

Photoelectron spectroscopy

Studies of intrinsic surface states and of adsorbate surface states, both at ultraviolet and x-ray photon energies, are among the many applications of this versatile probe.

Dean E. Eastman and Marshall I. Nathan

The surge of growth in surface science, demonstrated by this special issue of *PHYSICS TODAY*, can be attributed to several complementary factors. First, the gas-solid interface is amenable to investigation by many new research tools that involve various combinations of electrons, photons, ions, electric fields and so on. Second, the insights and information obtained from modern surface-science experiments are useful to many technologically important fields, such as catalysis, corrosion and semiconductor devices among others. Third, two-dimensional interfaces such as the gas-solid interface constitute a distinct phase of condensed matter with unique properties that we are only beginning to understand—thus, studies of solid surfaces are an attractive “new frontier” for materials scientists and are being vigorously explored.

As pointed out by Charles Duke and Robert Park in their recent review,¹ a complete description of a surface involves answering several questions, including:

- ▶ What atomic species are present?
- ▶ What is their structural arrangement?
- ▶ How are their valence electrons distributed in space and in energy?

In this article we will address the third of these questions, and attempt

through several selected examples to illustrate the interesting and important types of surface phenomena where ultraviolet and x-ray photoelectron spectroscopy can provide understanding of electronic structure.

Photoelectron spectroscopy is an extremely simple and versatile method for probing the electronic structure of a variety of surfaces. Several tunneling-type surface-electron spectroscopies, each with unique advantages and disadvantages, can also probe valence electrons, and they are described by E. Ward Plummer, John W. Gadzuk and David Penn in this issue. In addition, there are many other surface spectroscopies involving photons or electrons that can be used to probe valence electrons.

Types of surfaces

Before turning to a description of photoelectron spectroscopy and its applications, let us schematically characterize several types of surface complexes in terms of their electronic and spatial structure. We define the surface of the solid as the outermost atomic layer or two including any foreign atoms adsorbed onto it or absorbed into it, either substitutionally or interstitially. When adsorbed species exist over several layers into the solid, such as occurs in oxidation, we shall loosely call this complex a surface compound.

The physical and chemical properties of a surface are largely determined by electronic interactions whose characteristics are reflected in the spatial charge distribution² and energy distribution of

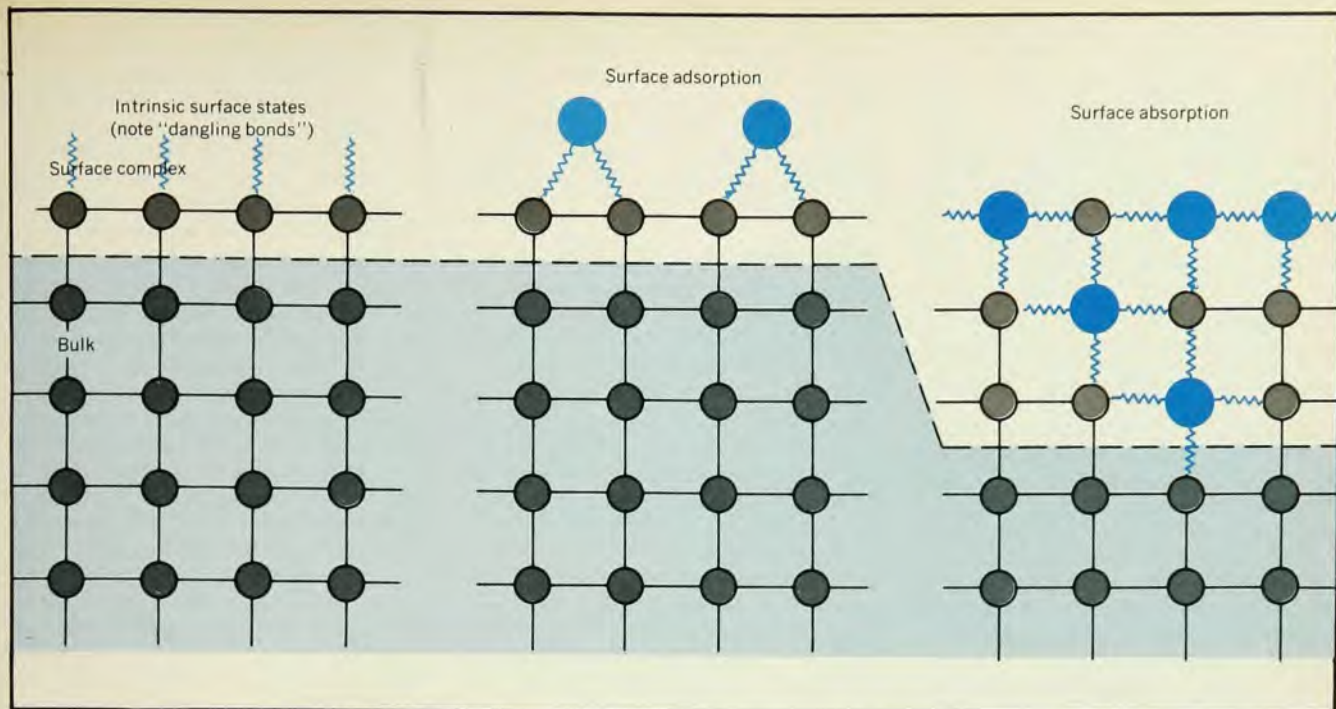
the electronic states of the surface atoms.

As an example, the termination of a solid (figure 1a) can result in the occurrence of new electronic states, confined to the surface region, which have physical properties and energy levels different from those of the underlying bulk. As we shall describe, these new “intrinsic” surface states occur both in and near the forbidden band-gap energy for semiconductors. Charge transfer involving these states causes bending of the bulk energy bands near the surface. These states can also influence electron barriers at metal-semiconductor contacts (Schottky barriers) and play an important role in metal-oxide-semiconductor devices. Atoms and molecules adsorbed on the surface (figure 1b) or absorbed a few layers deep (figure 1c) play an important role in heterogeneous catalysis, corrosion, and so on. Energy-level measurements can provide insight concerning the interactions involved in chemical reactions at surfaces, and can also be used as a “fingerprint” to identify what molecular or atomic species are present at the surface, even during a reaction.

Energy-level measurements

In photoelectron spectroscopy, photons of a given energy are used to excite electrons above the vacuum level ϕ ; some of these excited electrons are emitted into the vacuum, where their energy distribution, or photoelectron spectrum N , is measured with an electron energy analyzer (figure 2). Parameters that can be varied include the

Dean Eastman and Marshall Nathan are both at IBM's Thomas J. Watson Research Center, Yorktown Heights, N.Y., where Eastman is an IBM Fellow and manager of the photoemission and surface-physics group and Nathan is consultant to the director of research.



