

UHV ESR AND CREMSEE: TWO NOVEL SURFACE TECHNIQUES^{*}

Mark NILGES and Jack H. FREED

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

Received 15 June 1981; in final form 31 July 1981

The complementary surface techniques of ultra-high vacuum (UHV) ESR and CREMSEE (cyclotron resonance from microwave-induced secondary electron emission) are described. It is shown in a study of a stable paramagnetic molecule on Cu and Ag surfaces, that it appears to lose its paramagnetism while forming a chemisorbed complex with the metal surface. Control experiments on air-oxidized Cu are also presented.

Current spectroscopic techniques for the study of the interaction of adsorbed species on metal surfaces include electron spectroscopies such as ultraviolet photoemission [1] (UPS) and high-resolution loss spectroscopy [2] (EELS) and conventional infrared [3] and Raman [4] spectroscopies. Recently IR [5] and Raman [6] spectroscopy have been performed under ultra-high vacuum (UHV) conditions. ESR, like IR and Raman, has high resolution, but it is limited to the detection of unpaired electron spins, and few studies have been performed under UHV conditions on insulators [7–10]. Recently we have performed experiments on metal surfaces prepared under UHV conditions, and that work focused on chemical reaction of the reactive paramagnetic gas NO₂ with a clean Cu surface [11,12]. We wish, in this letter, to present new experimental results with our UHV ESR technique, which relate to the nature of the interaction between a paramagnetic species and clean metal surfaces. Specifically, we address the question whether a (stable) paramagnetic species can retain its paramagnetism on a relatively unreactive (e.g. inert) metal surface. ESR is clearly the method of choice to resolve this hitherto unresolved question. In addition, we have, in the course of our UHV ESR experiments, observed and characterized a new phenomenon we call

CREMSEE (cyclotron resonance from microwave-induced secondary electron emission), which we find is very sensitive to surface bonding as described below. This CREMSEE technique has proved invaluable in our study of the nature of interaction between stable paramagnetic species and a clean metal surface.

First we summarize our experimental design. We use mostly conventional stainless steel UHV equipment, except for the microwave cavity. The system is roughed using a cryosorption pump and is pumped to UHV with an ion pump and titanium sublimation pump. It has a base pressure of 3×10^{-10} Torr after bakeout to 150°C. Pressure measurement may be performed between 10^{-11} and 20 Torr using a combination of ionization, cold cathode, and thermocouple gauges, while a quadrupole mass analyzer is used for examining gas purity and desorption species. The UHV microwave cavity is constructed from thin wall titanium, and is an integral part of the UHV system. It is a cylindrical TE011 mode cavity with a substantial fraction of its end walls removed, so that pumping conductance through the large openings is maximized, yet it has a high $Q_u \approx 13000$ after electroplating a 0.1 mil film of Cu. The thin titanium wall permits passage of 25 kHz field modulation with only $\approx 1/3$ attenuation. While one end of the cavity leads to the pumping system, the other end admits a tungsten filament and assembly with electrical feedthroughs, which are driven into the cavity with a bellows. In these experiments either 99.999% Cu or Ag wire was

^{*}Supported by Grant No. DE-AC02-80ER04991 from the Office of Basic Energy Sciences of DOE, by the Cornell Materials Science Center (NSF), and PRF Grant No. 10935-N5.

wrapped around the tungsten filament, so that fresh Cu or Ag film of 10^2 – 10^3 Å thickness could be evaporated onto the inner cavity surface. The filament must be removed prior to ESR (or CREMSEE) measurements. We find that the sensitivity of this UHV ESR system corresponds to a minimum detectable number of spins of 5×10^{11} spins per gauss linewidth (or 1×10^{10} spins/cm² of cavity surface), which is close to theoretical for a filling factor based on wall loading. Further design details will appear elsewhere [12].

We now wish to briefly describe the CREMSEE phenomenon. It is an intense electron cyclotron resonance (ECR) signal ($g = 2$) seen when the UHV ESR cavity is at a pressure less than 10^{-2} Torr. The signal intensity is extremely non-linear in microwave power, such that there is a threshold power, P_t below which no ECR signal is observed. Below 10^{-6} Torr there is no pressure dependence of the ECR signal. This fact, plus the sensitivity of P_t to the nature of the metal, as described below and in ref. [12] shows that the source of electrons is from the surface and not from residual gas molecules. We propose that we are seeing the ECR of secondary electrons emitted from the surface.

