

PHOTOELECTRIC DETERMINATION OF WORK FUNCTION VIA CREMSEE ENHANCEMENT. PHOTO-CREMSEE †

Mark NILGES and Jack H. FREED

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853 USA

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CREMSEE (cyclotron resonance from microwave-induced secondary electron emission), operated at a microwave power level just below threshold for self-sustaining signals may be used as an electron-amplifier and detector of photoelectrons. A determination of the work function of air-oxidized Ag on the interior surface of a UHV-microwave cavity yields 4.06 ± 0.05 eV.

In recent studies [1–3] we have shown the considerable potential of two novel surface techniques: UHV ESR and CREMSEE. Both these techniques are based upon methods we have developed whereby *in situ* studies of adsorption on metal (and oxide) surfaces can be performed in a microwave cavity, the interior of which is under ultra-high vacuum (UHV) and is, in fact, part of the UHV system. We have provided details of our techniques elsewhere [2]. CREMSEE, or cyclotron resonance from microwave-induced secondary electron emission, was shown to complement ESR studies on metal surfaces, because it is a very sensitive indicator of chemisorption of molecules on metal surfaces, and it does not require the existence of any paramagnetic species. Thus, in a study of NO_2 on clean Cu surfaces [1,2], it was shown by CREMSEE that pure NO_2 oxidizes the Cu surface even though no ESR signal is obtained from surface Cu^{II} species, while the presence of H_2O in the NO_2 permits the formation of Cu^{II} -aquo complexes with distinct exchange-narrowed microcrystalline types of ESR spectra. In another study of a stable nitroxide di-tertiary butyl nitroxide (DTBN), it was shown that this radical appears to lose its paramagnetism when adsorbed on a clean Cu or Ag surface (except perhaps below -100°C),

while this is not the case if the surface is first air oxidized [3]. CREMSEE was used to demonstrate the existence of a (presumably diamagnetic) chemisorbed bond between the DTBN and the Cu or the Ag (below $\approx -30^\circ\text{C}$) surface [3]. The experiment of monitoring of the CREMSEE microwave power threshold P_t , as a surface is dosed with a molecular species, is similar in some respects to performing work function measurements [4] with surface dosage. The latter is also sensitive to the formation of chemisorbed bonds with some polarity (or charge separation). The advantage of CREMSEE is the almost order-of-magnitude changes in P_t that are observed [1–3], compared to relatively smaller changes typically observed in work function (usually up to 25–50% changes) [4].

As yet we do not have a rigorous formal theory for CREMSEE. It is basically a self-sustaining, steady-state electron cyclotron (ECR) signal ($g = 2$) seen when the UHV ESR cavity is under vacuum (i.e. pressure $< 10^{-2}$ Torr) and is present in the empty cavity (i.e. at 10^{-10} Torr). One must, however, maintain the microwave power level above P_t , the threshold level. Our experiments [1–3] show that the electrons are from the surface, and the steady-state presence of free electrons ($\approx 10^3$ at P_t) in the cavity undergoing ECR is due to their colliding with the cavity walls, and, because of their excited orbits from the ECR, they cause secondary electrons to be emitted from the surface. That is, when the secondary electron yield is greater than uni-

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ty, there is electron multiplication until surface charge effects oppose further net emission of electrons (1 e the secondary electron yield becomes unity)

Clearly, then, any chemisorbed species which causes a surface dipole, either due to the permanent dipole of the adsorbed molecule and/or charge transfer with the surface, should influence CREMSEE leading to a change in P_1 . Similarly, the work function ϕ is modified by an adsorbed species, and this is attributed to the formation of an electrical double layer [4,5]. Now the secondary emission yield δ is known to depend on ϕ according to $\partial \ln \delta / \partial \ln \phi = -(\bar{E}_s)^{-1}$ where \bar{E}_s is the average emission energy and is between 5 and 10 eV [6-9]. However, the predicted increase in δ from this relation [3] shows it is much too small (only a factor of 1.6 at most) to explain the nearly order-of-magnitude increase in P_1 . Somewhat better agreement is obtained when P_1 is related to E_{p1} , the incident electron energy necessary for $\delta = 1$ (1 e secondary electron emission yield of unity) [3], but further analysis is required.