Three types of surface complexes. Gray dots denote "bulk" lattice atoms, and colored dots denote atoms (or molecules) adsorbed on the

surface or absorbed into the surface region. Colored wiggly lines denote valence bonds associated with the surface. **Figure 1**

photon energy $h\nu$, polarization ϵ_p and direction Ω_i of the incident radiation and the energy E and direction Ω_f of the emitted electron. Thus photoelectron spectra depend on all these parameters in general, and we can say that $N = N(E, \Omega_f, h\nu, \epsilon_p, \Omega_i)$. For magnetic samples, N may depend on electron spin polarization as well. In practice, what is usually measured is the electron energy distribution $N(E, h\nu)$ averaged over a range of emission angles Ω_f for one or more fixed photon energies.

We show the photoemission process in the energy-level diagram of figure 3, where the energy levels for a nickel surface with an adsorbed layer of oxygen are sketched schematically. A photon of energy $h\nu$ is absorbed by exciting one of the filled valence or core level electrons upwards in energy by $h\nu$, thereby giving rise to an energy distribution of excited electrons (colored lines). Some of these electrons are sufficiently close to the surface that they can leave the solid without loss of energy (that is, without inelastic scattering). The kinetic-energy distribution, or photoelectron spectrum $N(E, h\nu)$, of these unscattered electrons is measured (colored levels), together with the smooth background of secondary electrons that occurs because of strong inelastic electron-electron scattering. This energy distribution directly reflects the distribution of initially filled states for both the nickel surface and the adsorbate. (In figure 3 these are the d-band states and core level for nickel and the 2p states of oxygen.) Since the photoemission process involves the excitation of

a single electron for each absorbed photon, we can directly determine the one-electron binding energies $E_B = h\nu - E - \phi$ (where ϕ is the work function), level widths and line shapes of these filled electron levels.

If the photon is in the ultraviolet energy range, say between 4 and 50 eV, the technique is called "ultraviolet photoelectron spectroscopy"; if it is in the x-ray energy range (commonly 1486 eV (aluminum x-rays) or 1253 eV (magnesium x-rays)), it is called "x-ray photoelectron spectroscopy."

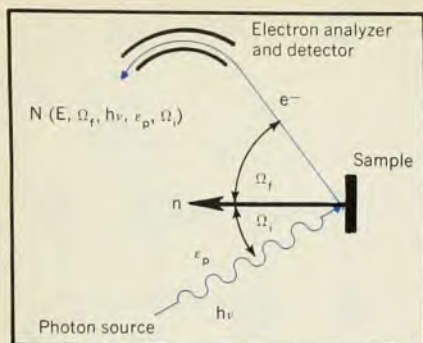
Important ultraviolet sources for this purpose are hydrogen discharge lamps (4–11.6 eV) and, for surface studies, helium (21.2 and 40.8 eV) and neon (16.8 and 26.9 eV) resonance lamps³. The resonance lamps are very simple, intense, and of sufficiently high energy to permit the valence electron energy levels of adsorbed species to be measured. Such sources yield high electron counting rates (around 10^4 – 10^5 /sec) and typically permit photoelectron spectra to be taken for samples of about 1 mm² area in a few minutes, with an energy resolution of about 0.2–0.3 eV. Electron-energy distributions are typically measured in an electrostatic deflection-type energy analyzer with an electron multiplier for electron counting. In photoelectron spectroscopy with x rays, which is generally less surface sensitive than with uv, it is possible to measure energy levels of core electrons of atoms as well as the energy levels of valence electrons.

Recently, radiation produced by accelerating electrons in a synchrotron has been used for photoemission mea-

surements that span both the ultraviolet and x-ray regions, and the distinction between the two types of photoelectron spectroscopy has become blurred.⁴ These synchrotron-radiation sources provide an intense continuum of linearly polarized radiation in an ultrahigh vacuum environment and have many exciting and unique applications,⁵ including that of photoelectron spectroscopy.

The surface sensitivity of photoelectron spectroscopy is determined by two main factors. First, only those electron states that have nonvanishing wave functions within an escape depth $l(E)$ of the surface can contribute to the unscattered photoelectron current. This escape depth, which is determined by inelastic electron-electron scattering, is much shorter than the photon absorption depth, and typically varies in the range 5 to 20 Å for electrons in the energy range of a few electron volts to a thousand electron volts. Thus, the outermost layers of a solid contribute to the photoelectron current in an exponentially diminishing manner for successively deeper layers with a characteristic decay distance $l(E)$ of about 5 to 20 Å. Because several layers are typically sampled by photoelectron spectroscopy, the largest fraction of the photocurrent is usually associated with bulk states rather than intrinsic (adsorbate-induced) surface states. Also, photoelectron spectroscopy cannot usually determine whether or not sorbed species are on the surface or incorporated into the outer few layers.

For adsorbed species, or species ab-



Photoelectron spectroscopy apparatus shown schematically, with definitions of the parameters involved: incident photon energy $h\nu$, polarization ϵ_p , angle of incidence Ω_i , electron energy E and angle of emission Ω_f of the emitted electrons. Figure 2

sorbed within $l(E)$ of the surface, the most important factor that determines surface sensitivity is usually the ratio of photoionization cross sections of the adsorbate levels to those of the host solid.⁴ As an example, for common residual gases or organic species adsorbed on transition metals, maximum surface sensitivity for probing valence levels occurs at low energies (between 15 and 50 eV) because of the relative cross sections involved.

We now turn to a discussion of some

experimental results for several of these types of surfaces. All data are for surfaces prepared and measured in ultra-high vacuum (pressures in the mid- 10^{-10} Torr range or better), so that adsorption of unwanted species is negligible during the time required to perform the experiment.

Intrinsic surface states

One might expect that electronic states of the chemically bonding valence electrons of surface atoms would be severely affected by the surface discontinuity—that is, that they can be quite different from their counterparts in the bulk solid. Indeed, this is the case for many materials, particularly for the covalently bonded semiconductors (Si, Ge, GaAs, etc.), where the bonds in the bulk are each made up of two electrons shared by adjacent atoms. The surface can leave dangling bonds, each with only one electron (figure 1a). Thus, both filled and empty electron surface-state energy levels, which are different from bulk energy levels, occur for these “dangling” bonds.

