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THE OPTICAL PROPERTIES OF PLATINUM AND GOLD IN THE VACUUM ULTRAVIOLET

by Roger C. Linton

George C. Marshall Space Flight Center
Marshall Space Flight Center, Ala. 35812

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16. Abstract

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INTRODUCTION

The optical constants of platinum and gold thin films have been determined in the spectral region of 40 to 200 nm by reflection measurements. The highly polarized continuum of synchrotron radiation emitted by the 240-MeV electron storage ring at the Physical Sciences Laboratory of the University of Wisconsin was used as a light source for the spectrum below 120 nm, while a windowless gas-discharge lamp coupled to a normal incidence monochromator provided a source for the longer wavelengths. Reflection measurements were made as a function of the angle of incidence for opaque films of platinum and gold deposited on quartz substrates. Optical constants were determined by a computer program that was based on iterative solutions to the Fresnel equations.

In the vacuum ultraviolet, very few materials can surpass thin films of platinum or gold as highly efficient reflectors for grating coatings or mirrors and as highly stable coatings minimally subject to oxidation, tarnishing, or general aging. As a result of their widespread use, considerable study has been made of optimal preparation techniques to produce optically efficient reflectors, particularly in the ultraviolet [1]. The optical constants, n and k, of a material comprise the real and imaginary parts of the complex dielectric constant, providing complete information for defining the reflection, refraction, and transmission of unpolarized light through a given thickness at a given wavelength. The varied applications of multilayered thin film optics are based primarily on knowledge of these constants. For basic physical studies of materials, the n and k values contribute information about energy absorption processes such as interband transitions and collective oscillations of electrons.

The optical constants of gold have received more attention in the literature than those of platinum. While platinum is generally a much better material for vacuum ultraviolet applications, particularly for the shorter wavelengths, a gap exists in the literature concerning the optical constants and derived atomic properties. Several investigators have measured the optical properties of platinum for normal incidence radiation in this spectral region, and the optical constants have been obtained at a very few selected

wavelengths [2]. The primary objectives of this report are to fill in the existing gaps and to obtain the spectral dependence of the optical constants in the vacuum ultraviolet for platinum thin films. The constants for gold in the region of 120 to 200 nm were calculated from measured reflectances to provide a comparison with the literature and to indicate the validity of the general approach.

Since few materials transmit appreciable radiation in the vacuum ultraviolet, it is generally necessary to employ reflection measurements in determining optical constants. A Kramers-Kronig analysis [3] of normal incidence reflectance measurements on an opaque film over a sufficiently wide spectral region can lead to quite accurate values of these constants at the longer wavelengths. The method requires, however, an extrapolation of the data at the extreme ends of the spectrum and is fairly difficult to employ satisfactorily at the shorter wavelengths of the ultraviolet.

For many materials, the occurrence of total reflection at some "critical angle" provides a useful means of determining one of the optical constants, the index of refraction. If the other optical constant, the extinction coefficient, is very small, the critical angle is sharply defined as an inflection point on the curve of reflectance as a function of the angle of incidence; and the resulting value calculated for the refractive index will be accurate. The extinction coefficient is calculated separately by transmittance measurements. Obviously, the method is limited in applicability to materials and wavelengths satisfying the defining criteria and is generally used only when the normal incidence reflectance is very small.

Another method of determining the optical constants of a material is referred to as the "two-angle method," requiring the measurement of specular reflectance from the material at two or more angles of incidence. This is the most widely used method of obtaining optical constants at the shorter wavelengths and is the technique employed in the data to be described.

THEORY

The optical constants of a material are the index of refraction, n, and the extinction coefficient, k. The index of refraction $n = c/u$, where c is the velocity of light in a vacuum and u is the phase velocity of light in the material under investigation. The extinction coefficient is related to the

amplitude damping of an electromagnetic wave E as it propagates through the material:

$$E = E_0 \exp\left(-2\pi kz/\lambda\right) \quad ,$$

where z is the axis of propagation, E_0 is the amplitude at $z = 0$, and λ is the wavelength (measured in vacuum). These two constants form the real and imaginary parts of the complex index of refraction, $n^* = n + ik$.

For a given wavelength, the values of n and k are constant and must be experimentally determined. The formulas for determining these constants from reflectance measurements as a function of the angle of incidence will be derived.

The relations expressing a functional dependence of the optical constants to reflectance are derived by the application of boundary conditions to solutions of Maxwell's equations. Maxwell's equations, in the rationalized meter-kilogram-second (mks) system, may be stated as [4]

$$\vec{\nabla} \cdot \vec{D} = \epsilon \vec{\nabla} \cdot \vec{E} = \rho \quad , \tag{1}$$

$$\vec{\nabla} \cdot \vec{B} = \mu \vec{\nabla} \cdot \vec{H} = 0 \quad , \tag{2}$$

$$\vec{\nabla} \times \vec{E} = \frac{\mu \partial \vec{H}}{\partial t} \quad , \tag{3}$$

and

$$\vec{\nabla} \times \vec{H} = \sigma \vec{E} + \frac{\partial \vec{D}}{\partial t} \quad . \tag{4}$$

Taking the curl of equation (3), and substituting for $\vec{H}$ from equation (4), one obtains

$$\nabla^2 \vec{E} = \frac{\mu\sigma \, \partial \vec{E}}{\partial t} + \frac{\epsilon\mu \, \partial^2 \vec{E}}{\partial t^2} \quad , \tag{5}$$

with a similar equation for $\vec{H}$ obtained by the same operation.

Considering initially a nonconducting medium ($\sigma = 0$), one has

$$\nabla^2 \vec{E} - \frac{\epsilon\mu \, \partial^2 E}{\partial t^2} = 0 \quad . \tag{6}$$

This is the general wave equation for a nonconducting medium, with velocity of propagation $u = 1/\sqrt{\epsilon\mu}$.

Since the index of refraction $n = c/u$,

$$n = c\sqrt{\epsilon\mu} \quad .$$

Since for most nonmagnetic materials the magnetic susceptibility is aproximate unity, one obtains, converting to the centimeter-gram-second (cgs) system of units to conform to literature usage,

$$n = c\sqrt{\frac{\epsilon\mu}{c^2}} = \sqrt{\epsilon\mu} \cong \sqrt{\epsilon} \quad ,$$

so that for most materials $\epsilon = n^2$, relating the real index of refraction to the real dielectric constant.

A plane wave solution of equation (6), propagating in the z direction, has the form

$$\vec{E} = \vec{E}_0 \exp\left[i\,(Kz - \omega t)\right]$$

and

$$\vec{H} = \frac{\vec{K} \times \vec{E}}{\mu\omega} \quad ,$$

where $\vec{K}$ is a vector in the direction of propagation defined by

$$\vec{K} = \frac{\omega}{u^2} \vec{u} \quad ,$$

so

$$K = \frac{\omega}{u} = \omega \sqrt{\epsilon\mu} \quad .$$

To derive reflection coefficients for a wave incident on a plane surface, the boundary conditions (that the tangential components of $\vec{E}$ and of $\vec{H}$ must be continuous at the boundary of the surface) are applied to the solutions for both $\vec{E}$ and $\vec{H}$.

Referring to Figure 1, one must have

$$\vec{N} \times (\vec{E} + \vec{E}_1) = \vec{N} \times \vec{E}_2$$

and, substituting for $\vec{H}$,

$$\vec{N} \times (\vec{K} \times \vec{E} + \vec{K'} \times \vec{E}_1)/\mu_1 = \vec{N} \times (\vec{K'} \times \vec{E}_2)/\mu_2 \quad .$$

Generally, $\mu_1 = \mu_2$ to further simplify this expression. The vector $\vec{E}$ can be written as the sum of two orthogonal components, resulting in two cases to consider.

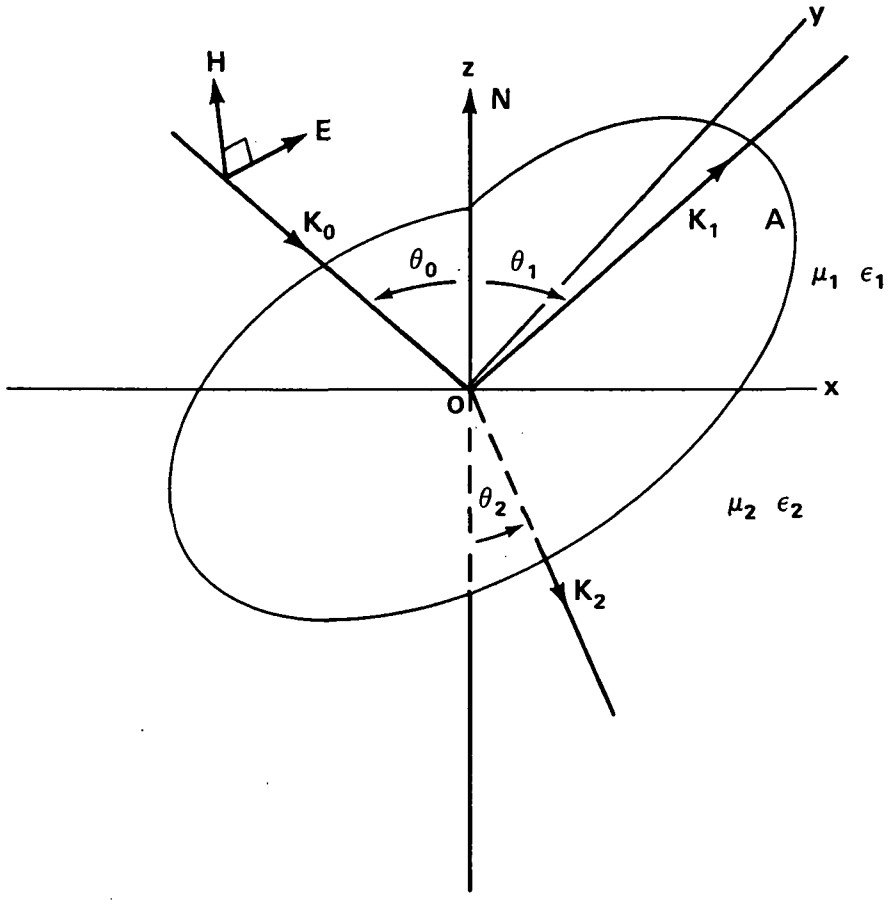

Figure 1. Reflection and refraction of an incident plane wave (propagation vector K_0) at the boundary of a surface in the (x, y) plane.