When electrons absorb enough successive microwave quanta before colliding with the cavity walls (≈ 100 eV for Cu and Ag), then there will be a secondary electron yield greater than unity [13]. This leads to electron multiplication until a steady-state number of electrons is achieved due to surface charge effects opposing further net emission of electrons. The intense signal just above threshold corresponds to $\approx 10^3$ electrons. In fact, for $T = 298^\circ\text{C}$ and 9.5 GHz frequency we estimate a ratio of susceptibilities [14] $\chi''_{\text{ECR}}/\chi''_{\text{ESR}} = 4mc^2kT/(\hbar\omega)^2 = 3.4 \times 10^{13}$ (assuming an electron transit time $\tau \approx$ the ESR T_2), implying even a *single steady-state* electron can be detected. We do not know the source of the initiating electron(s), but the CREMSEE is always obtained above P_t .

The CREMSEE can be very effectively suppressed by applying a negative voltage on the electrically isolated end rings of the cavity relative to the cavity walls, according to $P_t(V)/P_t(V=0) \approx e^{AV}$ such that for $V \geq 200$ V it cannot be observed at any available power level. We have measured the rise and decay times for CREMSEE just above P_t with periodic square wave modulation of the electric field applied to the end rings, and we find they are ≈ 20 and ≤ 3 μs ,

respectively. We have not attempted to determine if there is any additional incubation time when microwave power is first admitted into the UHV ESR cavity.

The CREMSEE signal depends upon the number of electrons $N_e(\Delta\omega)$ which is a function of $\Delta\omega \equiv \omega - \omega_c$ (ω is microwave while ω_c is cyclotron resonance frequency), and upon the distribution of transit times [represented by normalized distribution function $f(\tau)$], so that

$$\chi''_{\text{CREMSEE}} = \int N_e(\Delta\omega) \chi''_{\text{ECR}}(\Delta\omega, \tau) f(\tau) d\tau,$$

where χ''_{ECR} is the ECR susceptibility per electron.

The well-known and stable paramagnetic molecule we have used is DTBN (di-*t*-butylnitroxide, $[(\text{CH}_3)_3\text{C}]_2\text{N}^+\text{O}$) [15]. The bulky *t*-butyl groups protect the nitroxide group from chemical attack. It has the further advantage that it does not dimerize in the condensed phase as do NO and NO₂, but rather it exists as a paramagnetic liquid at room temperature. It has a vapor pressure of 1.4 Torr at room temperature permitting it to be leaked into the cavity using a stainless steel bakeable leak valve.

Initial experiments were performed on a Cu surface that was previously air-oxidized to serve as a basis for comparison with the clean metal surfaces. First we note that an air-oxidized Cu surface gives a CREMSEE P_t that is an order of magnitude lower than the clean Cu surface. DTBN was leaked in till the desired pressure at room temperature. A single ESR line is observed (cf. fig. 1a) in which the ¹⁴N hyperfine structure is absent due to exchange narrowing. The derivative linewidth decreases with pressure to a limiting value of 11 G at 700 mTorr and above. From spin concentration measurements we estimate 3×10^{14} spins/cm² at 1.4 Torr, which corresponds to about a monolayer coverage given an estimated cross section for DTBN of ≈ 70 Å². Since the pressure of the UHV system must be raised to just below the vapor pressure of DTBN to see this signal, we conclude that the DTBN is physisorbed, and the exchange narrowing at fractional monolayer coverage is probably due in part to surface diffusion of the weakly adsorbed DTBN. The physisorbed DTBN was removed by pumping out to 10^{-8} Torr leaving only the chemisorbed species, which shows no appreciable exchange narrowing and corresponds to ≈ 20 – 30% of a monolayer coverage (cf. fig. 1b). At