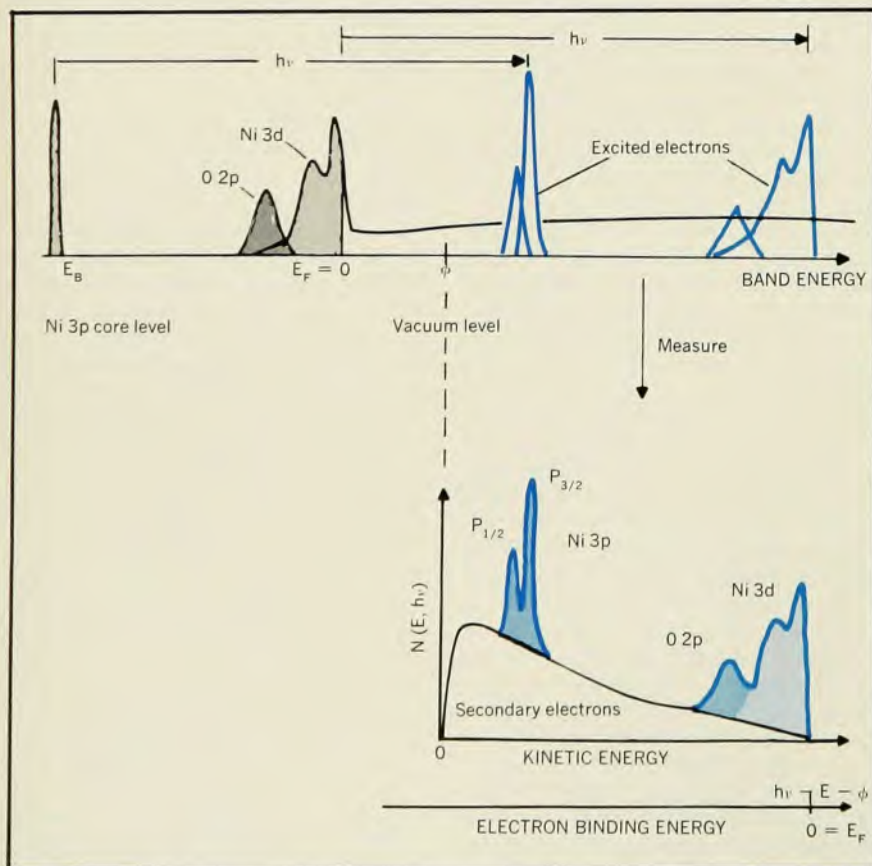
Such surface states have long been known to play an important role in determining electron barriers at semiconductor interfaces. The elegant pioneering measurements of band bending, surface work functions, photoemission

yields and energy distributions for clean semiconductor surfaces by Fred Allen and Garth Gobeli represent a significant contribution of photoelectron spectroscopy to surface science.⁶

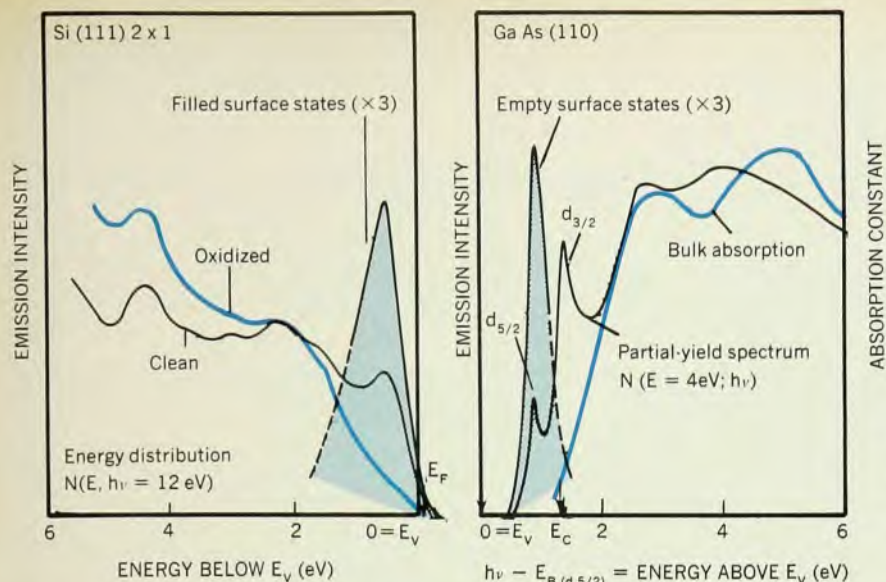
The energy distribution of filled surface states can be seen directly with ultraviolet photoelectron spectroscopy.^{7,8} The example shown in figure 4a is of a (111) silicon surface for both a freshly cleaved surface and for a surface that has been saturated with oxygen.⁷ The oxygen bonds chemically to the silicon surface and saturates the dangling bonds, thereby eliminating these intrinsic surface states and giving rise to new extrinsic silicon-oxide states, which appear at much lower energy. By subtracting the spectrum for the oxidized surface from that of the clean surface, the density of filled surface states is obtained for (111) silicon as shown in figure 4a. This band of surface states has a peak just below the top of the bulk valence-band states (E_v) and a diminishing tail of states extending up to the Fermi energy E_F , which is pinned in the bulk band gap⁷ about 0.3 eV above E_v .

Empty surface states can also be observed with photoemission in certain cases, with a continuous source of uv radiation such as synchrotron radiation from a storage ring.⁹ To observe unoccupied states, as shown for (110) GaAs in figure 4b, one measures the number of slow secondary electrons $N_{\text{sec}}(h\nu, E)$ at a fixed final-state kinetic energy E as the photon energy $h\nu$ is scanned through the threshold for transitions from a sharp core level to the conduction band and empty surface states. Basically, this yield spectrum is indirectly measuring the photon energy dependence of core-level excitations, and thus it reflects the empty final state density near the surface; it is roughly equivalent to an optical absorption measurement on a very thin sample with a thickness equal to an escape depth $l(E)$. This indirect process involves optical excitation, de-excitation of the core level by an Auger process (see Robert Park's article in this issue), and subsequent secondary electron emission.⁹