Case 1: Electric Field Vector $\vec{E}$ Perpendicular to the Plane of Incidence. The first boundary condition gives

$$E_0 + E_1 = E_2 \quad . \tag{7}$$

The second boundary condition, upon expansion of the vector cross product, gives

$$\{(\vec{N} \cdot \vec{E}_0)\vec{K} - (\vec{N} \cdot \vec{K})\vec{E}_0\} + \{(\vec{N} \cdot \vec{E}_1)\vec{K}_1 - (\vec{N} \cdot \vec{K}_1)\vec{E}_1\} = (\vec{N} \cdot \vec{E}_2)\vec{K}_2 - (\vec{N} \cdot \vec{K}_2)\vec{E}_2 \quad .$$

Since, in this case, $\vec{E}$ is perpendicular to the plane of incidence, $\vec{N} \cdot \vec{E}$ vanishes for all three field vectors, and the expression becomes

$$(\vec{N} \cdot \vec{K})\vec{E}_0 + (\vec{N} \cdot \vec{K}_1)\vec{E}_1 = (\vec{N} \cdot \vec{K}_2)\vec{E}_2 \quad .$$

Propagation vectors in the same medium are equal, so that $|\vec{K}| = |\vec{K}_1|$, and $|\vec{K}|/|\vec{K}_2| = u_2/u_1$. Thus, one has

$$E_0 \cos \theta_0 - E_1 \cos \theta_1 = \frac{u_1}{u_2} E_2 \cos \theta_2 \quad . \tag{8}$$

Combining equations (7) and (8) and simplifying by acknowledging that $\theta_0 = \theta_1$ for reflection at a boundary gives

$$E_1 = -E_0 \left\{ \frac{(u_1/u_2) \cos \theta_2 - \cos \theta_1}{(u_1/u_2) \cos \theta_2 + \cos \theta_0} \right\} \quad .$$

Since $u_1/u_2 = n_2/n_1$ and assuming the incident medium is vacuum ($n_1 = 1$),

$$E_1 = -E_0 \left\{ \frac{n \cos \theta_2 - \cos \theta_0}{n \cos \theta_2 + \cos \theta_0} \right\} \quad . \tag{9}$$

This is one of the Fresnel formulas for light with $\vec{E}$ perpendicular to the plane of incidence. The other Fresnel equation for this case expresses a relationship between E_2 and E_0 and is derived similarly.

The expression for reflectance of light with the electric field vector perpendicular to the plane of incidence is

$$R_s = \frac{|E_1|^2}{|E_0|^2} \quad .$$

From Snell's Law, one has $(n_i = 1)$, $\sin\theta_0 = n \sin\theta_2$. Squaring both sides and using the trigonometric identity that $\cos^2\theta + \sin^2\theta = 1$, one obtains

$$\cos\theta_2 = \sqrt{\frac{n^2 - \sin^2\theta}{n}} \quad .$$

Substituting in equation (9) and squaring both sides gives

$$R_s = \left|\frac{E_1}{E_0}\right|^2 = \left|\frac{[n^2 - \sin^2\theta]^{1/2} - \cos\theta}{[n^2 - \sin^2\theta]^{1/2} + \cos\theta}\right|^2 \quad . \tag{10}$$

Case 2: Electric Vector $\vec{E}$ Parallel to Plane of Incidence. The tangential components of $\vec{E}$ satisfy the boundary condition $\vec{N} \times (\vec{E}_0 + \vec{E}_1) = \vec{N} \times \vec{E}_2$ such that

$$E_0 \cos\theta_0 - E_1 \cos\theta_1 = E_2 \cos\theta_2 \quad . \tag{11}$$

Since the magnetic field vectors $\vec{H}$ are perpendicular to the electric field vectors, one must have, from the boundary conditions,

$$H_0 + H_1 = H_2 \quad .$$

However,

$$\vec{H} = \frac{\vec{K} \times \vec{E}}{\omega u} \quad ,$$

and for $\vec{E}$ parallel to the plane of incidence the boundary condition gives

$$\frac{|\vec{K}|\, E_0}{\omega u_1} + \frac{|\vec{K_1}|\, E_1}{\omega u_1} = \frac{\vec{K_2}\, E_2}{\omega u_2} \quad .$$

For the usual case of $u_1 = u_2$, and since the propagation vectors in the same medium are equal ($|\vec{K}| = \vec{K_1}$), one has

$$|\vec{K}|\,(E_0 + E_1) = |K_2|\, E_2 \quad .$$

Now $|\vec{K}|/|\vec{K_2}| = u_2/u_1 = n_1/n_2$, so

$$E_0 + E_1 = \frac{n_2}{n_1} E_2 = nE_2 \quad , \tag{12}$$

if the incident medium is vacuum and one lets $n_2 \equiv n$.

Substituting equation (10) into equation (12), one obtains, since $\theta = \theta_1$ for reflection at a boundary,

$$(E_0 - E_1) \cos\theta_0 = \frac{(E_0 + E_1) \cos\theta_2}{n} \quad .$$

Thus,

$$E_1 = E_0 \frac{(n \cos\theta_0 - \cos\theta_2)}{(n \cos\theta_0 + \cos\theta_2)} \quad .$$

This is one of the Fresnel formulas for light with $\vec{E}$ parallel to the plane of incidence. The other equation relates E_2 and E_0 and is derived similarly.

The reflectance of light polarized parallel to the plane of incidence is then

$$R_p = \left| \frac{E_1}{E_0} \right|^2 = \left| \frac{n \cos \theta_0 - \cos \theta_2}{n \cos \theta_0 + \cos \theta_2} \right|^2 \quad . \tag{13}$$

From Snell's Law, with the incident medium vacuum ($n_1 = 1$), one has

$$\sin \theta_0 = n \sin \theta_2 \quad .$$

Referring to equation (13), one has, on substitution,

$$R_p = \left| \frac{n \cos \theta_0 - \frac{\sqrt{n^2 - \sin^2 \theta}}{n}}{n \cos \theta_0 + \frac{\sqrt{n^2 - \sin^2 \theta}}{N}} \right|^2 = \left| \frac{n^2 \cos \theta_0 - (n^2 - \sin^2 \theta)^{1/2}}{n^2 \cos \theta + (n^2 - \sin^2 \theta)^{1/2}} \right|^2 \quad . \tag{14}$$

For a conducting medium, including metals, the wave equation is equation (5).

Assuming the time dependence of the wave in the form

$$\vec{E}(r, t) = \vec{E}(r)\, e^{-i\omega t} \quad ,$$

one has

$$\vec{\nabla}^2 \vec{E} = (-i\mu\sigma\omega - \epsilon\omega^2) \vec{E}$$

or

$$\vec{\nabla}^2 \vec{E} = -K^{*2} \vec{E} \quad ,$$

where

$$K^{*2} = \epsilon\mu\omega^2 + i\mu\sigma\omega = \mu\omega^2\left(\epsilon + \frac{i\sigma}{\omega}\right) \quad .$$

Since the real wave vector $K = \sqrt{\epsilon\mu\omega}$, we have, by analogy, the complex wave vector K^*:

$$K^* = \sqrt{\mu\epsilon^*} \quad ,$$

where ϵ^* is the complex dielectric constant given by $\epsilon^* = \epsilon + i\sigma$. Since

$$n = c\sqrt{\mu\epsilon} \quad ,$$

we must have for the complex index of refraction (which inherently includes absorption)

$$n^* = c\sqrt{\mu\epsilon^*} \quad .$$

Recognizing the unity of μ for most nonmagnetic materials and again converting to cgs units,

$$n^{*2} = \epsilon^* \quad .$$

Let

$$\epsilon^* = (\epsilon_1 + i\epsilon_2)$$

and

$$n^* = n + ik \quad ,$$

then

$$\epsilon_1 = n^2 - k^2$$

and

$$\epsilon_2 = 2nk \quad .$$

Solutions to the wave equations for conducting media can be found for both $\vec{E}$ and $\vec{H}$; by application of the boundary conditions, the Fresnel formula for calculating reflectance can be obtained. The expressions, however, become very cumbersome. In the case of an infinitely thick absorbing film, the expressions for the polarized components of reflected light reduce to

$$R_p = \left| \frac{[(n + ik)^2 - \sin^2\theta]^{1/2} - (n + ik)^2 \cos\theta}{[(n + ik)^2 - \sin^2\theta]^{1/2} + (n + ik)^2 \cos\theta} \right|^2 \qquad (15)$$

and

$$R_s = \left| \frac{[(n + ik)^2 - \sin^2\theta]^{1/2} - \cos\theta}{[(n + ik)^2 - \sin^2\theta]^{1/2} + \cos\theta} \right|^2 \quad , \qquad (16)$$

where R_p and R_s represent the components of reflected light polarized parallel and perpendicular, respectively, to the plane of incidence; θ is the angle of incidence; and n and k are real. These same expressions are obtained more directly by substituting the complex index of refraction $n^* = n + ik$ for n in equations (10) and (14).

For unpolarized light, the reflectance is given by

$$R = \frac{R_p + R_s}{2} \quad .$$

For partially plane polarized light, the reflectance is given by

$$R = \frac{(PR_p + R_s)}{1 + P} \quad ,$$

where $P = I_p/I_s$ is the ratio of parallel to perpendicular intensities in the incident light [5].