We wish, in this letter, to address ourselves to two matters. First, it will be important for future applications of UHV ESR and of CREMSEE to surface science to be able to perform some of the more familiar surface experiments [5] to characterize the surface and to interrelate the results with those from the more familiar techniques. It is very difficult to design experiments to perform, e.g. Auger, work function, or other spectroscopic measurements (e.g. UV photoemission (UPS) [10]) in situ in the microwave cavity. Thus we first wish to consider how some of these measurements might be performed in conjunction with UHV ESR and CREMSEE studies. Secondly, we wish to study the "electron-amplifier" and detector properties of CREMSEE described above. In fact, we wish to show that these very "electron-amplifier" and detector properties can be used to perform accurate in situ work function measurements (and possibly other measurements such as UPS). In particular we examine the photoelectric effect in the presence of CREMSEE.

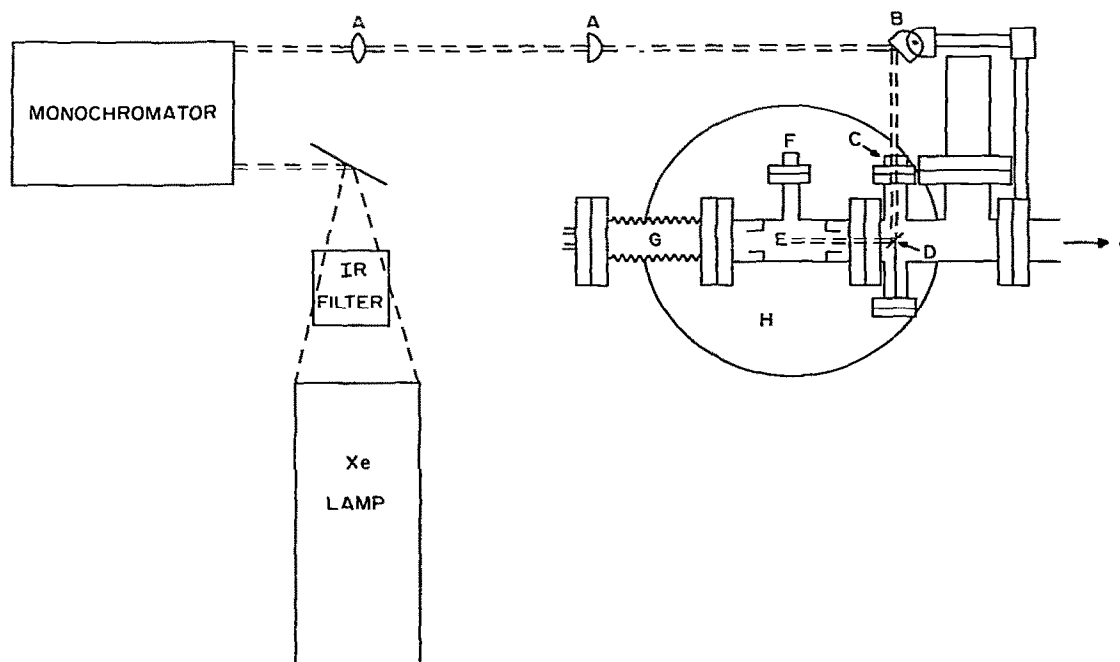


Fig. 1. Experimental arrangement for photo-CREMSEE. Dashed lines represent light beam. Also A = UV lens, B = UV mirror, C = sapphire UHV window, D = mirror in UHV system, E = UHV ESR cavity, F = UHV microwave feedthrough, G = bellows and tungsten filament arrangement for metal evaporation (cf. ref. [2]), H = magnet pole face, J = to UHV pumps, etc.

We show our experimental arrangement in fig. 1. Light from an XBO 150 W Xe lamp mounted in a PAR ALH215 housing which is placed ≈ 13 inches from the monochromator (a 1/4 m Amunco with a grating blazed at 300 nm), so as to focus a spot of $\approx 1/4$ inch diameter on the entrance slits of the monochromator, after passing through an IR filter. The output as a function of wavelength λ was calibrated by use of a quantum counter. This was done by measuring the fluorescence of a concentrated solution of rhodamine B (in ethylene glycol) at a direction perpendicular to the beam incident from the monochromator. To eliminate background scattered visible radiation when making intensity measurements, two Corning 9863 (1 mm thick each) filters were used. Absorption curves for these filters were obtained by running an absorption spectrum on a Cary 14. Light exiting from the monochromator is directed through two quartz convex lenses as shown in fig. 1. It is necessary to adjust the position of the monochromator so that the light beam just passes by both the magnet yoke and the microwave coaxial cable (cf. fig. 1). These lenses focus a beam onto the UHV sapphire window (with effective diameter of 5/8 inch). This beam was then directed into the UHV ESR cavity with a mirror inside the vacuum system but is directed unevenly over its cylindrical surface, a matter requiring future improvements. Only the electrons emitted from the cylindrical cavity surface, which have linear momentum in the direction parallel to the magnetic field contribute to CREMSEE, and furthermore they form a narrow beam in the center of the cavity (cf. ref. [2]). Therefore only photoelectrons from the prepared surface can contribute to our observation. Data were collected with the monochromator slits left wide open (≈ 8 nm resolution).