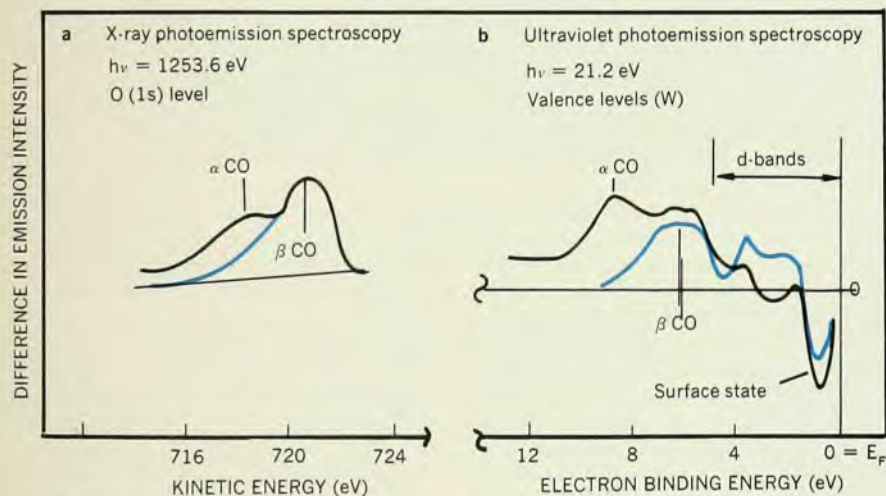
We can see intrinsic empty surface states for a (110) GaAs surface in the partial yield spectrum of figure 4b. An optical absorption spectrum,¹⁰ which probes a thickness of approximately 1000 Å and thus does not show surface-state transitions, is also shown in figure 4b. The sensitivity for observing surface states in the yield spectrum occurs because only optical excitations within an effective escape depth (roughly 10–25 Å) from the surface can contribute to the measured photocurrent. In figure 4b we see two peaks, corresponding to transitions into a narrow empty surface band, with the Ga 3d core level being left in either of two spin-orbit split



Schematic energy-level diagram for adsorbed oxygen on nickel. This figure illustrates the photoemission process, showing the direct one-electron relation between observed kinetic energies for valence and core-level electrons (color) and their initial energy states (black). Figure 3



Photoelectron spectra showing on the left the filled intrinsic surface states on (111) silicon (ref. 7) and on the right the empty surface states on (110) GaAs (ref. 9). The latter lie in the 1.4-eV-wide band gap between the valence-band edge E_v and conduction-band edge E_c . Figure 4



X-ray photoelectron spectra (a) and ultraviolet photoelectron spectra (b) for a saturated layer of CO adsorbed on (100) tungsten (black curves). Both the oxygen 1s core-level and valence-level spectra show the molecular α -phase and dissociated β -phase of adsorbed CO. The colored curves show the remaining β -phase after removal of the weakly bound α -phase. (Part a is from reference 12, figure 11, and part b is from reference 11.) Figure 5

states ($d_{5/2}$ and $d_{3/2}$, with about 0.5 eV splitting). The shape of these surface states is shown by the colored region, which corresponds to $d_{5/2}$ transitions. To determine the energy position of these surface states one subtracts the measured $d_{5/2}$ core-level binding energy ($E_{B(d_{5/2})} = 18.6 \text{ eV}$) from the photon energy. We observe a band of surface states in the bulk 1.4-eV energy gap between the valence bands (E_v) and conduction bands (E_c), with a peak at 0.9 eV and edge at 0.6 eV above E_v . These empty surface states determine the Fermi energy position at the surface and cause the energy bands to bend up in n-type III-V semiconductors, both for vacuum-semiconductor interfaces

and for metal-semiconductor interfaces (for example, Schottky barriers).

"Simple" adsorbate surface states

Adsorption of simple molecules on metal surfaces has long been a favorite subject of surface scientists. Among the many surface techniques available, photoelectron spectroscopy has seen extensive use since its first application to molecular adsorption.³ Both x-ray and uv techniques give directly the ionization energies of the electronic states of adsorbed molecules, from which we can infer information about the molecular identity, electronic interactions and structure of the molecule on the surface. Ultraviolet photoelectron spectroscopy

enjoys advantages in resolution, intensity, and surface sensitivity in probing valence electrons of adsorbates; with x rays, on the other hand, one can measure chemical shifts of adsorbate core levels (changes in core-level energies due to valence-electron interactions). Such core level measurements can provide information about the chemical state of the adsorbate and its bonding to the surface.

From the voluminous photoelectron-spectroscopy literature on simple adsorbates, we have chosen for our example (figure 5) measurements for adsorbed carbon monoxide on single-crystal (100) tungsten, which has been studied both with uv¹¹ and with x rays.¹² This system has been extensively studied, and it is well known that CO adsorbs in two distinct types of states, α and β . Figure 5 shows difference curves (the spectra for CO adsorbed on W minus that of clean W) for both x ray and uv photoelectron spectroscopy. Note the adsorbate-induced change in emission for the O(1s) level and valence-electron energy region. A saturation coverage of about one atomic layer (shown by the black curves) contains both α - and β -phase CO. As we can see in both the core levels and valence levels, these two phases have quite different electron binding energies. The weakly bound α -phase is easily removed by heating, leaving the more strongly bound β phase (colored curve).

If we compare the β -phase spectra with those obtained for oxygen and carbon adsorbed on (100) W, we find that β -phase CO is essentially dissociated upon adsorption.^{11,12} In contrast, the α -phase level—which is very similar to levels seen for CO adsorbed on many metals—is characteristic of molecular CO rather than dissociated CO. We have no space here for discussion of the additional information about adsorbed CO on W that has been obtained; it includes correlations with surface structures, surface phase transitions, identification of the α -CO orbitals, and much else.^{11,12}

Surface oxidation of nickel

We show some observations³ of the formation of a surface compound on nickel by oxidation in figure 6. At low oxygen exposures (figure 6a), emission from a level characteristic of adsorbed oxygen is observed at 5 eV below the Fermi energy, in addition to the emission from the metallic d-bands of nickel within 3 eV of the Fermi energy. Further exposure (figure 6b) results in the spectrum losing its metallic character and becoming insulator-like—in other words, the density of states at the Fermi energy has nearly vanished. By comparison with the spectrum for bulk NiO in figure 6c we can identify the levels for oxidized Ni near 2 eV and 5 eV with

those of the d-electrons of oxidized Ni^{2+} and with surface oxide "p" bands. Thus, the spectra show that oxidized Ni is similar to bulk NiO.

An important difference between x-ray¹³ and uv spectra for bulk NiO is seen in figures 6c and 6d. Namely, with x rays the p-bands are absent and only the d-states are visible, together with a multielectron transition satellite.¹³ On the other hand, with uv we observe both p and d states. This occurs as a result of the energy dependence of the relative photoionization cross-sections. Generally, the states that are either more localized or possess higher angular momentum, (or both)

have larger cross sections at higher photon energies. Thus x-ray photoelectron spectroscopy is usually much less surface sensitive than the uv technique for adsorption of common residual gases on transition metal surfaces.

