such as Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and appearance potential spectroscopy (APS). These techniques utilize low-energy electrons and have high surface sensitivity but cannot be used at high pressures [$\gtrsim 10^{-4}$ Torr($\gtrsim 10^{-2}$ Pa)]. Optical techinques can be used at high pressures but their surface sensitivity is poor. It is proposed to combine these approaches by using the high-pressure gas as a converter. Two situations are considered. First, variable-energy x-rays are used to produce variable-energy photoelectrons from the gas which impinge on the sample; these electrons constitute a suitable source for APs. Second, the variable-energy x-rays produce photoelectrons from the sample (XPS) of variable energy; these electrons can be detected using the gas for APS. In both cases, the derivative of the x-ray yield from the gas-sample cell is measured as a function of incident x-ray energy; features in the derivative spectrum can be correlated with the core levels of surface atoms of the sample. Design calculations based on x-ray intensities from available sources indicate that the proposed method could be useful for specialized applications.

PACS numbers: 82.80.Pv, 07.35.+k, 79.60.−i, 07.85.+n

I. INTRODUCTION

Many techniques are currently being used for the analysis of surfaces to solve a great variety of scientific and technological problems.[1] Most of these techniques require that the sample be placed in a region with pressure less than about 10^{-4} Torr (10^{-2} Pa) but there are many applications for which it would be desirable to maintain the sample in a region of much higher pressure. Catalytic reactions, for example, frequently occur at pressures above one atmosphere and it would be desirable to monitor the composition of the catalyst surface *in situ* under its operating conditions (rather than evacuating a high-pressure chamber to low pressures for surface analysis[2] with the consequent risk of surface modifications). Also, there is interest in the conversion of SO_2 and oxides of nitrogen to sulfate and nitrate species in or on atmospheric aerosols and pollutant particulates (at atmospheric pressure).[3,4]

The surface-analysis methods with the greatest surface sensitivity utilize low-energy (~0.1 to 5 keV) electrons or ions, as in Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), appearance-potential spectroscopy (APS), secondary ion mass spectroscopy (SIMS), and ion scattering spectroscopy (ISS).[1] These spectroscopies can be successfully employed (without differential pumping) only at relatively low pressures [$\lesssim 10^{-4}$ Torr ($\lesssim 10^{-2}$ Pa)]. On the other hand, optical techniques (such as attenuated total reflectance, ellipsometry, x-ray fluorescence, internal reflectance spectroscopy, and surface-reflectance spectroscopy) can operate satisfactorily at high pressures but generally have less surface sensitivity or elemental specificity than the charged-particle methods.

The purpose of this paper is to describe and discuss a surface-analysis method involving a combination of optical and electron spectroscopies that could be used in a high-pressure environment. X rays are used for excitation and fluorescent x rays are detected (with minimal attenuation in the gas); low-energy electrons in the vicinity of the sample surface give surface sensitivity. The method is described in Sec. II and some design calculations are presented in Sec. III. The results of these calculations are discussed in Sec. IV.

II. DESCRIPTION OF METHOD

We consider the schematic geometry shown in Fig. 1. The sample of interest is located in a cell with two thin beryllium windows W. The sample is irradiated by x rays of variable energy $\hbar\omega$ from a monochromator coupled to a synchrotron or storage-ring source. Fluorescent x rays are detected by the solid-state detector. The sample is exposed to the gas environment of interest which may also be "seeded" if necessary by selected gases.

The major part of the detected x-ray signal arises from fluorescence from the "bulk" of the specimen (information depth ≈ 1 μm) and from the gas in the cell. Conventional pulse-height analysis of the detector output will thus identify the elements present in the bulk of the sample and/or the gas.