In the case of normal incidence, for an unpolarized incident light beam, the expression for the reflectance is particularly simple:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

With equations (15) and (16), knowing the polarization of the incident beam and measuring experimentally the reflectance for at least two angles of incidence leads to two equations in two unknowns for n and k. Because of the form of equations, it is necessary to solve for the optical constants by iterative techniques, using a computer to handle the numerous tedious computations required to achieve convergence to a set of n and k giving best agreement with the measured reflectances. The accuracy in determining n and k is obviously limited to the accuracy in measuring R; however, if R is measured for multiple angles of incidence from normal to grazing incidence, the results are often improved.

INSTRUMENTATION

Wavelengths 120 to 200 nm

The optical schematic of the equipment used for measuring optical properties in this spectral region is shown in Figure 2. The light source was a commercial Hinteregger gas-discharge lamp, operated windowless with a current-regulated dc power supply. The source gas was hydrogen, flowing into and out of the windowless lamp capillary at a nominal pressure of 1 mm.

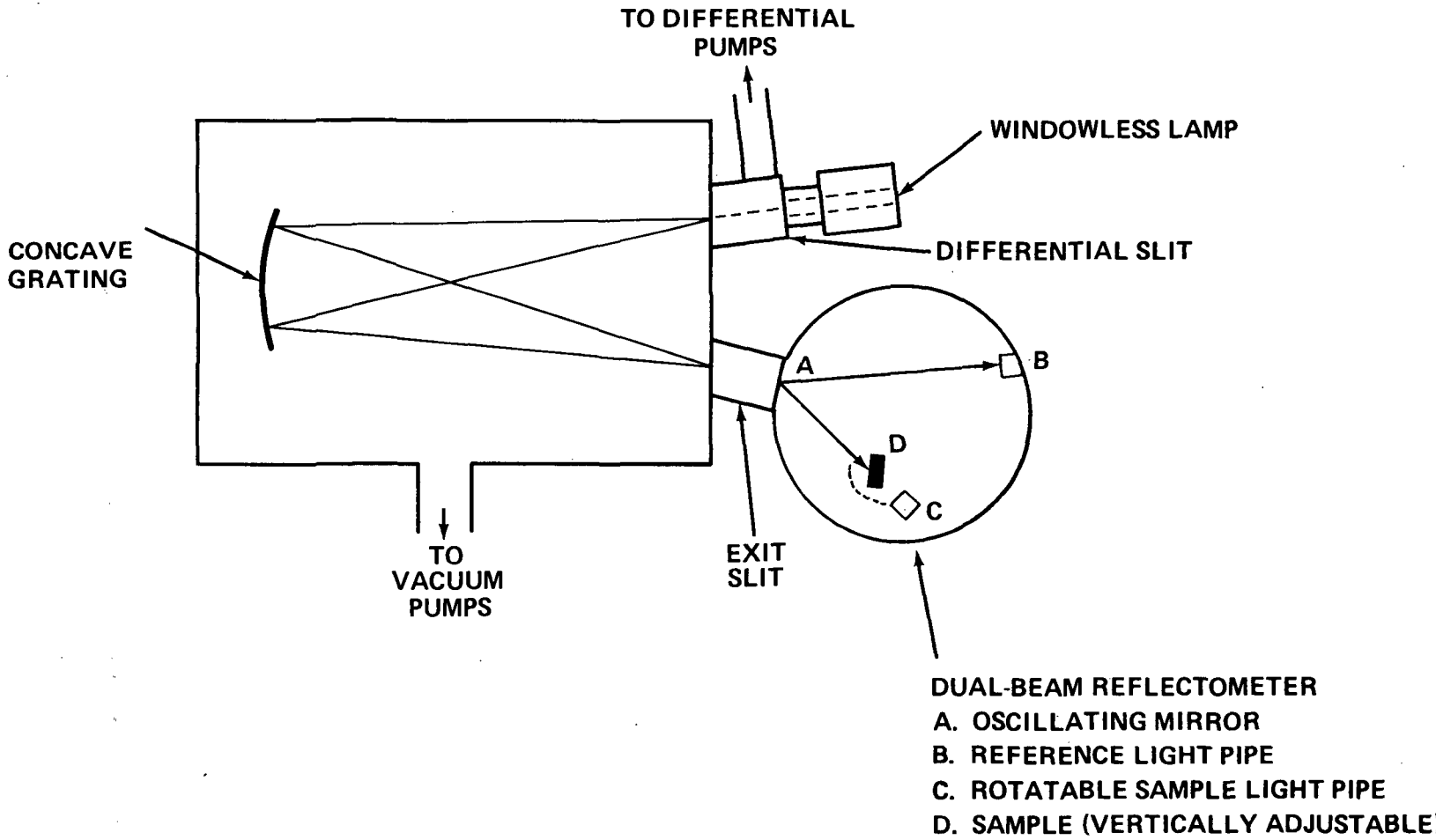

Figure 2. Optical schematic of equipment for vacuum ultraviolet studies.

The differential pumping system, indicated in Figure 2, pumps directly on the monochromator entrance slit to minimize the leakage of the source gas into the main chamber. The dc-excited discharge is maintained in a water-cooled, constricted glass capillary in the lamp.

The monochromator is a 1-m, normal incidence McPherson 225. The concave grating is coated with magnesium fluoride over aluminum, ruled with 1200 lines/mm, and blazed at 220.0 nm. The exit slit is bilaterally adjustable and is maintained at a nominal setting of 20 μm. The monochromator and the detector assembly are maintained at a vacuum of 10^{-5} N/m^2 by a 15.24-cm (6-in.) oil diffusion pump with a liquid nitrogen trap. The spectrum of hydrogen obtained with the Hinteregger lamp and this monochromator is shown in Figure 3. This type spectrum was employed in the optical properties measurements.

The detector assembly, shown schematically in Figure 2, is a McPherson dual-beam reflectometer. The light from the monochromator exit slit, after passing through a rotatable filter wheel, is incident on a focusing mirror (Fig. 2) which, by oscillating at 6.5 Hz, alternately reflects the beam to the sample and reference channels. In the reference channel the beam strikes a sodium-salicylate-coated light pipe and is detected by a photomultiplier tube (EMI Model 9635B). The phosphor coating luminesces at visible wavelengths when ultraviolet light is incident, providing a means of detecting short wavelength radiation without windowless detectors. When the light beam is deflected to the phosphor-coated sample channel light pipe, the signal is detected by a matched photomultiplier at the base of the unit. When these two signals are made equal by gain adjustments, the I_0, or 100 percent, is set. If the sample is placed in the beam at some angle of incidence and the sample light pipe rotated to twice that angle, the assembly provides a ratio signal equal to the reflectance. Scanning the wavelength range with the monochromator then provides a spectral reflectance curve for one angle of incidence. The electronic ratioing is accomplished by two Brower Model 131 lock-in voltmeters and a Brower Model 151 ratiometer. The output is displayed on a Hewlett-Packard two-channel strip-chart recorder. Figure 4 is a photograph of the vacuum ultraviolet facility, which includes the lamp power supply and the dual-beam electronics.

Wavelengths 40 to 120 nm

Optical data in this spectral region were obtained using the 240-MeV electron storage ring of the Physical Sciences Laboratory (PSL) of the

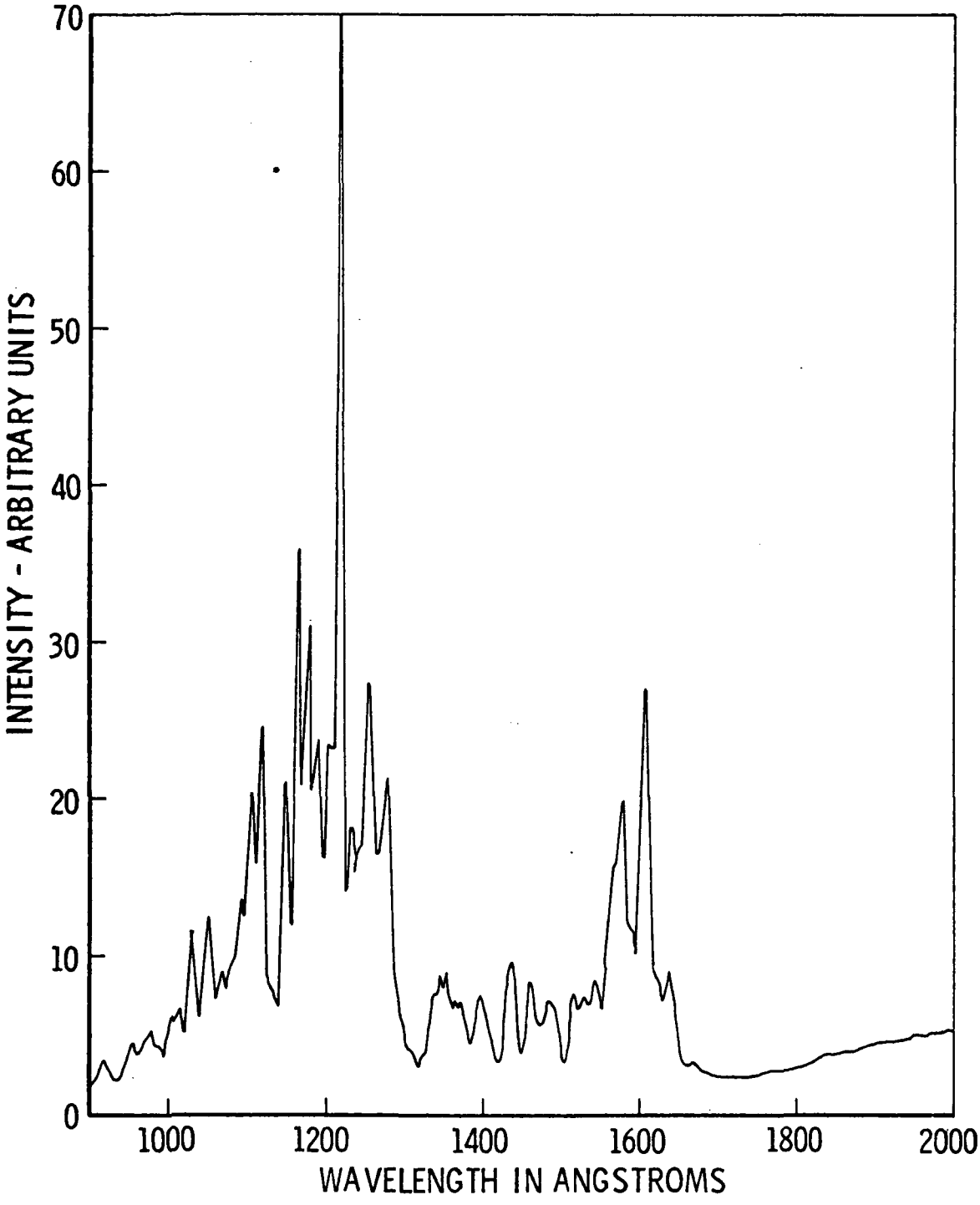

Figure 3. Lamp spectrum with hydrogen gas.