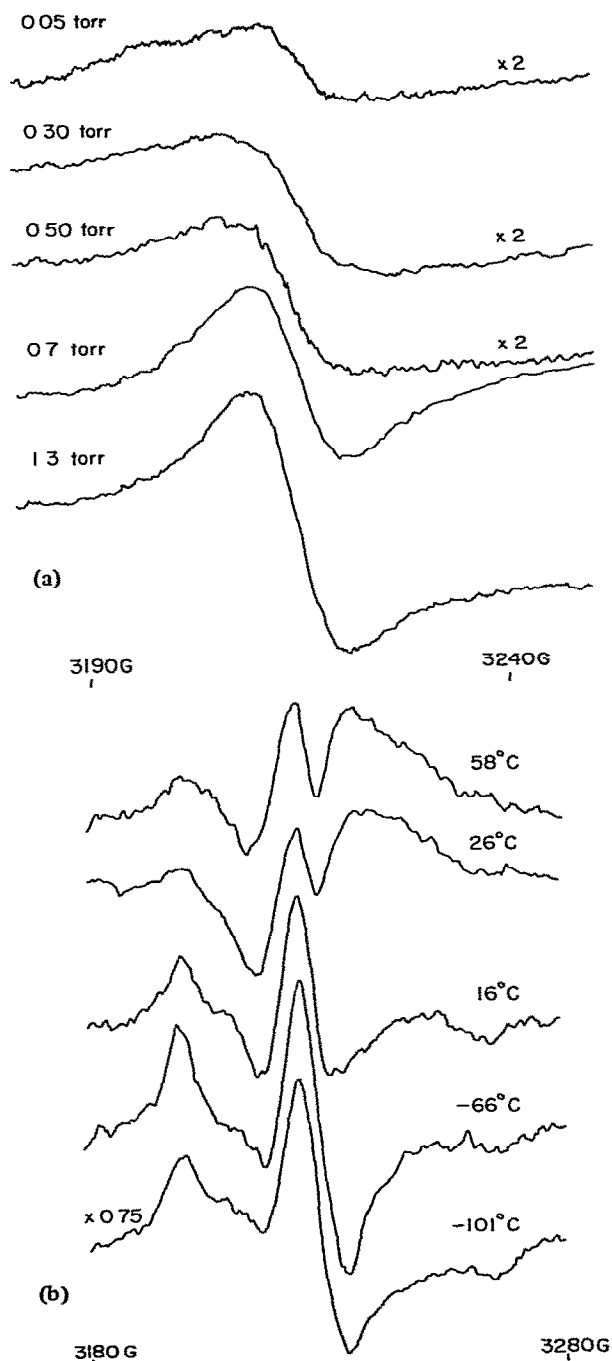


Fig. 1. ESR spectra of DTBN adsorbed on Cu (air-oxidized); (a) physisorbed DTBN at 26°C as a function of pressure; (b) chemisorbed DTBN at 10^{-8} Torr as a function of temperature.

-101°C a rigid limit spectrum is obtained with ESR parameters ($g_{\parallel} = 2.003$, $g_{\perp} = 2.007$, $A_{\parallel} = 33$ G, $A_{\perp} \approx \Delta H = 6$ G) similar to DTBN in various solvents, and on silica and zeolite surfaces [15,16]. Above -101°C the lineshapes are quite temperature dependent. Preliminary interpretation based on computer simulation, is in terms of two components, one of which shows substantial exchange narrowing with increased T .

When experiments are performed with DTBN adsorbed on a clean Cu surface at -20°C , no ESR signals are seen[‡]. However, the observation of a dramatic decrease in CREMSEE P_t when DTBN is leaked in at 10^{-8} – 10^{-7} Torr (cf. fig. 2a) clearly demonstrates

[‡] Conduction ESR is too broad to be observed in our experiment (cf. ref. [17]).

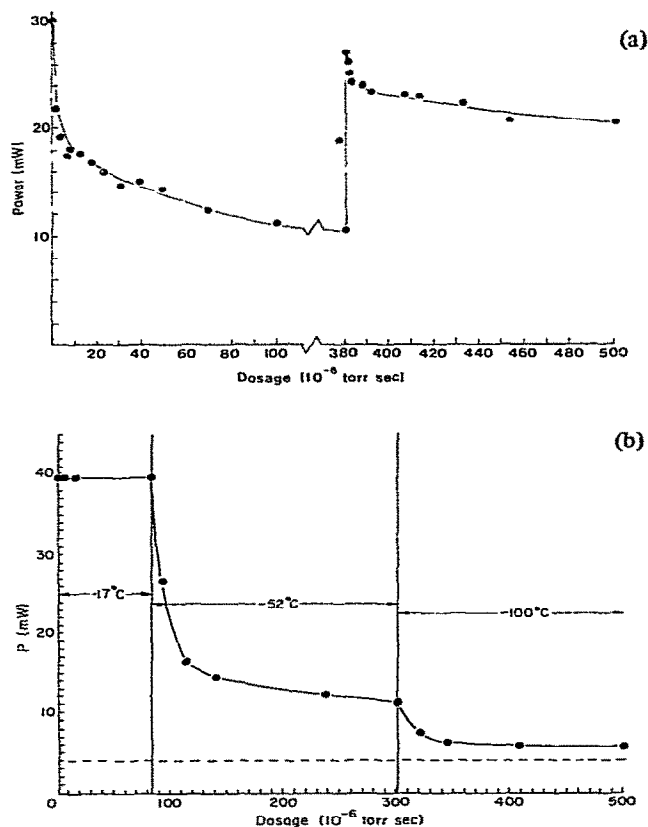


Fig. 2. CREMSEE threshold: P_t versus dosage of DTBN: (a) on clean Cu surface, at -20°C , except for vertical marked by * corresponding to heating at $+150^{\circ}\text{C}$; (b) on clean Ag surface at various temperatures.