Adsorbed hydrocarbons

Photoelectron spectra for clean single-crystal Ni(111) and for Ni(111) with a chemisorbed layer of benzene (C_6H_6) are shown in figure 7, together with spectra for several layers of condensed benzene and for gas phase benzene.^{14,15} Part b of the figure shows the difference spectrum $\Delta N(E)$ between the spectra for chemisorbed benzene on Ni(111) and for clean Ni(111); here the five lower-lying peaks are associated with benzene energy levels. Several important points are illustrated by figure 7, including the role of π -d bonding in hydrocarbon chemisorption, the use of photoemission spectra as a "fingerprint" of the adsorbed molecular species, and the large changes in ionization energies of a non-chemical bonding nature (relaxation shifts) that occur for adsorbed species.¹⁴

Before discussing the spectrum for chemisorbed benzene, we should compare the spectra for gas-phase benzene and condensed benzene (figures 7c and 7d). Relative to the gas-phase spectrum, we see that all levels for condensed benzene shift to smaller ionization energies, with relative level positions and intensities largely unchanged. This behavior usually occurs when weak bonding is involved; the uniform relaxation shift to lower ionization energy is due not to chemical bonding but rather to increased screening of the excited state by surrounding electrons for the condensed phase.¹⁴ Such relaxation effects (typically in the range 1–3 eV) also occur for adsorbed species and complicate theoretical descriptions of their absolute ionization energies.

When we compare chemisorbed benzene (figure 7b) with condensed benzene (figure 7c) we again observe that the ionization energies of all lower-lying σ orbitals are further reduced due to relaxation effects, but the ionization energy of the uppermost doubly-degenerate π orbital is increased. This shift signifies π -d bonding, which is involved in the strong chemisorption bonds for unsaturated hydrocarbons on transition metals. Also, the spectra in figure 7 serve as a "fingerprint" of what species are present; that is, the similarity of the spectra for chemisorbed and gas phase benzene indicates that most of the adsorbed benzene remains structurally as benzene. This is often not the case, as we next illustrate with an example of a surface reaction, the dehydrogenation of chemisorbed ethylene (C_2H_4) to acetylene (C_2H_2) on Ni(111).

Photoelectron difference curves

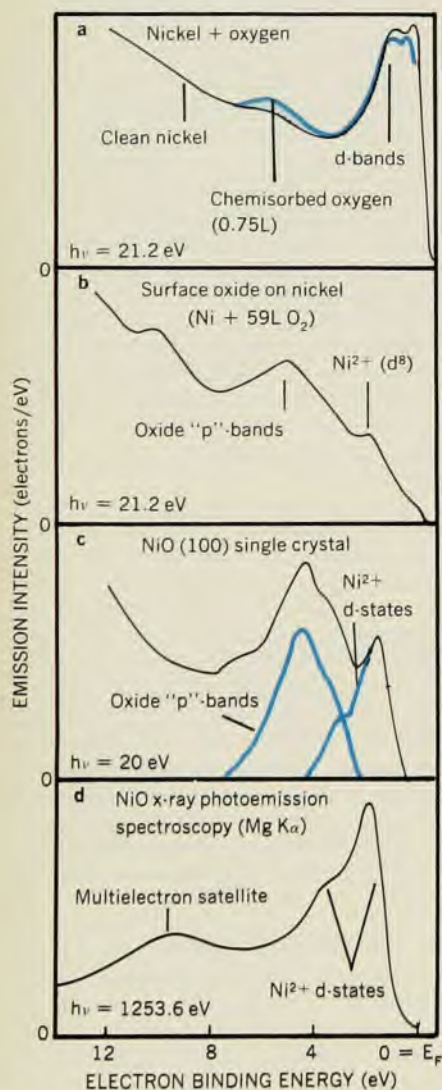
$\Delta N(E)$ for chemisorbed acetylene and ethylene on (111)Ni are shown in figure 8. Molecularly adsorbed acetylene has three energy levels between 4 and 12 eV, whereas molecularly adsorbed ethylene has four levels. The molecular nature of these adsorbates has been established by comparison with gas-phase spectra.¹⁴ For ethylene, molecular adsorption only occurs at low temperatures (about 100 K for the data in figure 8). Upon heating to 230 K, hydrogen is evolved and the spectrum for chemisorbed ethylene is dramatically altered (figure 8b), changing to a spectrum identical to that of chemisorbed acetylene. At room temperature, exposure to ethylene results in only an adsorbed acetylenic species. These results clearly show that chemisorbed ethylene undergoes thermally activated dehydrogenation to chemisorbed acetylene for temperatures above about 230 K. This question as to the chemical nature of adsorbed ethylene on nickel has been the subject of many earlier investigations (roughly half of all hydrocarbon chemisorption-catalysis work done to date), which were inconclusive. At higher temperatures, further dehydrogenation occurs; we find that chemisorbed acetylene is stable for temperatures below about 470 K, and above this temperature it completely dehydrogenates and forms carbonaceous species.¹⁴

Photoelectron spectroscopy allows us to understand the driving mechanism for this ethylene dehydrogenation reaction. The observed π -level bonding shifts for chemisorbed acetylene and ethylene show that the π -d bonding strength of adsorbed acetylene is much greater than that of adsorbed ethylene, thereby causing an exothermic reaction that results in a lower energy state.

A very desirable feature of ultraviolet photoelectron spectroscopy for chemisorption and surface-reaction studies is that photodissociation and photodesorption cross sections are very small for adsorbed species, including sensitive adsorbates such as organics. Thus surface complexes usually are not affected by the measurement probe. This is in contrast with techniques such as Auger electron spectroscopy, appearance-potential spectroscopy and low-energy electron diffraction, which involve incident electron beams that can often alter the adsorbed species.