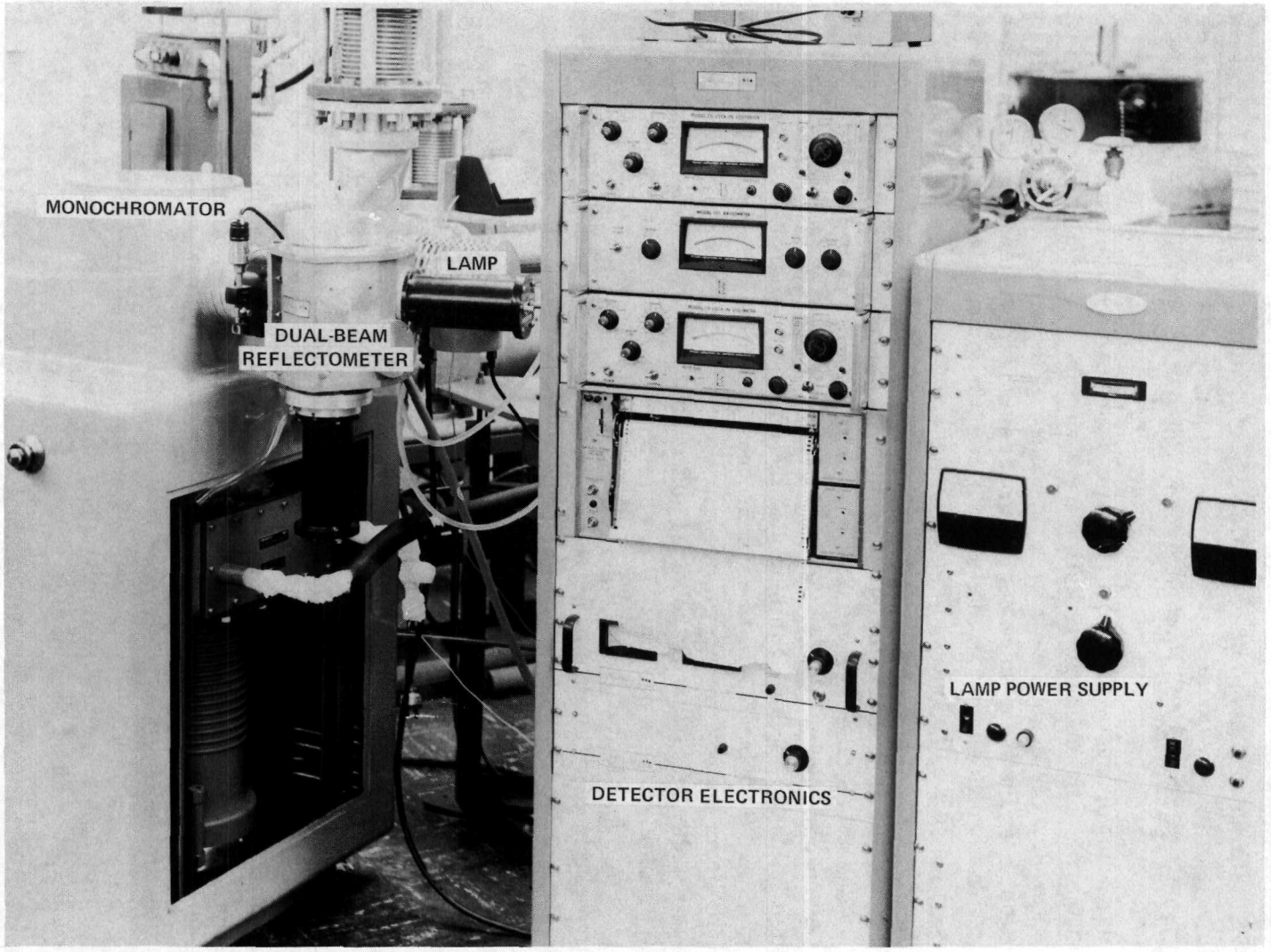

Figure 4. Vacuum ultraviolet laboratory.

University of Wisconsin as a source of highly polarized synchrotron radiation[1]. The PSL storage ring, fed by a 45-MeV injector synchrotron, accelerates the injected electron beam to the maximum energy and, by focusing fields of eight bending magnets and four quadrupole magnets, confines the beam to a nearly circular orbit. The centripetal acceleration of the electrons in the circular orbit produces the synchrotron radiation which is then available as a source of electromagnetic radiation for a variety of investigative purposes. While the electron beam loses energy because of the emission of the synchrotron radiation, a radio-frequency accelerator restores this energy on a continual basis. The orbiting beam is then maintained for hours as a stable source of soft X-ray and far ultraviolet light for optical studies.

The detailed characteristics of the PSL storage ring have been adequately described elsewhere [6, 7], and only the most pertinent features will be reviewed here. One of the most useful features of the storage ring is the high intensity spectral continuum of the emitted synchrotron radiation. The spectral distributions of the synchrotron radiation for several values of electron beam energy are shown in Figure 5 [8]. There is no other type system capable of sustaining spectral continuum at these wavelengths for any appreciable length of time. Polarization of the synchrotron radiation is also a significant factor which must be considered since the flux is almost totally polarized in the orbital plane of the storage ring, although there is a wavelength dependency and some variation as a function of the spectrometer's inclination angle with respect to the orbital plane. The level of stray light was measured by inserting a quartz optical filter into the beam with a transmission cutoff at much longer wavelengths than those under study.

The synchrotron radiation can be observed at a number of ports. A system of grazing incidence mirrors focuses the beam into the desired optical apparatus. For these data, the north port of the PSL storage ring was used, which included a normal incidence monochromator designed by the Physical Sciences Laboratory for optical studies down to 30 nm. The optical characteristics of this monochromator are very similar to those of the monochromator described previously, except that the grating, with 1200 lines/mm, was coated with gold and blazed for 80 nm. The detector was, again, a McPherson Model 665 dual-beam reflectometer but was modified in size to accommodate a separate vacuum-pump assembly. The signals were detected with the same electronics described previously.

1. This facility is supported by Air Force Contract F44620-70-C-0029.

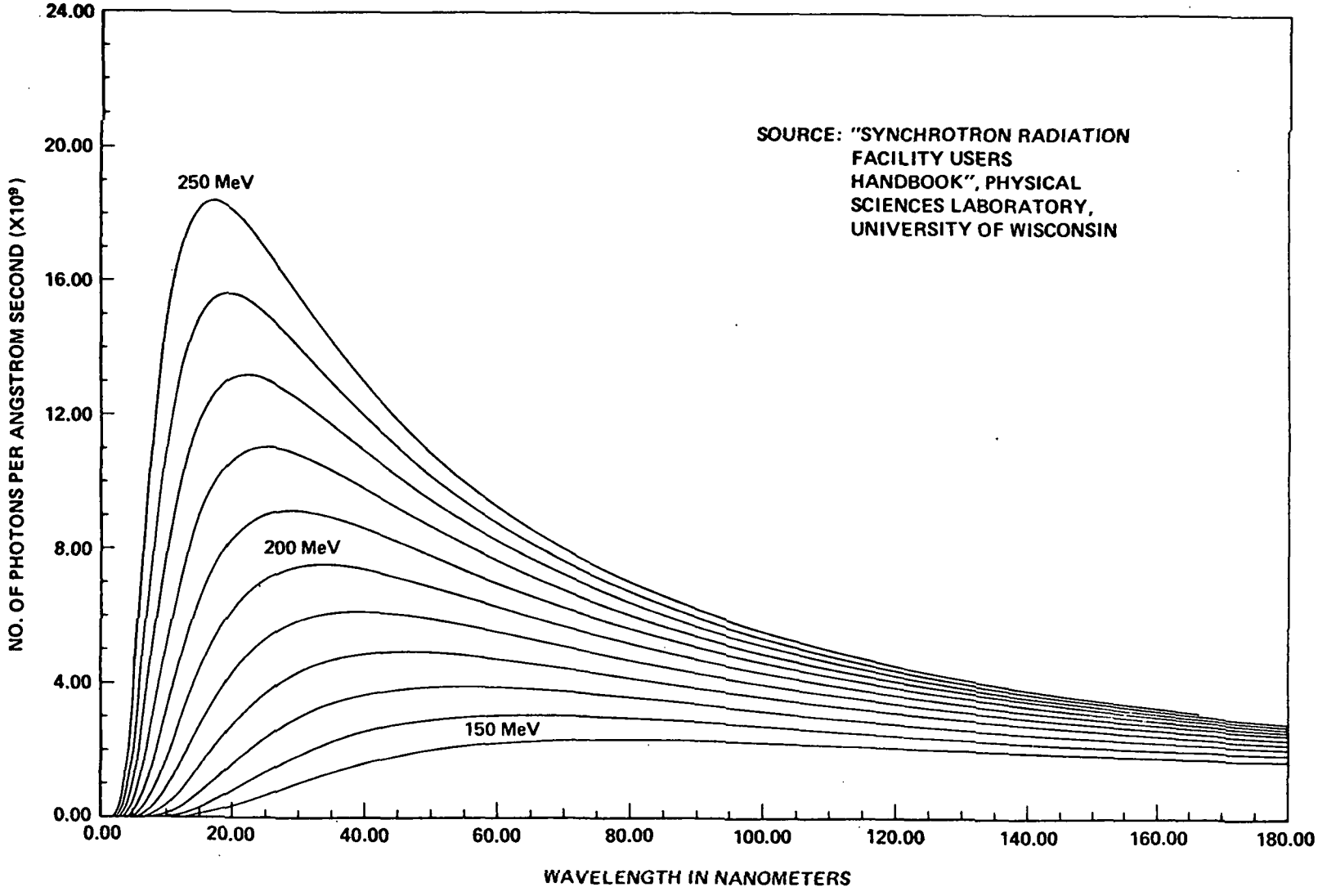

Figure 5. Photon flux into 1 mrad versus wavelength, 1-mA beam, E = 250, 240, ... 150 MeV.

