

SPECTROSCOPIC MEASUREMENTS OF SURFACES USING VACUUM ULTRAVIOLET RADIATION*

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Abstract. Recent research on surface properties of materials using X-ray and vacuum ultraviolet radiation suggest some relationships in common to lunar research. New and intense sources of vacuum ultraviolet continuum radiation may offer the possibility of probing the surface properties of lunar materials and may permit some experimental demonstrations of the surface phenomena observed on the Moon.

1. Introduction

At the Lunar Interactions Conference this author confined his presentation to the utility of synchrotron radiation as a research tool in the vacuum ultraviolet. A portion of this paper will repeat those observations in the hope that they may be of value to others. As a result of this conference this author learned a great deal about the complexity of the problems facing lunar scientists and came away with a clear conviction that a number of the problems were identical to those facing any scientist doing research in the VUV area. This short exposure to lunar problems, even coupled with prior and subsequent reading, has not provided the perspective however, which permits integration of prior lunar experimental results in the design of new experiments. Neither is it at all clear which lunar problems must have a quantitative answer and which can be satisfied with an order of magnitude estimate. With this warning in mind, and with the aim of stimulating further research ideas, the following sections have been written.

2. Sources of Vacuum Ultraviolet Radiation

Scientific investigations employing vacuum ultraviolet radiation have achieved tremendous encouragement from the ESCA (Electron Spectroscopy for Chemical Analysis) work of Siegbahn and his group at Uppsala, and the PES (Photoelectron Spectroscopy) work of Turner and his group in England (Siegbahn *et al.*, 1967, 1969; Price and Turner, 1970; Turner *et al.*, 1970; Shirley, 1972). In addition to these two main areas, numerous chemistry, physics, and astronomy research groups are employing this region of the electromagnetic spectrum for studies involving absorption, reflectance, transmission, ionization, fluorescence, and intensity calibration experiments (Hercules and Carver, 1974; Betteridge and Williams, 1974; Marr *et al.*, 1973, 1974; Codling, 1973; Watson and Perlman, 1972; Perlman *et al.*, 1974; Taylor, 1974). In each of these experiments the source of the vacuum UV radiation dictates, in part,

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the type and quality of the information which can be obtained. Those experiments which rely on line sources are relatively easy to perform in the laboratory, whereas those which require a continuum below 600 Å are much more difficult. Samson (1967) and Zaidel and Shreider (1970) provide excellent reviews of the methods of generation of laboratory line sources to include those which can be operated with windows. Below 1040 Å, where LiF absorbs, these sources are operated windowless unless a thin-metal window can be constructed to transmit the desired radiation. One example is the 1500 Å aluminum window for PES applications which was adapted from some of the work of Ausloos at NBS (Kinsinger *et al.*, 1972).

For continuum VUV radiation below 600 Å (and at longer wavelengths as well) the high velocity centripetal acceleration of electrons can be employed. It produces a continuum which starts in the X-ray region and extends through the infrared. Two devices have been used to achieve this continuum. In a synchrotron, electrons are repetitively produced, accelerated to velocities approaching the speed of light, and deflected in a magnetic field to produce light pulse intensities related to the number of electrons in a given pulse, the radius of the electron trajectory, the energy of the electrons, and the acceptance angle of observation. The operation of a storage ring is conceptually similar except that a single bunch of electrons may be injected into a closed structure which can capture the injected bunch and cause it to circulate for a long time period. The photon signal from the storage ring appears as pulses of short duration but the intensity of succeeding pulses decreases slowly and uniformly as electrons are slowly lost from the circulating bunch (Codling, 1973; Marr, 1974; Perlman *et al.*, 1974; Taylor, 1974).

The following characteristics explain the spectroscopic interest in synchrotron radiation as a light source. (1) The spectrum is a true continuum and devoid of line structure. (2) The intensity of the photon flux, particularly from the X-ray to 1000 Å, can be greater than any other available source and can approximate the peak intensity of many intense line sources. (3) The light is polarized with the electric vector oriented in the plane of the electron orbit. (4) The light arrives at an experimental port in short time pulses, on the order of nanoseconds, with a highly precise pulse repetition frequency in the megahertz range. (5) The light is produced from a vacuum environment in the 10^{-10} to 10^{-11} torr range. (6) If a given experiment requires a line source, a suitable wavelength isolation device can be employed. If the wavelength must be variable, the wavelength can be scanned. New facilities for light research are primarily storage rings and at the present time there are major installations in England, France, Germany, Italy, Japan, the U.S.S.R. and the United States (Perlman *et al.*, 1974; Taylor, 1974).