Future prospects

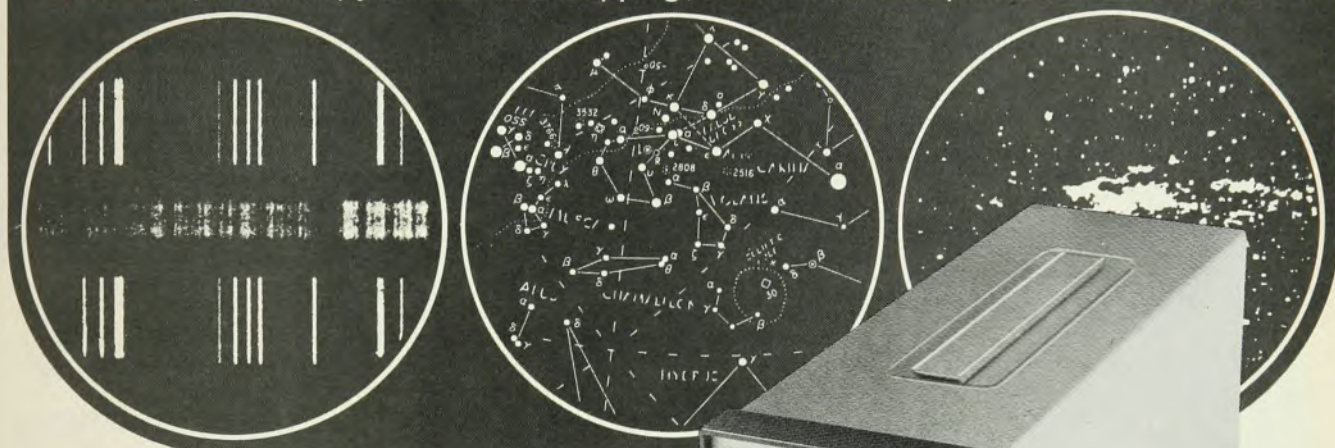
In addition to the primary applications of photoelectron spectroscopy to surfaces that we have described, namely energy-level measurements and molecular "fingerprinting" with uv resonance lamps and x-ray sources, exciting new applications and extensions of photoelectron spectroscopy are currently underway in many laboratories. These include



Oxidation of nickel. Part a shows uv photoelectron spectra for clean Ni and for Ni with about half a monolayer of chemisorbed oxygen (ref. 3). Part b is the spectrum for a surface oxide formed by oxygen exposure (ref. 3). This spectrum shows features similar to that of bulk (100) single-crystal NiO (part c); that is, both spectra show Ni^{2+} 3d-state emission near 2 eV and oxide p-band emission centered near 5 eV. Part d is the x-ray photoelectron spectrum (ref. 13) for bulk NiO, showing Ni^{2+} 3d-state emission but no oxide p-band emission. Figure 6

Let the EMR Optical Data Digitizer Talk to Your Computer about star tracking...

or stellar spectroscopy, or star field mapping, or real time solar phenomena measurement



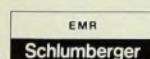
**the result of their conversation
will mean faster, more useful
information for you!**

The EMR Optical Data Digitizer is a versatile aspect sensor that automatically converts visual information into computer digital language in response to computer controlled image scan and dwell. This complete computer interfacing eliminates the time-consuming need for manual or mechanical preprocessing.

The O.D.D. is capable of tracking targets within the same field of view and, with your computer, it can compare star fields with previous photographic plates. Its ability to measure spectral intensity makes it ideal for stellar and solar spectroscopy.

EMR Optical Data Digitizer — more information, faster!

For technical specifications on the EMR Optical Data Digitizer, fill out the coupon and mail to:



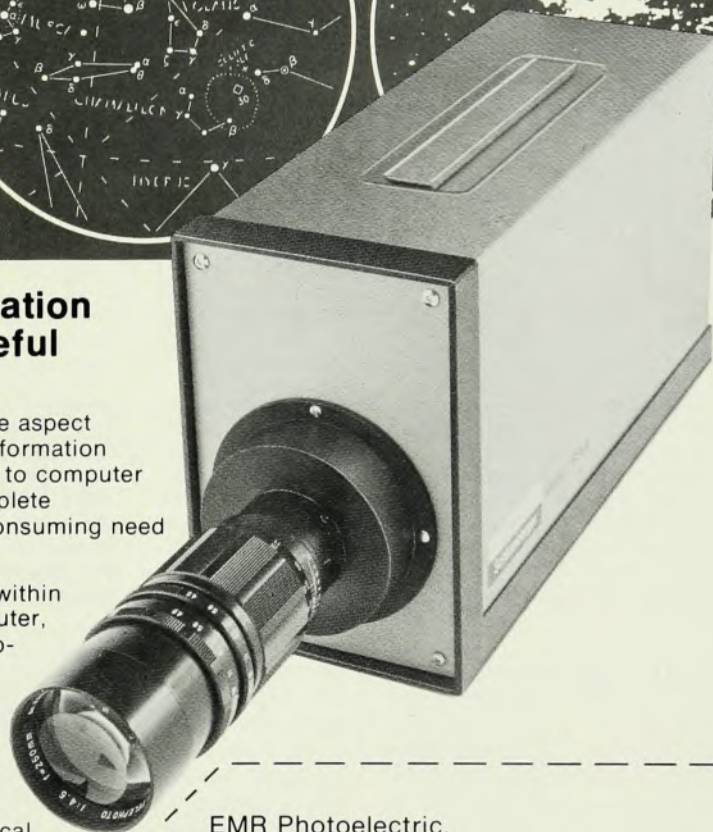
EMR PHOTOELECTRIC

Box 44, Princeton, New Jersey 08540
Telex 84-3459 • Telephone 609-799-1000

Eastern
11315 Lockwood Drive
Silver Spring, Maryland 20904
301•593-7171

Western
4676 Admiralty Way
Marina del Rey, California 90291
213•822-1441

Circle No. 27 on Reader Service Card



EMR Photoelectric.

Box 44

Princeton, New Jersey 08540

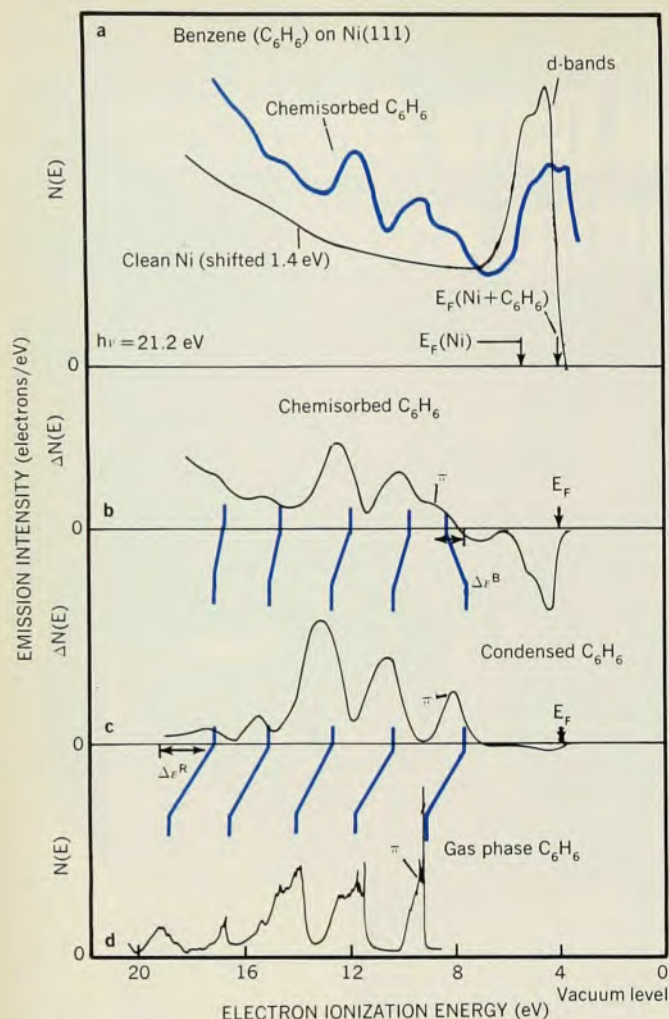
- ☐ Send technical specifications.
☐ Have sales representative call.