To identify the surface atoms of the sample, we consider fluorescent x rays that can result from either of the following two mechanisms; in both cases, the gas in the vicinity of the sample surface is used as a "converter."[5] First, x rays produce photoelectrons from available core levels X of gas molecules (as in XPS of gases). If the x-ray energy is scanned, there will be a corresponding variation in the kinetic energy of the photoelectrons. If these photoelectrons reach the sample surface without inelastic scattering, they constitute an electron source of well-defined energy that can be used for APS. There will be an increase in fluorescence as the photoelectron energy rises above the binding energies (BE) of the core levels Y of the surface atoms. Second, the incident x rays can cause

 0022-5355/78/1502-0549$01.00

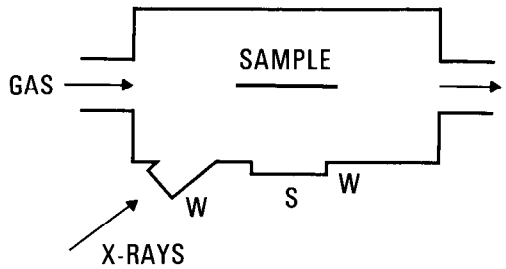

FIG. 1. Schematic outline of proposed experimental arrangement. W denotes a thin Be window and S denotes a solid-state x-ray detector.

photoemission from the core levels Y of surface atoms (as in XPS of solids). Again, if the x-ray energy is scanned, there will be a corresponding variation in the kinetic energy of the photoelectrons that leave the surface without inelastic scattering. These photoelectrons of variable energy can be detected by APS from the gas. There will be an increase in fluorescence from the gas molecules as the photoelectron energy increases above the binding energies of the gas core levels X.

Both processes are energetically equivalent, as illustrated in Fig. 2, although the increases in fluorescence will occur at the different x-ray energies corresponding to the most probable radiative decay channels of the levels X and Y of the gas and surface atoms, respectively. In each case, the surface atoms would be detected from a change in the fluorescence as a function of the incident x-ray energy; that is, the derivative of the total fluorescence radiation would be measured as a function of x-ray energy. Structure would be expected when

$$\hbar\omega = (\mathrm{BE})_X + (\mathrm{BE})_Y. \tag{1}$$

The core levels Y of surface atoms would be identified from knowledge of the energy $\hbar\omega$ and of the levels X of the gas converter.

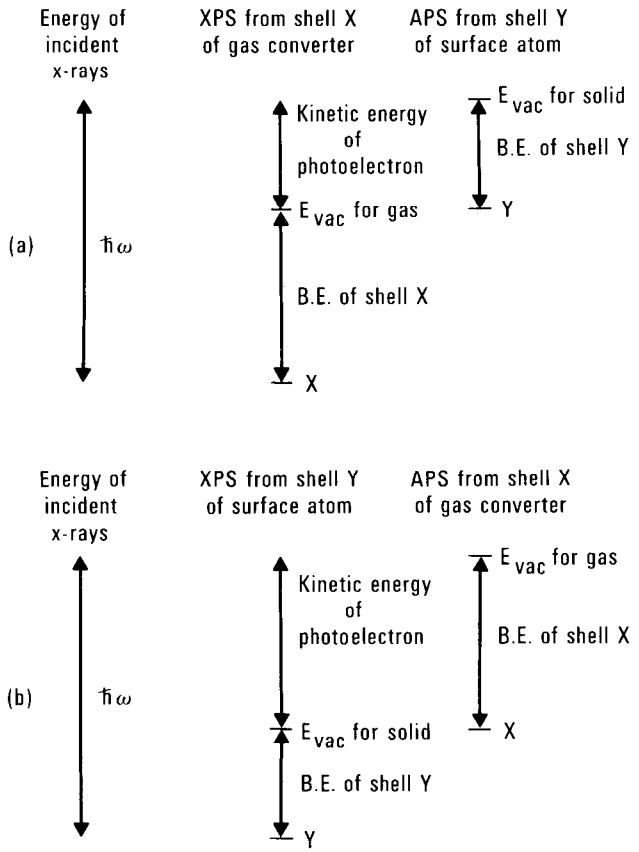

FIG. 2. Illustration of energy relationships for the processes of (a) XPS in the gas followed by APS from the sample surface and (b) XPS from the sample surface followed by APS from the gas.