3. The Problem of Surface Effects in Determining Photoelectron Yields and Distributions

Several speakers at the conference stressed the dynamic nature of the events which occur at the lunar surface as a consequence of photon, ion, and electron bombardment, gas absorption from the solar wind and gas release from the lunar soil. We know from

the laboratory use of ESCA and PES that the electron kinetic energies are a function of the energy of the bombarding photon and the energy levels of the chemical species interacting with the photons. Hercules and Carter (1974) in their review of electron spectroscopy list six references to chemical identification of lunar material using the electron binding energy as a probe. These were: the reducing effect of solar wind on iron oxides (Yin *et al.*, 1972); an ESCA examination of Luna 16 and Apollo 11 samples for aluminum, silicon, iron, and oxygen (Vinogradov *et al.*, 1971) with a comparison to terrestrial minerals (Huntress and Wilson, 1971; or Vinogradov *et al.*, 1972); a comparison of the difference in concentration of principal elements on the surface and inside particles of lunar material which was thought to arise from the shock effects by micro-meteorites (Nefedov *et al.*, 1972); and the variation of metallic iron *versus* the oxidized iron content in samples taken from the Ocean of Storms (Vinogradov and Nefedov, 1972).

In answering some of the major questions raised at the conference, however, it is the timing and magnitude of the electron release which becomes important in explaining some of the phenomena observed by site instruments and in rationalizing the observed electric field variations. Along these lines, one paper has reported the photoelectric yield, secondary electron yield, and energy distribution of returned Apollo 14 and 15 dust samples for photon energies between 4 to 21 eV and for electron energies between 50–2500 eV (Willis *et al.*, 1973). These workers were careful in attempting to minimize surface contamination of their samples and used Auger electrons as a probe to monitor that surface. They heated their samples at 150°C for one week at vacuums in the range 10^{-7} to 10^{-9} torr before measurement.

We know from laboratory experiments involving deliberate layering of samples that the X-ray generated photoelectron mean free path for escape is on the order of 10–40 Å for a variety of materials (Steinhardt *et al.*, 1972; Carlson and McGuire, 1973). Hagstrom's work (Hagstrom, 1972; Hagstrom and Becker, 1972) suggests that a somewhat smaller depth is sampled for PES and that ion bombardment (a technique called ion-neutralization spectroscopy or INS) samples at an even smaller depth. Some more recent data from ESCA, PES, and INS research (Fadley *et al.*, 1974; Frazer *et al.*, 1973; Hagstrom and Becker, 1972) has shown that not only is the mean free path for electron escape a strong function of electron energy, it is also a function of the observation angle from the surface. At smaller observation angles, the photoelectron arises from fewer monolayers on the surface. More pertinent to lunar samples, however, is the observation that the angle of the photon beam to the surface also has a strong effect on the electron yield and sampling depth (Fadley *et al.*, 1974). The variation in photon angle would be expected to be important at sunrise and at sunset on the lunar surface.

There are two questions which arise from these observations. Do we want electron yields from absolutely clean lunar material (and, of course, how do we get them), or we want information on the electron yield with the surface absorption still intact? It is fairly clear that any meaningful measurement must also include some consideration of the dynamics of the sample material. At 10^{-8} torr it requires approximately

100 s for a monolayer to appear on a clean surface. If a surface were covered by nitrogen to 20 or so monolayers, no photoelectrons should be observed from $L\alpha$ radiation at 1216 Å. The ionization potential for nitrogen is approximately 796 Å (or 15.58 eV). The same sort of insulation condition can occur with hydrogen and the rare gases. Although it is reasonable to expect that the lunar surface exposed to high energy bombardment at 10^{-12} torr and temperatures up to 150°C would outgas the samples, the question remains as to what happens to the surface as the Moon rotates and is no longer exposed to sunlight and solar wind. Hoffman and Hodges at the Lunar Interactions Conference did report evidence for argon absorption during this period and estimated temperatures on the order of 150 K.