The storage ring is maintained by an ion-pump vacuum system at a pressure in the 10^{-10} torr range. All equipment that is coupled to the ring and is open must be maintained at a pressure of at least 10^{-8} torr. Thus, the monochromator and the reflectometer had separate vacuum ion-pump assemblies to minimize the pressure differential with the storage ring and to prevent contamination. The monochromator was evacuated with a 200 liter/sec Ultek D.I. pump and an air-cooled sublimation chamber. The reflectometer had the same type pumping system, although the ion pump was smaller, with a 100 liter/sec capacity.

The optical constants of those mirrors subjected to the synchrotron facility measurements were calculated for reference purposes at three wavelengths in the vacuum ultraviolet from data obtained on a separate experimental facility at Marshall Space Flight Center. Using the same windowless Hinteregger lamp with helium and neon as source gases, a McPherson Model 247 grazing-incidence monochromator, and a specially designed single-beam reflectometer, the optical data at 58.4, 73.5, and 121.5 nm on these type mirrors were obtained. These data were used, in a manner to be discussed in the next section, to determine the magnitude of polarization present in the synchrotron data.

MEASUREMENTS AND RESULTS

Measurement Approach

The specular reflectances of opaque thin films of platinum and gold were measured as a function of the angle of incidence in the vacuum ultraviolet. In the wavelength region of 40 to 120 nm, the synchrotron radiation continuum was scanned at a speed of 200 Å/min, and the ratio of the reflected to the incident light intensities was recorded from the output of the Brower 151 ratiometer. At the longer wavelengths to 200 nm, the many-lined spectrum of hydrogen was scanned at 100 Å/min and 200 Å/min by the same equipment, and the reflectances were recorded.

The results to be described are the average obtained from measurements of many samples of the same type. The mirrors consisted of thin films of 99.999 percent pure metal evaporated in a vacuum of 10^{-5} N/m^2 by an electron gun to a nominal thickness of 500 Å on polished (1/10 λ flat) quartz substrates. The substrates were not externally heated during evaporation.

It was necessary to correct the measured data for incident light polarization that was introduced in varying degrees as a function of wavelength by grazing incidence transfer optics, the monochromator grating, and, at the short wavelengths, by the nature of the generation of the synchrotron radiation. That polarization is a significant factor in the reflectance of a material, particularly at angles of incidence far from the normal, can be seen by inspection of Figure 6, which was calculated for platinum at 58.4 nm using the literature values of the optical constants [2].

The magnitude of polarization of the incident light at the synchrotron facility was approximated by comparison of the observed reflectances to curves of the type shown in Figure 6; the curves of reflectance as a function of the incident light polarization were calculated, based on optical constants of similar mirrors determined at 58.4, 73.5, and 121.5 nm, using a grazing-incidence monochromator whose polarization properties were known. (See "Instrumentation.") Since the synchrotron polarization was within 20 percent of the total over the short wavelength region, the uncertainty introduced by this correctional procedure had minimal effect on the resulting calculated values of the optical constants.

At the longer wavelengths, the polarization of the McPherson 225 monochromator has been studied in the literature [9] and found to be, at worst, about 10 percent at the shorter wavelengths.

The presence of longer wavelength stray or scattered light was checked by inserting a quartz filter into the beam at wavelengths below the transmission cutoff. In the synchrotron beam, components of stray light were generally less than 2 percent of the available intensity in this spectral region.

Results for Gold Thin Films

Thin films of gold deposited on fused silica substrates were measured in the wavelength region of 110 to 200 nm to obtain a comparison with literature data, thus providing a check on the validity of the optical measurements and the calculations of the optical constants. The study of gold thin film mirrors has received extensive attention in the literature, for both theoretical and practical reasons. Gold has a reflectance in the vacuum ultraviolet superior to many materials, and the stability of a gold coating after extended use and storage is excellent. It has been shown that the highest reflectances with gold in the vacuum ultraviolet are obtained with semitransparent coatings, by taking advantage of interference effects between the gold film and glass

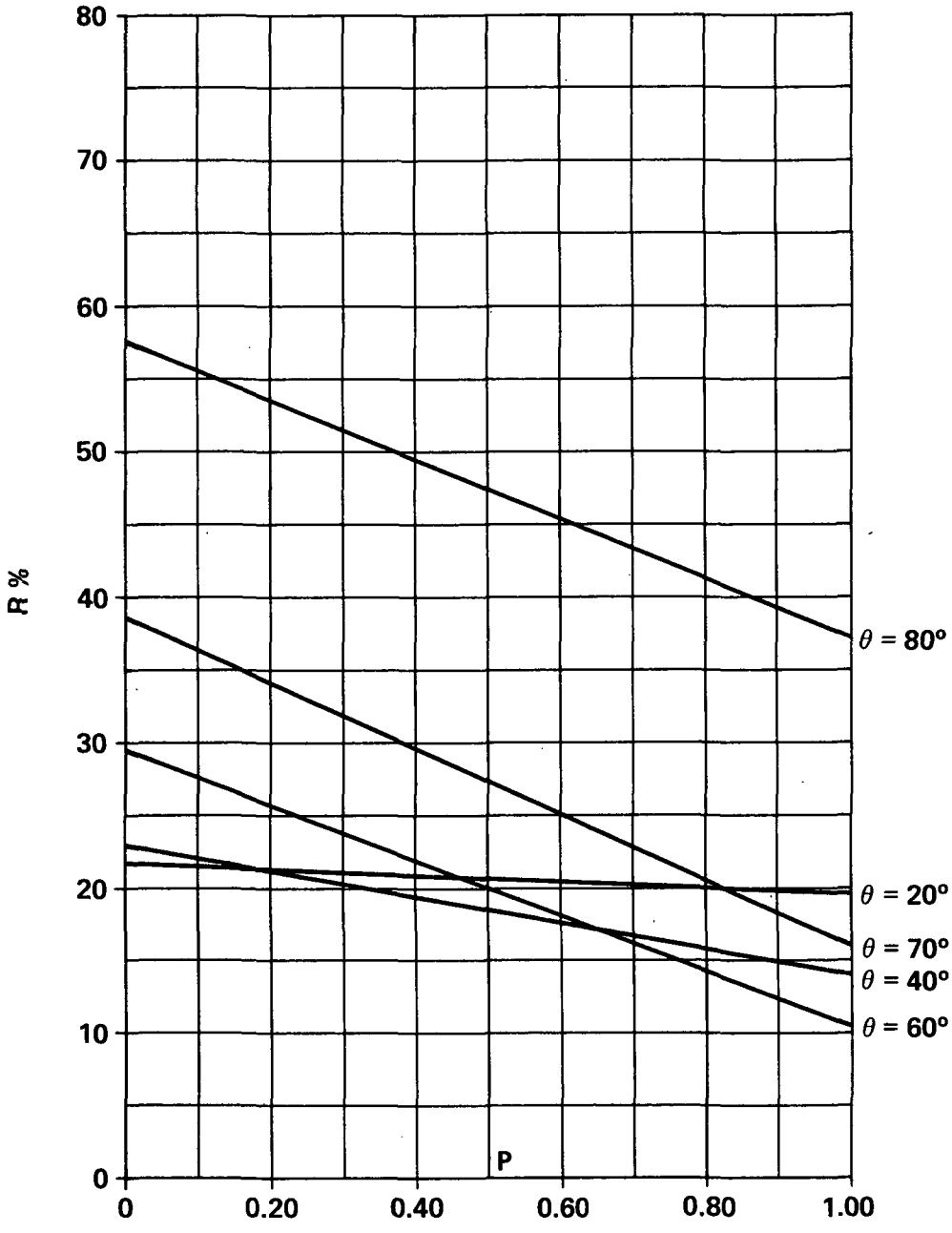

Figure 6. Reflectance of platinum, 1215 Å, as a function of polarization for various angles of incidence.

substrates [10]. For calculating the optical constants n and k, however, an opaque film of the coating material is desired to simplify the calculations by eliminating the effects of the substrate. A further complication arises in

that surface roughness generally increases with thickness, an undesirable factor for specular reflectance measurements. Canfield, Hass, and Hunter [10] have approached this problem for gold by measuring the minimal thickness required for 99.9 percent opacity as a function of wavelength in the ultraviolet. Considering these data, the selected thickness of the measured gold film mirrors was about 600 Å.