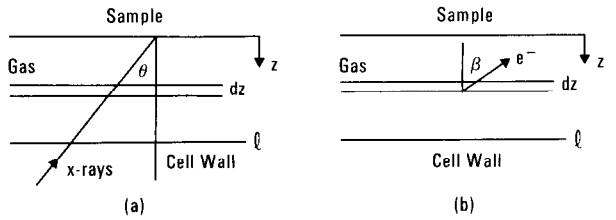

FIG. 3. Geometry for the case of XPS in the gas to be followed by APS from the sample.

III. CALCULATIONS OF PHOTOELECTRON CURRENT

A. XPS from the gas

We consider the geometry illustrated in Fig. 3(a). X rays of energy $\hbar\omega$ are transmitted through a window in the cell wall and then have an intensity I_0. The intensity of the x-ray beam in the gas (assumed here to be a single component) will be

$$I_g = I_0 \exp[-\mu_{xg}(\ell - z)/\cos\theta], \tag{2}$$

where μ_{xg} is the total linear absorption coefficient in the gas, θ is the angle of incidence on the sample, z is distance normal to the surface, and $\ell/\cos\theta$ is the total x-ray path length in the cell. If $\ell/\cos\theta = 1$ cm, x-ray absorption data[6] indicates that the gas cell pressure can be about 1 atm for x-ray attenuation by $(1/e)$ for light gases (N,O) with $\hbar\omega \gtrsim 1.5$ keV. The rate of photoionization events from a level X of gas atoms or molecules in an element dz at distance z from the surface will be

$$R_X = I_g N_g \sigma_X dz/\cos\theta, \tag{3}$$

where N_g is the number density of gas atoms and σ_X is the appropriate photo-ionization cross section. The probability of a photoelectron created at z reaching the surface without inelastic scattering in the gas, for emission in a solid angle $d\Omega$ at an angle β to the surface normal [Fig. 3(b)], is

$$P_g = \exp(-z\mu_{eg}/\cos\beta), \tag{4}$$

where μ_{eg} is the inverse inelastic mean free path of the photoelectrons in the gas. If we assume for simplicity that the photoemission is isotropic, the photoelectron current reaching the surface without inelastic scattering will be

$$I_{eg} = \int d\Omega \int_0^{\ell} R_X P_g \, dz/4\pi$$

$$= \frac{I_0 N_g \sigma_X \exp(-\mu_{xg}\ell/\cos\theta)}{2\cos\theta}$$

$$\times \int_0^{\pi/2} \sin\beta d\beta \left[\frac{\exp[-\ell\mu_{eg}/\cos\beta] - 1}{(\mu_{xg}/\cos\theta) - (\mu_{eg}/\cos\beta)}\right] \quad (5a)$$

$$\approx \frac{I_0\sigma_X \exp(-\mu_{xg}\ell/\cos\theta)}{4\sigma_{eg}\cos\theta}, \quad (5b)$$

where $\sigma_{eg} = \mu_{eg}/N_g$. Equation [5(b)] follows from Eq. [5(a)] if $(\ell\mu_{eg}/\cos\beta) \gg 1$ and if $(\mu_{eg}/\cos\beta) \gg (\mu_{xg}/\cos\theta)$; both conditions will usually be satisfied.

B. XPS from the surface

We now consider the geometry shown in Fig. 4. If x-ray reflection and refraction at the sample surface are neglected,[7] the x-ray intensity as a function of depth z' from the surface will be

$$I_s = I_0 \exp(-\mu_{xg}\,\ell/\cos\theta) \exp(-\mu_{xs}\,z'/\cos\theta), \quad (6)$$

where μ_{xs} is the x-ray absorption coefficient in the sample. The rate of photoionization from a level Y of atoms in an element dz' at z' is

$$R_Y = I_s N_s \sigma_Y \, dz'/\cos\theta, \quad (7)$$

where N_s is the number density of surface atoms and σ_Y is the relevant photoionization cross section. The probability of a photoelectron created at z' reaching the surface without inelastic scattering in the sample, for emission in a solid angle $d\Omega'$ at an angle β' to the surface normal (Fig. 4) is

$$P_s = \exp(-z'\,\mu_{es}/\cos\beta'), \quad (8)$$

where μ_{es} is the inverse inelastic mean free path of the photoelectrons in the gas. If we assume for simplicity that the photoemission is isotropic, the photoelectron current reaching the surface without inelastic scattering will be