The basic idea of the experiment is to sweep the wavelength of the light till $h\nu > \phi$, at which point photo-induced electrons lead to a CREMSEE signal. We have found that the CREMSEE P_t is very slightly lowered by the photoelectric effect (< 0.01 mW), so this lowering cannot be used as a sensitive indicator of this effect. Instead we found that by keeping the microwave power just below P_t , i.e. $P_t - 0.01 > P > P_t - 0.1$ mW, a photo-induced or "photo-CREMSEE" signal may be observed due to the photoelectric effect.

We now wish to summarize the observed properties of this photo-CREMSEE signal.

(1) At a given frequency the signal height S is pro-

portional to the UV light intensity expressed as number of photons W , i.e. $S \propto W$. (In the following W will be on a relative, and not absolute scale).

(2) $S \propto P/(P - P_t)$ to a rough approximation (cf. fig. 2a).

(3) Two sharp signals are observed corresponding to $g = 1.9997$ and $g = 1.9970$, each with derivative peak-to-peak widths of slightly less than 0.2 G (≈ 170 mG). The positions of the two peaks correspond to the two maxima in the CREMSEE absorption [2]. The peaks appear to be symmetric, and show no disconti-

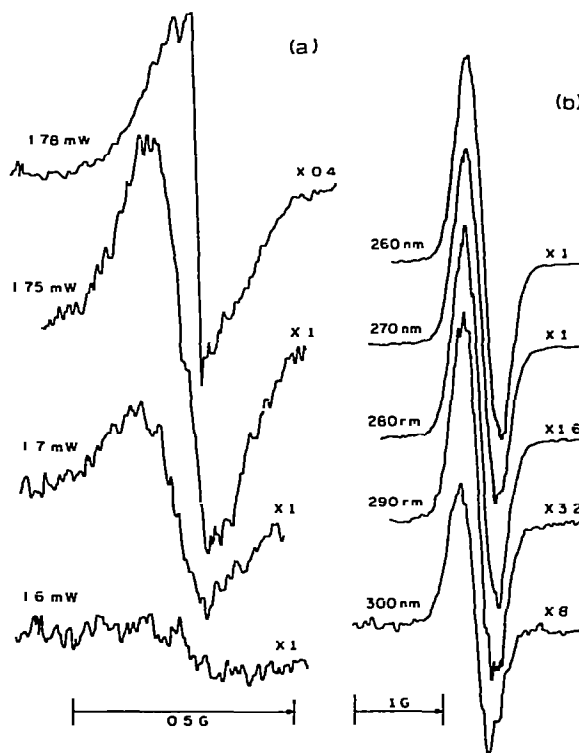


Fig. 2. Photo-CREMSEE signals for an air-oxidized Ag surface at room temperature (A) versus microwave power using light at $\lambda = 270$ nm. The microwave power incident on the UHV ESR cavity is shown as is the relative receiver gain. Normal CREMSEE appears just above 1.8 mW microwave power (B) versus light wavelength using an incident microwave power of 1.75 mW. The values of λ and relative receiver gain are indicated. All signals (A and B) were observed at $g = 1.9970$ (cf. text) and 25 kHz field modulation of ≈ 1.5 G amplitude was used.