It would appear to this author that any improvement in the laboratory measurement of the electron yield and distribution would require that some attempt be made to duplicate the dynamic environment where the sample is maintained at 10^{-12} torr with traces of hydrogen, argon, and helium comprising the residual gas above the sample, the photon source is scanned from 100 Å–2000 Å, the sample is cycled through a temperature range of 425 K down to 150 K, and the electron spectrometer yield function is known for all the electrons of various energies. These experimental requirements can be met with a synchrotron radiation source. The problem remains, however, to choose a sample which would be representative of the surface material, one which could duplicate the surface absorption conditions, and also one which could approximate the loss from scattering from a non-uniform surface.

4. The Sample Charging Effect and Its Relationship to Lunar Observations

Freeman and Ibrahim at this conference (and Freeman *et al.*, 1973) discussed the surface suprathreshold ion detector (SIDE) response which showed a dayside 10 V positive surface potential and a zero potential as the terminator is approached from the dayside. Gold and Williams (1973) and Criswell (1973) also discussed at the conference the various possible mechanisms of electrostatic dust transport and the consequences of such motion. Bombardment with ions, photons, or electrons all could conceivably produce the observed charge.

Both these phenomena have been observed in ESCA and PES research where the surface potential arises solely from photon bombardment. Release of the electron leaves behind a positive surface charge which must eventually be neutralized. In conductors this neutralization occurs quickly and no net accumulation is observed. For non-conductors, however, the problem can become serious. The relationship which defines the electron binding energy (E_b) and hence the chemical identity of the observed species is given by

$$E_b = E_{X\text{-ray}} - E_{\text{kin}} - \phi_{\text{sp}} - C,$$

where $E_{X\text{-ray}}$ is the irradiating photon energy, E_{kin} is the measured kinetic energy of the electron, ϕ_{sp} is the work function of the spectrometer (and is usually a constant), C is the correction for charging effects, and the recoil energy has been neglected

(Johansson *et al.*, 1973). The net effect on the measurement is to make the observed binding energy larger when sample charging effects are operative. Because the instrument can be calibrated (Johansson *et al.*, 1973) it is possible to have some estimate of the value of C for various types of non-conducting samples. For most of the samples the values range from a few tenths of a volt up to a maximum of about four volts (Johansson *et al.*, 1973).

Ebel and Ebel (1974) have attempted to analyze the charging problem systematically using glass, glass coated with thin gold films, Teflon and Teflon coated with thin silver films. Their observations were that increasing the photon flux increased the amount of surface charge; that electrons generated from the X-ray window could, under some operating conditions, be sufficient not only to neutralize the surface charge but drive it to negative values as well; and that the amount of charge depended on the thickness of the sample or distance the charge had to move before being neutralized.

To this author's knowledge there is no experimental ESCA or PES data on what values of charging to expect from lunar materials because neither the appropriate compositions, thicknesses, nor physical states have been measured. Johansson *et al.* (1973) found that a 20 Å evaporated NaCl layer showed 0.2 eV, a 2000 Å NaCl layer showed 0.6–0.8 eV and a pellet (≈ 1 mm thick) showed 2–3 eV. A log-linear extrapolation of these data would predict a maximum of 5 eV charging for the Moon's surface, but the shape of the curve is unknown, the NaCl is not comparable to lunar material, and the evaporated salt is not equivalent to the lunar fines. How these values would differ in the VUV compared to radiation with Mg K α at 1253.64 eV also is not clear. It is perhaps reasonable to speculate, however, that the charging effect for the relatively loose lunar dust would not be the same as that for the more compact rocks found on the surface. If the rate of charge neutralization for a levitated dust particle were slower than that for a rock on the surface, it is reasonable to expect an attraction between the two.

If one were anxious to test the similarity of some of these relationships, it should be possible to measure the charging as a function of thickness for materials comparable to lunar soil, to initiate particle migration under the influence of photon impact similar to the way in which Gold and Williams (1973, and Lunar Interactions Conference) have demonstrated motion under electron impact. For a prototype experiment, a windowless line source could replace the electron source. Lithium fluoride would be an applicable window for hydrogen and argon discharges and 1500 Å aluminum for discharges in neon and helium. The aluminum window would also produce electrons which would have to be retarded to prevent them from reaching the sample.

If the laboratory extrapolation on sample materials were not convincing, there is the possibility of performing a PES experiment directly on the lunar surface. In this case the charging effect could be measured directly from the shift in peak position as a function of lunar rotation and the data compared to the results from the SIDE and the charged particle lunar environment experiment (CPLLE) (Reasoner and Burke, 1973) where the source is broad band rather than a narrow line. These and other ideas perhaps merit further discussion to determine feasibility and necessity.

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