NAME _____ TITLE _____

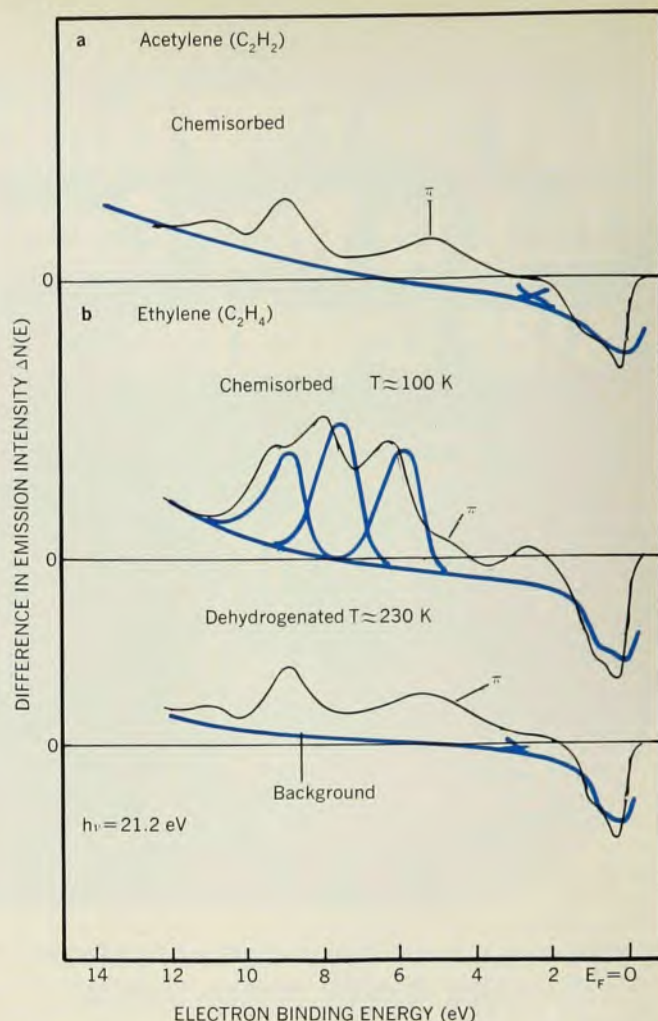
AFFILIATION _____

ADDRESS _____

CITY _____ STATE _____ ZIP _____



The effect of benzene chemisorbed on nickel. Part a shows photoelectron spectra $N(E)$ for clean (111) Ni and for (111) Ni with a chemisorbed layer of benzene (ref. 14). Part b shows the adsorbate-induced difference in emission, $\Delta N(E)$, from the clean surface for chemisorbed benzene—note the benzene-derived levels between 4 and 14 eV. Part c shows $\Delta N(E)$ for a weakly bound condensed layer of benzene, and part d illustrates $N(E)$ for gas-phase benzene (ref. 15). Compare parts b and c with the gas-phase spectrum (d) to see shifts due to relaxation ($\Delta\epsilon^R$) and chemical bonding ($\Delta\epsilon^B$). Figure 7



Acetylene and ethylene on nickel. Part a is the photoelectron difference spectrum $\Delta N(E)$ for chemisorbed acetylene on (111) Ni, showing C_2H_2 -derived levels between 4 and 12 eV (ref. 14). Part b shows $\Delta N(E)$ for chemisorbed ethylene on (111) Ni at a temperature of about 100 K and for dehydrogenated ethylene, which occurs on warming to above 230 K. Note that, upon dehydrogenation, ethylene becomes identical to chemisorbed acetylene. At higher temperatures still, further dehydrogenation occurs; the chemisorbed acetylene is stable up to about 470 K, above which it dehydrogenates completely. Figure 8

► angle-resolved and/or polarization-dependent uv photoelectron spectroscopy measurements
 ► energy-dependent photoionization cross-section measurements of both adsorbed and gas-phase molecules over an extended energy range (for example, 10–100 eV) exploiting synchrotron radiation, which can give new information concerning the identity of surface energy levels, and
 ► the combination and correlation of photoelectron spectroscopies with other spectroscopies such as mass spectroscopy or other electronic spectroscopy techniques.¹⁶ Such experiments will give additional information ranging from new insight on catalytic reactions to new information on surface electronic states.

The polarization ϵ_p of radiation incident at an oblique angle is an important parameter in determining the relative

strengths of photocurrents due to surface states and bulk states.¹⁷ Spectra taken with the light polarized out of the plane of the surface often show greatly enhanced surface-state emission relative to spectra taken with the light polarized parallel to the plane of the surface. The use of polarized radiation to enhance and identify surface features has not been widely recognized or used until now, and promises to be very useful.

Angular-resolved photoelectron spectroscopy measurements, in which energy distributions $N(E, \Omega_f)$ are measured as a function of electron emission angle Ω_f , promise to have several interesting applications. These include:

- determination of the geometrical orientation of adsorbed molecules or atoms¹⁸
- determination of the angular dispersion of intrinsic surface state emis-

sion,¹⁹ which can yield new information concerning the momentum-dependence of surface states, and

► angle-resolved photoemission measurements that contribute to our basic understanding of the photoemission process, including such important questions as how to distinguish between “bulk” and “surface” photoemission currents.