The measured specular reflectance at 20-degree and 70-degree angles of incidence for gold is plotted in Figure 7 as a function of wavelength, with the data of Canfield et al. shown for comparison. Since the original results shown in Figure 7 are the results of an average of many measurements of gold film mirrors and since it is known that the optical properties of a thin

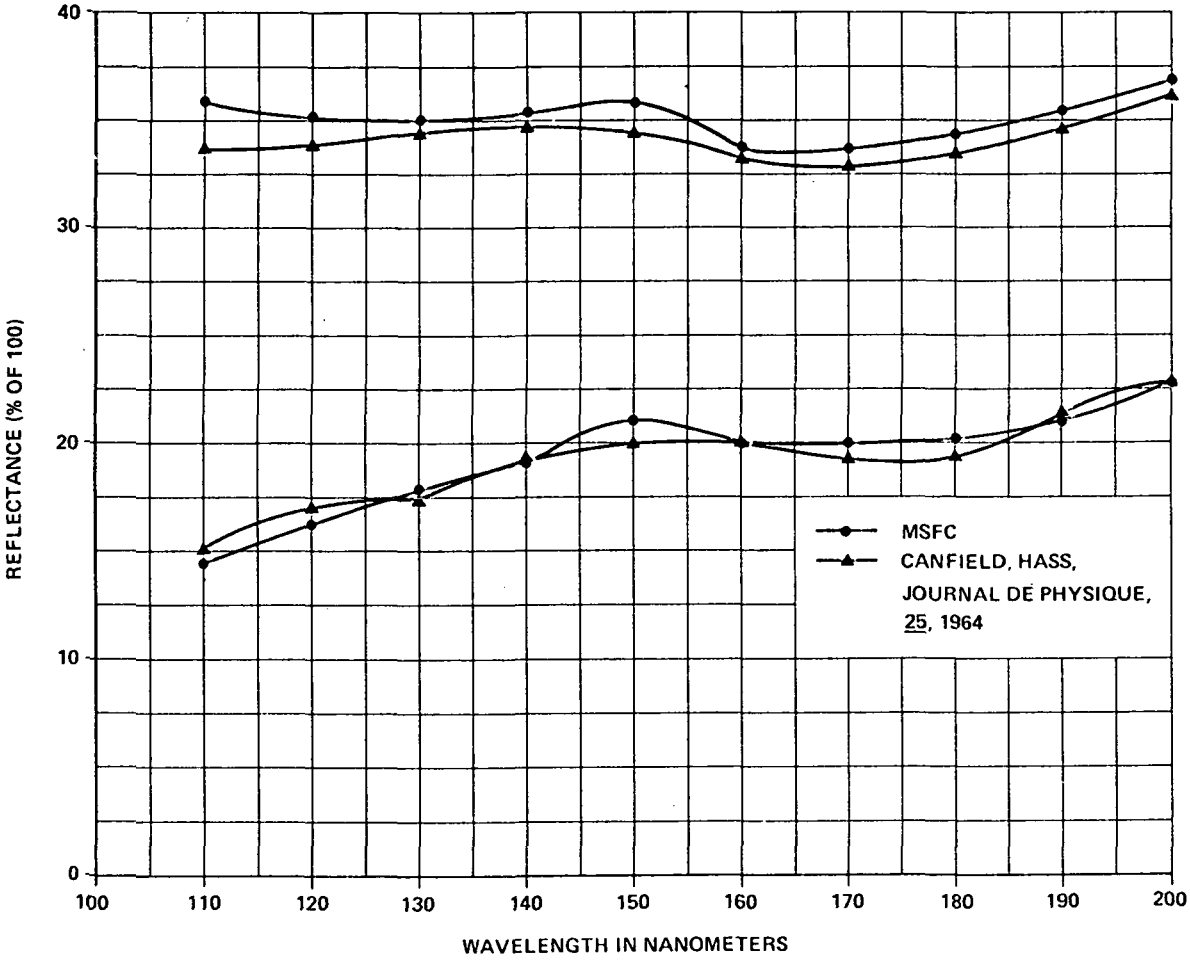

Figure 7. Reflectance of gold at 20 degrees and 70 degrees.

film mirror depend on material purity, evaporation conditions, thickness, and other factors, it is surprising that the agreement is so close. This does not mean that the original results are, therefore, that accurate, but that they are, at least, consistent in magnitude and spectral dependence with independent results in the literature.

By using the computer program to solve for n and k from these data (see "Introduction"), the results shown in Figure 8 were obtained. Again, in comparison with the data of Canfield et al. on a percentage deviation basis, the results are very close. Since the computer programs used depend on iterative techniques to achieve convergence to a "best" value and the differences shown in Figure 8 are generally about 5 percent or less, the different analytical approaches seem to lead to basically consistent results. Below 120 nm, however, the differences are greater and may be due to an incorrect value of polarization at these wavelengths in the original data.

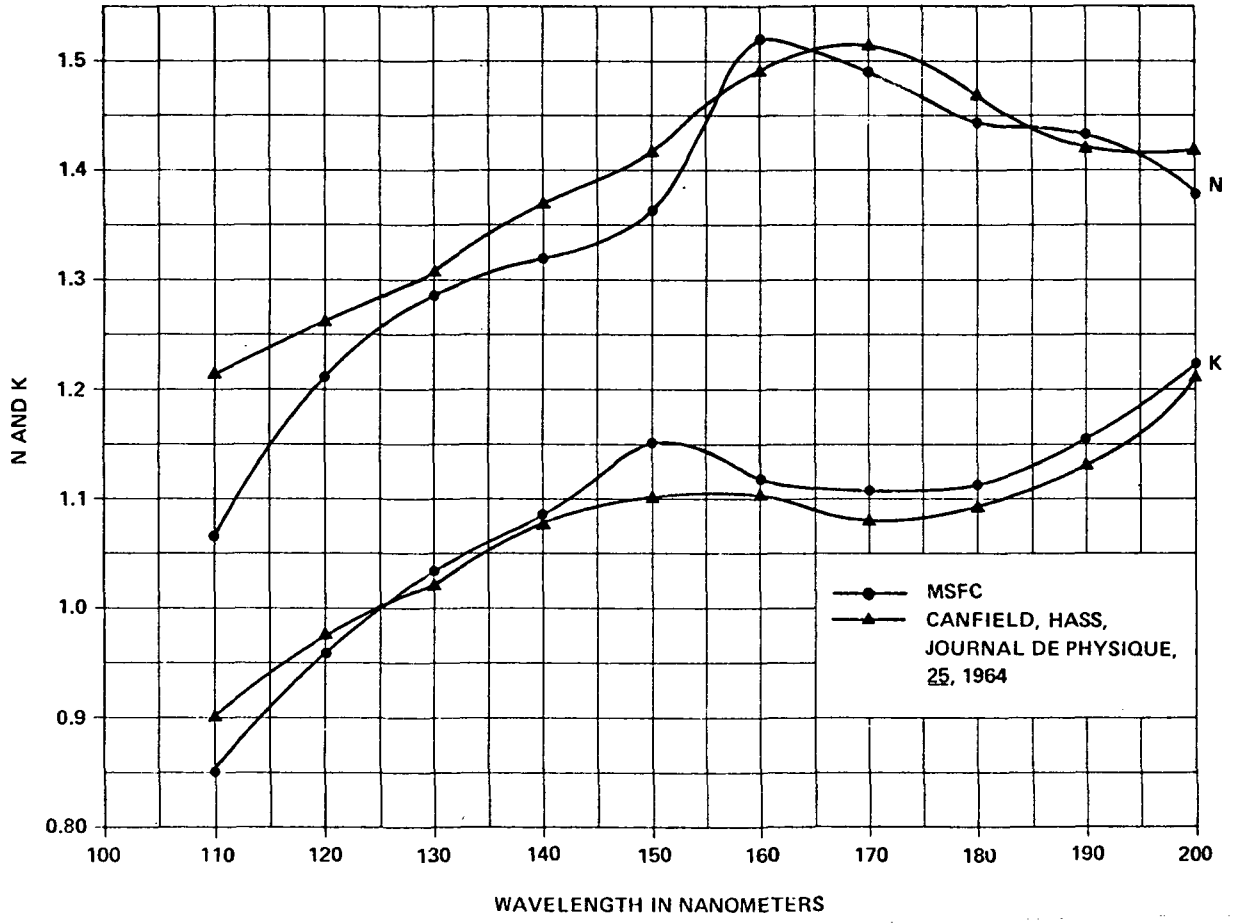

Figure 8. Optical constants of gold in the vacuum ultraviolet.

Since the results agree well with representative literature data on gold, the conclusion is that the approach taken in these measurements should lead to results reproducible by independent laboratories and valid to that extent.

Results for Platinum Thin Films

The reflectance values at 20-degree and 70-degree angles of incidence for platinum in the vacuum ultraviolet are shown graphically in Figure 9. The discontinuity in the curve for the 70-degree reflectance is directly attributable to the polarization differences of the instrumentation used above and below 120 nm. As discussed previously in the topic entitled "Instrumentation," optical properties below this wavelength were measured using the synchrotron facility of the University of Wisconsin, which produces a highly polarized light beam. At the higher wavelengths, the normal incidence monochromator with the gas-discharge lamp produced very little polarization. From Figure 6 it is obvious that polarization has minimal effect for low angles of incidence, while seriously affecting the reflected light intensities at higher angles from the normal.

For comparison, a representative curve of the normal incidence reflectance of platinum [2] is included in the previously mentioned Figure 9; data at higher angles were unavailable. While the absolute magnitudes of the reflectances are higher in the literature curve, the general spectral features are similar. The higher reflectances of the literature curve, particularly at the longer wavelengths, are attributed to interference effects resulting from using semitransparent layers of platinum. To insure that the measured reflectances were solely a property of platinum, thicker layers (600 Å) were employed in the samples used in this study to insure opacity.