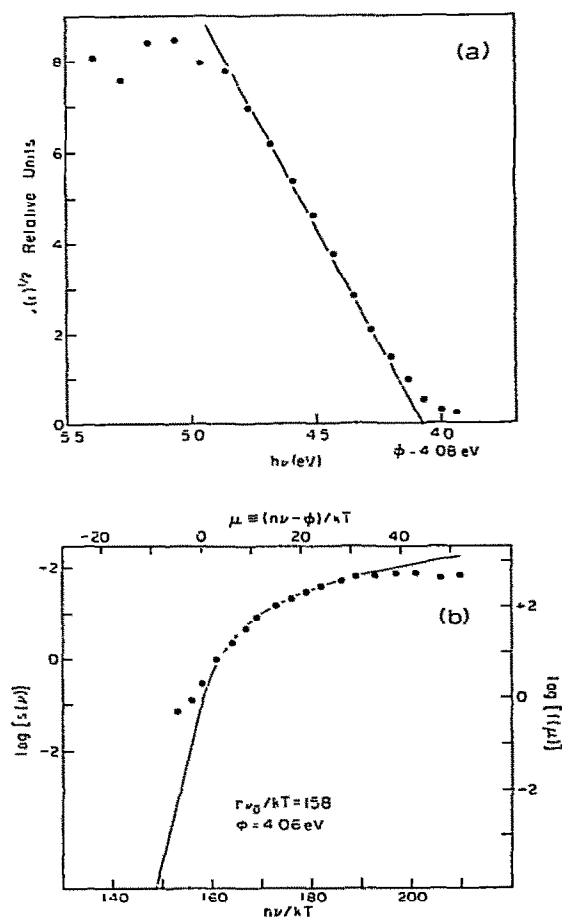


Fig. 3 (A) Photo-CREMSEE peak-height $s(\nu)$ in relative units plotted as $s^{1/2}(\nu)$ versus $h\nu$ in electron volts, the solid line shows least-squares fit through main points (cf. text). (B) Fowler plot of $\log[s(\nu)]$ versus $h\nu/kT$ (cf. text), the theoretical values of $\mu \equiv (h\nu - \phi)/kT$ and $f(\mu)$, which have been adjusted to coincide with the experimental data are shown and the solid curve shows the theoretical curve

nities in their first derivative (cf. fig. 2) (Discontinuities are seen in the CREMSEE absorption itself, cf. ref. [2].)

(4) The signal has the appearance of a normal first-derivative ESR signal, and its width and shape are independent of light wavelength λ (cf. fig. 2b).

(5) The photo-CREMSEE signal is stable, i.e. it

does not add any noise above the receiver level, unlike CREMSEE [2], which exhibits large fluctuations in amplitude. Thus, signals from low light levels can be observed even when S is on the order of the receiver noise.

(6) When both cavity end-rings are biased with a negative voltage [2], the signal becomes weaker and cannot be seen above 5 V. For positive biasing no large change in intensity is seen provided P is kept just below P_t . Also, small changes in the resonant field positions are induced by the biasing voltage.

We may conclude that this photo-CREMSEE signal differs from ordinary CREMSEE in that it is not a self-sustaining phenomenon. That is, the photo-CREMSEE signal disappears as soon as the light is turned off. Nevertheless, microwave power levels close to P_t are required to accelerate the photoelectrons to permit secondary electron emission, but the secondary electron emission yield δ is not quite sufficient to generate the self-sustaining CREMSEE signal. The presence of both primary and secondary electrons during light irradiation, which can engage in ECR, is the "electron-amplification" effect that we believe makes photo-CREMSEE a very sensitive technique.

We now describe the use of photo-CREMSEE to measure ϕ for an air-oxidized Ag surface. First P must be set to within 0.1 mW of P_t , preferably closer to P_t to maximize S/N . Also P must be maintained at a constant level during the experiment. Then the light-induced signal is recorded at 5 or 10 nm increments in λ . Since the photo-CREMSEE linewidth is independent of λ , the signal intensity, $S(\nu)$ is simply proportional to the peak-to-peak signal height. It is known that as $kT/(h\nu - \phi) \rightarrow 0$, then $I \propto (h\nu - \phi)^2/(\phi_0 - h\nu)^{1/2}$, where I is the photoelectron signal intensity (i.e. the induced photocurrent) per quantum of light absorbed [11]. Also $\phi_0 = \phi + \epsilon^*$, where to a first approximation ϵ^* is constant and equal to the electron energy at the Fermi level [11]. Thus for λ such that $h\nu \approx \phi$, we expect $h\nu - \phi$ to vary much more rapidly with λ (or ν) than $\phi_0 - h\nu$. Since we have found $S(\nu) \propto W(\nu)$, it then is reasonable that $I(\nu) \propto S(\nu)/W(\nu) \equiv s(\nu)$. Thus, a plot of $s^{1/2}(\nu)$ versus ν should yield a straight line (provided $h\nu - \phi \gg kT$), and when extrapolated to $s(\nu) = 0$ should give ϕ . This is shown to be the case in fig. 3a for the air-oxidized Ag surface at room temperature, for which we find $\phi = 4.08$ eV. For a clean Ag surface $\phi \approx 4.6$ eV, although non-annealed Ag films