We have briefly described here several applications of photoelectron spectroscopy to the study of the electronic properties of surfaces. As we mentioned, photoelectron spectroscopy can also be used to obtain surface-composition information (especially the x-ray technique) and, possibly, to obtain surface structural information. Photoelectron spectroscopy is attractive in that it is both simple and versatile; it is easy to illuminate any surface, and easily interpretable spectra of emitted electrons

Now Compatible with
UF₆, HF, F₂

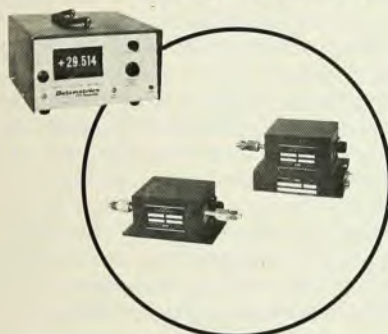
QUANTITATIVE VACUUM MEASUREMENTS

in the range of
10⁻⁵ to 5000 Torr.

**With 10 to 100 times
better accuracy than
McLeod, Ionization
or Thermal
Conductivity Gages.**

**And calibration
accuracy independent
of gas composition.**

With Type 1173
Electronic Manometer
and Barocel Sensor.



- Continuous direct reading.
- High level dc output signal.
- Sensors bakeable to 450°C.
- Digital outputs.
- Multi-Station inputs.

Applications include measurements of vapor pressure, cryogenic temperature, flow, surface area and adsorption in mass spectroscopy, fluid mechanics, leak testing, gas kinetics, freeze drying, vacuum metallurgy, and sputtering.

Datametrics offers a broad line of vacuum and pressure measurement systems for critical applications.

Write now for Bulletin 2005

Datametrics

A subsidiary of **ITE Imperial CORPORATION**

340 FORDHAM ROAD, WILMINGTON, MASS. 01887
(617) 658-5410

Circle No. 28 on Reader Service Card

can be measured over a wide range of energies with simple energy analyzers.

Such photoemission measurements, together with those of various other surface electronic spectroscopies, are stimulating—and being stimulated by—numerous theoretical models and methods (as J. Robert Schrieffer and Paul Soven explain in their accompanying article). Together, the multitude of new experimental techniques and theoretical models are resulting in rapid progress in our understanding of surfaces. We are only near the beginning of such an understanding, and there are innumerable challenges in extending it and applying it to useful fields.

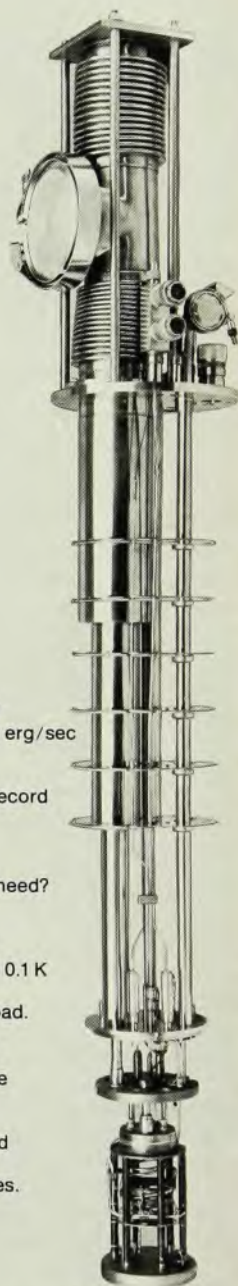
* * *

We are indebted to many colleagues at IBM for helpful discussions regarding this article, including Joseph E. Demuth, Warren D. Grobman, Norton D. Lang, James C. McGroddy, Erling Pytte, Gary W. Rubloff, Merrill W. Shafer, and John E. Smith, Jr.

References

1. C. B. Duke, R. L. Park, *PHYSICS TODAY*, August 1972, page 23.
2. N. D. Lang, in *Solid State Physics*, (F. Seitz, D. Turnbull, H. Ehrenreich, eds.) Academic, New York (1973); Volume 28, page 225.
3. D. E. Eastman, J. K. Cashion, *Phys. Rev. Lett.* **27**, 1520 (1971).
4. D. E. Eastman, in *Vacuum Ultraviolet Radiation Physics*, Proceedings of the IV International Conference on Vacuum Ultraviolet Radiation Physics, Hamburg, West Germany, July 1974, Pergamon/Vieweg, (1975).
5. M. L. Perlman, E. M. Rowe, R. E. Watson, *PHYSICS TODAY*, July 1974, page 30.
6. F. G. Allen, G. W. Gobeli, *Phys. Rev.* **127**, 1500 (1962).
7. D. E. Eastman, W. D. Grobman, *Phys. Rev. Lett.* **28**, 1378 (1972).
8. L. F. Wagner, W. E. Spicer, *Phys. Rev. Lett.* **28**, 1381 (1972).
9. D. E. Eastman, J. L. Freeouf, *Phys. Rev. Lett.* **33**, 1601 (1974).
10. W. Gudat, C. Kunz, *Phys. Rev. Lett.* **29**, 169 (1972).
11. J. M. Baker, D. E. Eastman, *J. Vac. Sci. Technol.* **10**, 223 (1973).
12. John T. Yates et al, in *The Physical Basis of Heterogeneous Catalysis*, Proceedings of Gstaad Conference, August 1975, Plenum, N.Y. (1975).
13. G. K. Wertheim, S. Hufner, *Phys. Rev. Lett.* **28**, 1028 (1972).
14. J. E. Demuth, D. E. Eastman, *Phys. Rev. Lett.* **32**, 1123 (1974).
15. D. W. Turner et al, *Molecular Photoelectron Spectroscopy*, Wiley Interscience, N.Y. (1970).
16. H. D. Hagstrum, *Science* **178**, 275 (1972).
17. B. Feuerbacher, B. Fitton, in *Vacuum Ultraviolet Radiation Physics* (see reference 4).
18. A. Liebsch, *Phys. Rev. Lett.* **32**, 1203 (1974).
19. J. E. Rowe, M. M. Traum, N. V. Smith, *Phys. Rev. Lett.* **33**, 1333 (1974). □

Incomparable Performance



The **DRI-334 SUPERFRIDGE** produces 2,400 erg/sec refrigeration at 0.1K a new world's record for dilution refrigerators.

More than you need? The **DRI-236** is guaranteed to reach 12 mK and to maintain 0.1 K with a 1000 erg/sec load.

Still too much? The inexpensive **Minifridge** offers rapid turn-around and short equilibrium times.

Need a custom design? The SHE staff has over 75 years total experience designing and building innovative refrigerators in the millikelvin range. Perhaps we can solve your cooling problems



S.H.E. CORPORATION

CRYOGENIC INSTRUMENTS AND SYSTEMS
11661 SORRENTO VY. RD. | SAN DIEGO, CA 92121
(714) 453-6300 | TELEX 697903

Circle No. 29 on Reader Service Card