Using the optical data of Figure 9 as input, the optical constants of platinum were calculated by a computer program based on iterative solutions to Fresnel's equation for reflectance as a function of n, k, the angle of incidence, and the polarization. (See "Theory.") The results are shown in Figure 10 with the only values found in the literature, at 58.4, 73.5, and 121.6 nm, given for comparison [1]. The values of Jacobus et al. agree fairly well at 58.4 nm, while the other two sets of n and k show some difference on the order of 10 to 15 percent. Such variations in magnitude are not uncommon in the literature for thin films, and the variations emphasize, upon investigation, the influence of evaporation conditions, material purity, and other factors on the resulting optical efficiency. Rather than the absolute

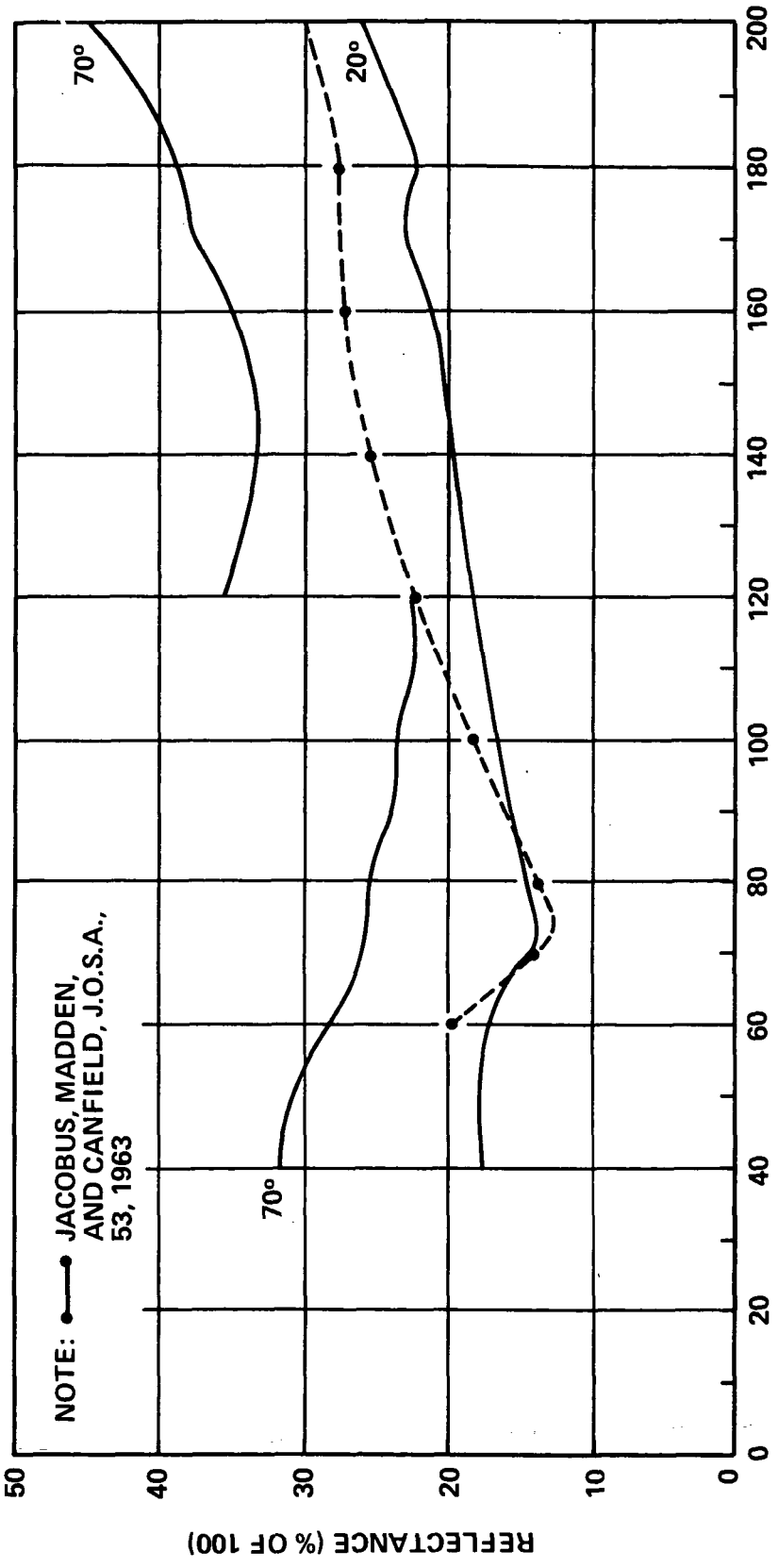

Figure 9. Optical properties of platinum.

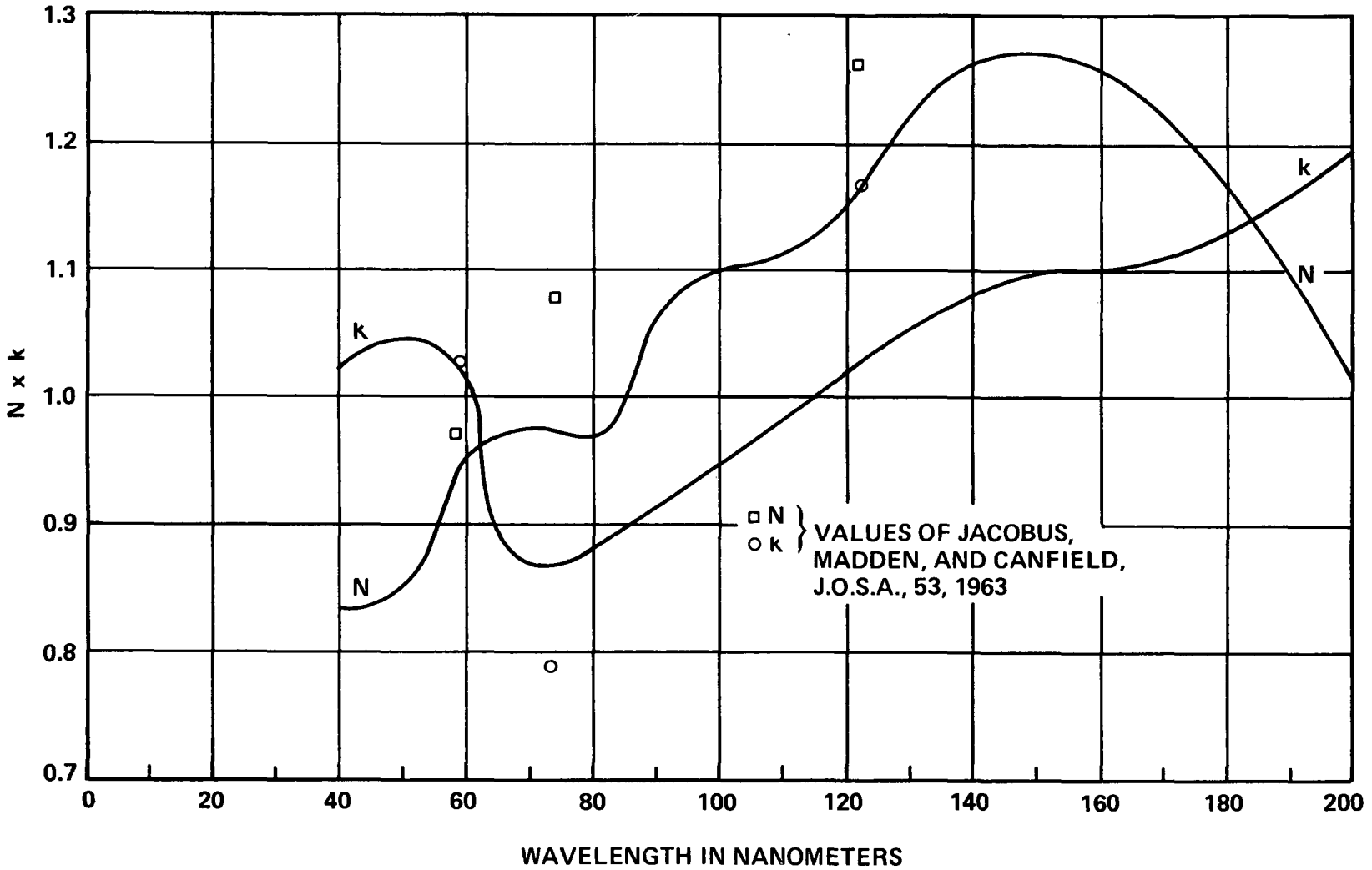

Figure 10. Optical constants of platinum.

magnitude of the values of n and k, the spectral dependence is often of more use in supplementing studies of basic properties of the materials.

The complex dielectric constant, $\epsilon = \epsilon_1 + i\epsilon_2$, is a function of n and k and, thus, varies with wavelength. The real and imaginary parts of ϵ, ϵ_1, and ϵ_2 are very useful in relating metallic spectra to atomic band structure. The spectral behavior of ϵ_2, particularly maxima and steep slopes, relates to optical transitions in the solid between filled and unfilled states [11]. It can be shown that the quantity ϵ_2 is proportional to the density of states in the material, so that the spectral dependence may reveal information about the existence of band gaps and the quantitative value may indicate the type of transition responsible and its strength.

The calculated real and imaginary parts of the complex dielectric constant for platinum are shown in Figure 11. Converting the wavelength to units of energy ($E = hc/\lambda$ eV), there are three relatively distinct features of the ϵ_2 curve for platinum occurring at about 20.7, 13.1, and 7.7 eV. The 13.1-eV value of ϵ_2 is an approximation of the "center" of the bump in the ϵ_2 curve between 80 and 110 nm. Whether through oversight, insufficient search, or lack of literature data on the band structure of platinum, the only feature of the ϵ_2 curve with some possibility of identification as a transition is the broad but intense peak at 7.7 eV. Klein and Rudberg [12] have reported results of electron energy loss measurements on platinum at 5.2 and 6.5 eV, respectively, pointing to the possible cause as an interband transition.