can yield φ as low as 4.3 eV [12,13]. Thus our result for an air-oxidized Ag surface seems quite reasonable, especially in view of the fact that P_t for CREMSEE is decreased significantly by air oxidation [2,3] (Note that P_t increases for adsorption of pure O₂ consistent with the known increase in φ in this case [3,13])

The tail of the $s(\nu)$ curve near the threshold in ν , which tails out to shorter ν values, is known to be due to the thermal population of electrons at the Fermi level (i.e. the inequality $h\nu - \varphi \gg kT$ is being violated) [11]. The points at shorter wavelength ($\lambda < 260$ nm) suffer from our large inaccuracies in measuring the low light intensity at these wavelengths.

A more general approach, which is not limited by the condition $h\nu - \varphi \gg kT$ is based on the graphical method of Fowler [11]. Here we use the result that $\log[s(\nu)/T^2] = B + f(\mu)$ where $\mu \equiv (h\nu - \varphi)/kT$ and

$$f(\mu) = \frac{1}{6}\pi^2 + \frac{1}{2}\mu^2 - f(-\mu), \quad \mu \geq 0,$$

$$= - \sum_{n=1}^{\infty} (-e^{\mu})^n / n^2, \quad \mu \leq 0$$

B is an unknown experimental constant independent of T and ν . One then plots the experimental data as $\log s(\nu)$ versus $h\nu/kT$ (since T is constant in our experiments). Theoretical curves are plotted for different values of μ and B until good correspondence with the experimental data is obtained. In this way we obtain (cf. fig. 3b) $h\nu_0/kT = 1.58$ corresponding to $\varphi = 4.06$ eV. Again the poor fit for $\lambda < 260$ nm is due to the low light intensities, while the poor fit at long λ is due to inaccuracies in measuring the small photo-CREMSEE signals when λ is near hc/φ .

This demonstration of the use of photo-CREMSEE to measure work function shows that this method should now enable us to correlate the observed dramatic changes in CREMSEE P_t [2,3] with φ , both to better understand how CREMSEE is affected by surface adsorption and to provide a basis for comparison with the results of other surface techniques. In this regard, we wish to suggest how photo-CREMSEE could be utilized to perform *in situ* UPS [10,14] in the microwave cavity. One would require a far-UV tunable source, which is swept to obtain $s(\nu)$ versus ν . This approach is usually referred to as photoemission total yield spectroscopy [14]. Then by differentiating $s(\nu)$ with respect to ν one would obtain results related to

UPS [14]. While such an approach may not be as accurate as electron velocity selection (and the use of a monochromatic laser source), it has the advantage of experimental simplicity in combination with UHV ESR and CREMSEE studies.

Finally, although our primary objective with photo-CREMSEE is to conveniently perform accurate *in situ* work function measurements in the UHV ESR cavity, it would be of interest to address the more general question of its ultimate sensitivity as a detector of photoelectrons. An accurate study of this matter awaits improvements in our experimental design (e.g. focusing most of the light beam onto the inner surface of the cavity and accurate measurement of this intensity), which are currently planned. The potential of the technique may, however, be indicated by noting that ECR yields an extremely strong signal such that only a fraction of a steady-state electron (under our conditions) could be observable [2]. The role of the secondary electron emission in photo-CREMSEE could, in this sense, be thought of not only as an electron multiplier of the photoelectron but also as a means of continuing to generate electrons over time periods longer than the lifetime of the photoelectron. In time, we hope to be able to compare this potential of photo-CREMSEE versus more conventional electron detection techniques such as a vibrating reed electrometer (with sensitivity of order 10^4 – 10^5 electrons/s or 10^{-15} – 10^{-14} amp), which would, in any event, *not* be appropriate for our UHV ESR cavity. Also, the potential of photo-CREMSEE for time-resolved [3] photoelectron detection remains to be explored.

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