$$I_{es} = \int d\Omega' \int_0^{\infty} R_Y P_s dz'/4\pi$$

$$= \frac{I_0 N_s \sigma_Y \exp(-\mu_{xg}\ell/\cos\theta)}{2\cos\theta}$$

$$\times \int_0^{\pi/2} \frac{\sin\beta' d\beta'}{(\mu_{xs}/\cos\theta) + (\mu_{es}/\cos\beta')} \quad (9a)$$

$$\approx \frac{I_0\sigma_Y \exp(-\mu_{xg}\ell/\cos\theta)}{4\sigma_{es}\cos\theta} \quad (9b)$$

where $\sigma_{es} = \mu_{es}/N_s$. Equation (9b) will be valid when $(\mu_{es}/\cos\beta') \gg (\mu_{xs}/\cos\theta)$.

IV. DISCUSSION

Equations (5b) and (9b) give the expected "elastic" photocurrents from the gas and solid that would be available for APS on the solid and the gas, respectively. These equations are of similar form and indicate that I_{eg} and I_{es} do not depend directly on the density of source atoms (i.e., the gas pressure or sample density) except through μ_{xg}.

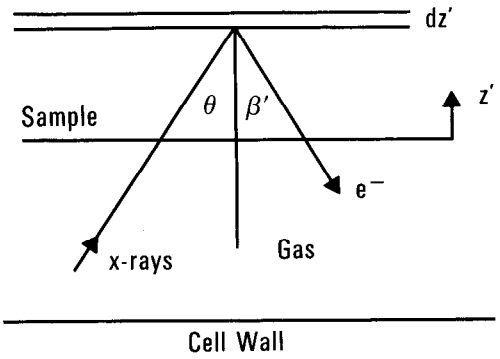

FIG. 4. Geometry for the case of XPS in the sample to be followed by APS from the gas.

The core levels of atoms provide a convenient means of elemental identification if they are in the range 50–1000 eV, as in XPS and APS. For efficient detection of the x-ray fluorescence, the x-ray energy should be at least 1 keV and preferably greater (from consideration of window transmission, typical fluorescence yields, and detector efficiencies); the photoionization cross sections σ_X and σ_Y, however, decrease with increasing x-ray energy.

For reasonable surface sensitivity, the photoelectron kinetic energy (Fig. 2) should be less than about 1 keV so that the electron attenuation length in the sample $(1/\mu_{es})$ would be less than about 20 Å for many materials.[8] The incident x-ray energy should therefore be greater than about 2 keV [Eq. (1)]. Suitable sources of exciting x radiation would be a rotating-anode x-ray tube or a synchrotron–storage-ring x-ray source.

The x-ray intensity at the Stanford Synchrotron Radiation Project is believed to be about 10^{13} photons s^{-1} mA^{-1} $mrad^{-1}$ at 10% bandwidth for energies between 2 and 10 keV (at the highest energies of the stored beam).[9,10] For a silicon-crystal bandwidth of 10^{-4} and a beam current of 30 mA, and a collection angle of 8 mrad in the x-ray optics, the x-ray intensity becomes 2×10^{12} photons s^{-1}. If we neglect x-ray absorption by the gas in the sample cell, the maximum photoelectron currents I_{eg} and I_{es} can be estimated from Eqs. (5b) and (9b):

$$I_{eg} \sim 10^{12}\sigma_X/2\sigma_{eg}\cos\theta \quad \text{electrons/s} \quad (10a)$$

and

$$I_{es} \sim 10^{12}\sigma_Y/2\sigma_{es}\cos\theta \quad \text{electrons/s}. \quad (10b)$$

The quantities σ_{eg} and σ_{es} are estimated to be about 10^{-16} cm^2 for 500–1000-eV electrons in gases and solids.[8,11] The cross sections for photoionization from favorable shells of transition metals such as Ni or Pt can be about 10^{-19} cm^2 for $\hbar\omega = 1.5$ keV.[12] The angle θ can be made large, in principle up to the critical angle for x-ray reflection, although the limited field of view of the fluorescence detector would require that $\theta \lesssim 80°$.