A different approach to the same type objective is available such that the spectral behavior of the quantity $-\mathrm{Im}\,(\epsilon^{-1}) = +2nk/(n^2 + k^2)^2$ should have peaks corresponding to characteristic absorption processes [13]. These absorption processes may alternatively be derived from analysis of characteristic electron energy loss spectra, which represent the energy spectra of electrons scattered in a given material; the peaks in the energy spectra, measured from the "central image" due to elastic scattering, represent the energy loss values in the scattering process. The energy loss values are characteristic of the given material, independent of the incident electron energy. The calculated values of the energy loss function $-\mathrm{Im}\,(\epsilon^{-1})$ are plotted in Figure 12 as a function of wavelength. From this plot three peaks whose values are about 24.4, 16.0, and 6.7 eV may be seen. A bump in the curve between 105 and 130 nm is centered about 10.8 eV. There have been numerous studies of the characteristic electron energy loss in platinum by scattering measurements, with peaks identified as shown in Table 1 and the corresponding peaks in the energy loss function found in this study included for comparison. Thus, the features found in this work do correspond well

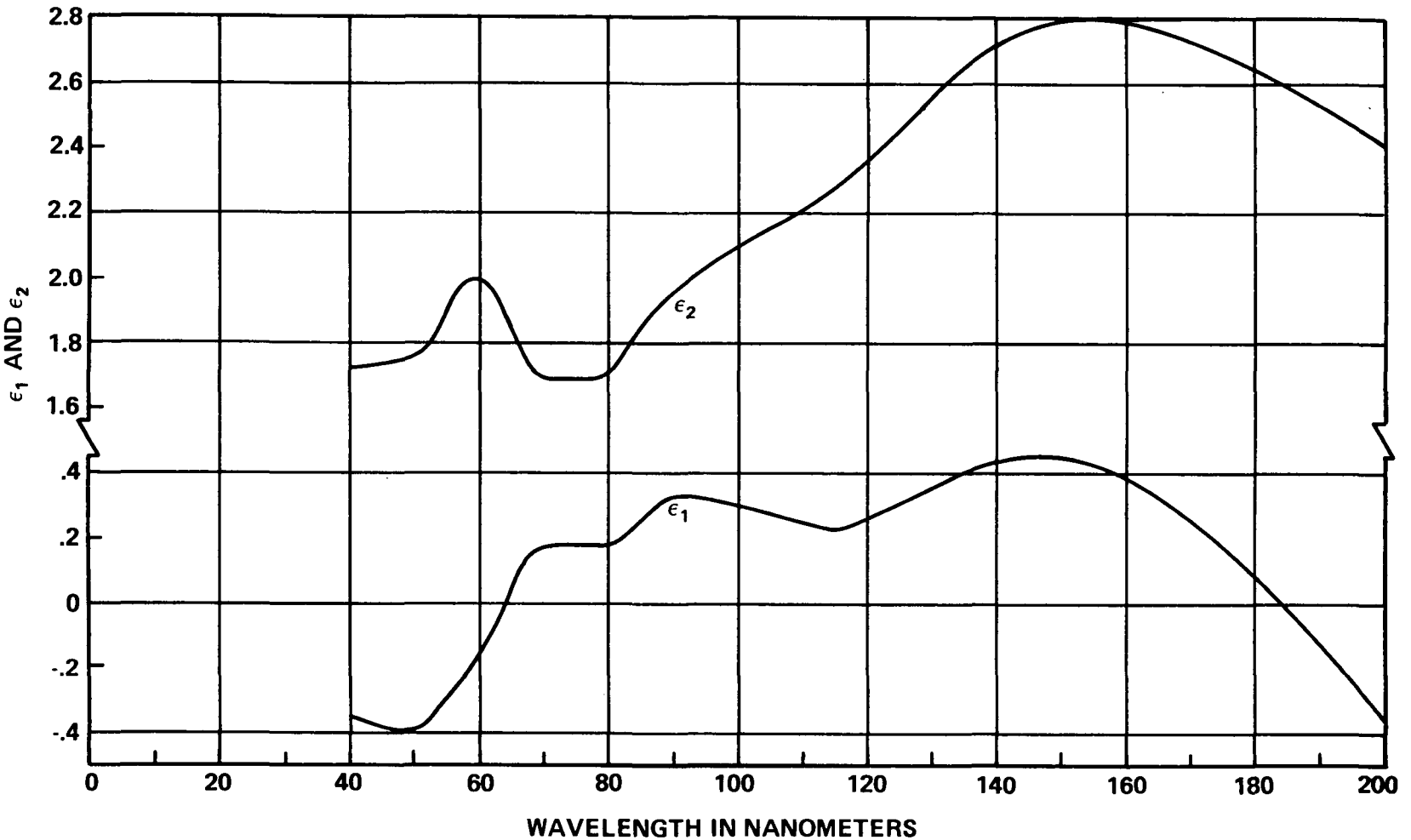

Figure 11. Dielectric constants of platinum.

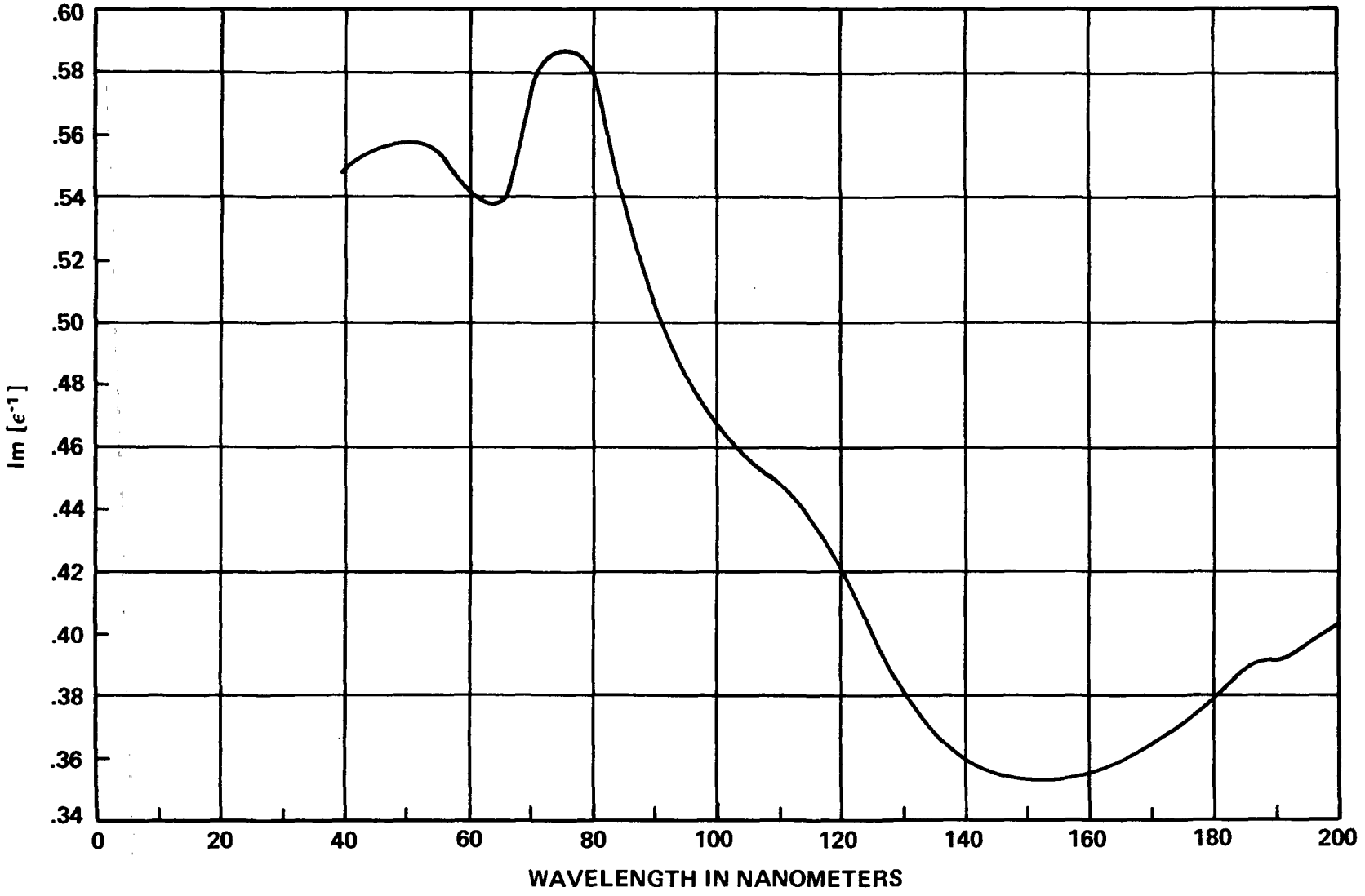

Figure 12. Energy-loss function of platinum.

TABLE 1. CHARACTERISTIC ELECTRON ENERGY LOSSES IN PLATINUM [13]

Powell	6.2	---	14.3	24.4	----	---	---	---
Rudberg	6.5	9.4	----	24.8	33.7	---	---	---
Mollenstedt	---	---	14	22.4	----	---	46	61.4
Klein	5.2	---	----	22.6	----	---	---	---
Gauthé	---	---	18.5	23.9	30	37	47	---
Peaks in the Energy Loss Function -Im (ϵ^{-1}) for Platinum								
Present Work	6.7	10.8	16.0	24.4	---	---	---	---

with existing energy loss phenomena discovered in the electron scattering measurements. The assignment of a particular atomic process, whether intraband transition or collective (plasma) oscillation, is more difficult. The condition for collective electron oscillation is satisfied when the value of ϵ_2 is small and ϵ_1 crosses zero (n + k). From the curves of ϵ_1 and ϵ_2 (Fig. 11), it appears that ϵ_1 crosses zero in this spectral range twice, at energies of about 19.2 and 6.8 eV. However, ϵ_2 has a minimal value of about 1.7 (dimensionless) over the given spectral range and is not as small as is generally required for ϵ_2 or ϵ_1. In this case, it would be difficult to interpret any of the features of either the curves of ϵ_1, ϵ_2, or -Im (ϵ^{-1}) as collective or plasma oscillations. The identification of the phenomena giving rise to the salient features of these data must await the reception and analysis of further information, such as band structure calculations.

In this work the optical constants of platinum in the vacuum ultraviolet were determined apparently for the first time. From analysis, agreement was found between observed energy losses from these optical data and results of electron energy scattering measurements.

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama, September 1, 1972
114-03-07

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