It therefore appears that I_{eg} and I_{es} would be less than about 10^{-9} A. These currents are appreciably less than the incident current of $\sim 10^{-2}$ A often used in APS measurements of solid surfaces in vacuum.[13] Surface sensitivity is obtained in the "double-event" spectroscopy discussed here with a serious reduction of observable signal (compared to conventional XPS

or APS). It may, however, be feasible to examine samples with a high density of unfilled states above the Fermi level which would be optimum materials for APS. Gerlach and DuCharme[14] have observed a very high cross section near threshold (about 10% of the maximum cross section) for the ionization of the L_{23} shell in Ti; similar high cross sections for ionization at threshold could be expected for other transition metals.

The scheme for surface analysis at high pressures described here will not be feasible as a routine analytical tool (unless the available x-ray intensities can be increased substantially). The method may nevertheless be useful for some highly specific investigations. For example, the degree of surface enrichment of one component of a bimetallic catalyst may need to be known in its working atmosphere. It might therefore be possible to determine in a reasonable time the relative amounts of several (expected) surface components, particularly for samples with surface atoms not present in the bulk. There could also be scope for further optimizations in considering specific solids and gases of particular interest. For example, it might be possible to minimize significantly the denominator of Eq. (5a).

Note added in proof: The author has received several suggestions which would lead to substantial increases in the desired signal.

The x-ray intensity at the Stanford Synchrotron Radiation Laboratory is expected to be increased by about an order of magnitude in 1980 when the storage ring is operated in a dedicated mode.[15] Further intensity increases of two orders of magnitude may be possible later with the use of a helical wiggler.[15]

The calculations of Sect. III were for a sample with a plane surface. There would be appreciable increases of signal intensity if the surface was very rough.[16] For example, if the sample was a highly dispersed catalyst, the effective surface area could be up to about four orders of magnitude greater than the geometrical area of the support.[16] It therefore could be worthwhile to test the method of surface analysis described here on catalyst samples at or near atmospheric pressure.

Finally, the surface signal of interest will also appear in a measurement of the net current to the sample.[17] Further calculations of signal and background levels for the fluorescence and absorbed-current modes of operation would be necessary to select the better method and preferred operating conditions.

ACKNOWLEDGMENTS

The author is grateful to P. I. Coheng, J. W. Cooper, R. D. Deslattes, R. E. LaVilla, I. Lindau, J. E. Houston, and T. E. Madey for useful discussions. Work for this paper was carried out at the National Bureau of Standards under the partial sponsorship of the U.S. Energy Research and Development Administration, Division of Biomedical and Environmental Research.

[1]C. J. Powell, Appl. Sur. Sci. (to be published).
[2]D. W. Blakely, E. I. Kozak, B. A. Sexton, and G. A. Somorjai, J. Vac. Sci. Technol. **13**, 1091 (1976).
[3]G. E. Likens and F. H. Bormann, Science **184**, 1176 (1974); L. Newman, Science **188**, 957 (1975).
[4]W. W. Kellogg, R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell, Science **175**, 587 (1972).
[5]M. O. Krause, *Advances in X-ray Analysis* (Plenum, New York, 1973), Vol. 16, p. 74.
[6]W. J. Veigele, At. Data **5**, 51 (1973).
[7]B. L. Henke, Phys. Rev. A **6**, 94 (1972).
[8]C. J. Powell, Surf. Sci. **44**, 29 (1974).
[9]P. Pianetta and I. Lindau, J. Electron Spectrosc. Relat. Phenom. **11**, 13 (1977).
[10]This intensity does not take into account expected losses in the beamline.
[11]L. J. Kieffer and G. H. Dunn, Rev. Mod. Phys. **38**, 1 (1966).
[12]J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976).
[13]J. E. Houston (private communication).
[14]R. L. Gerlach and A. R. DuCharme, Jpn. J. Appl. Phys. Suppl. **2**, Part 2, 675 (1974).
[15]I. Lindau (private communication).
[16]T. E. Madey (private communication).
[17]P. I. Cohen (private communication).