that the DTBN is adsorbing on the Cu and forming a strong enough chemical bond to affect secondary electron emission. The P_t reaches its asymptotic value by 100 L (1 L = 10^{-6} Torr s). After baking out the cavity at 150°C for ≈ 1 h, P_t almost returns to its initial value for clean Cu, implying that the DTBN has been effectively desorbed. Further dosage at room temperature results in only a much smaller drop in P_t probably because the surface has become contaminated (possibly from carbon deposit from DTBN decomposed by heating).

The drop in P_t for DTBN adsorbed on clean copper points to the formation of a diamagnetic surface species. Since silver is less reactive than copper, we repeated the experiment with a clean Ag surface. There is no observable ESR signal nor any change in CREMSEE P_t at -17°C . Clearly the DTBN is not interacting appreciably with the Ag surface compared to the Cu surface at the same temperature, nor is there any ESR evidence for adsorbed DTBN. When the temperature is lowered to -52°C and further DTBN is leaked in, a dramatic decrease in P_t is observed as shown in fig. 2b. After dosages of a few hundred langmuirs, P_t reaches an asymptotic value of 12 mW. (A small initial decrease of less than 5% in P_t is observed when the temperature is first lowered.) Lowering the temperature further to -100°C and leaking more DTBN causes a further drop in P_t , which reaches a new asymptotic value of 6 mW. These results show that DTBN is bonding to the Ag surface at lower temperatures than Cu, but is still not paramagnetic at -52°C , and that the saturation coverage of DTBN is temperature dependent. However, at -100°C an ESR signal (cf. fig. 3) does appear with a g factor of 2.0039 ± 0.0003 . It is a single exchange narrowed line of 11 G derivative width and corresponding to 2×10^{13} spins/cm² or a 10% coverage. This signal disappears when the cavity is heated to -80°C . (A similar signal with $g = 2.0038 \pm 0.0005$

is seen with the Cu surface at -90°C but only for very large dosages of DTBN.)

Given the steric structure of DTBN as well as the previous results on its adsorption on insulators [16], we expect that the DTBN is bonded via its oxygen atom to a surface (hydroxyl) group on oxidized Cu. The average g value is the same as for pure DTBN (2.0058). However, the single exchange-narrowed ESR line observed for DTBN on clean Ag (and Cu) at -100°C is at $g = 2.0039$ (and 2.0038), which is quite low, indicating that the unpaired spin is interacting with the metal surface (e.g. a weak bond). We expect that the apparently diamagnetic DTBN forms a strong bond and is present up to monolayer coverage on the clean metals. The paramagnetic DTBN observed below -100°C might be due to adsorption at remaining binding sites with a lower binding energy. The exchange narrowing of this signal for only 10% coverage might indicate either surface migration of this DTBN or that it is in clusters (or else there may be an indirect spin-exchange mechanism via the metal conduction band electrons).

We now wish to consider how the CREMSEE results relate to the surface bonding of DTBN on the metal surface. But first we must consider the general matter of how surface bonding affects CREMSEE.

The secondary electron emission yield, δ depends on the work function, ϕ according to [18–21]. $\partial \ln \delta / \partial \phi = -\bar{E}_s^{-1}$ where \bar{E}_s is the average emission energy and is between 5 and 10 eV. It is found that ϕ depends linearly on θ , the fractional coverage of adsorbed species, for low coverage, and this is attributed to the formation of an electrical double layer [22]. The surface dipole can result from the permanent dipole of the adsorbed molecule and/or charge transfer between the adsorbate and surface. Values of $\Delta\phi \approx -2$ to -3 eV have been observed for organic molecules adsorbed on Pt [23], and are attributed to partial electron donation to the metal surface. However, for Ag ($\phi = 4.5$ eV), a $\Delta\phi = -3$ eV yields a predicted increase in δ by a factor of ≈ 1.6 , or much smaller than the seven-fold decrease in P_t (cf. fig. 2b). If, however, we relate P_t to E_{p1} , the incident electron energy necessary for $\delta = 1$ (i.e. just at the threshold of electron multiplication), then from data on adsorption of Th and Na on W [18,20], one finds that E_{p1} is approximately linear in ϕ . This would correspond to a decrease in E_{p1} by a factor of 3 for $\Delta\phi = -3$ eV on Ag. Thus,

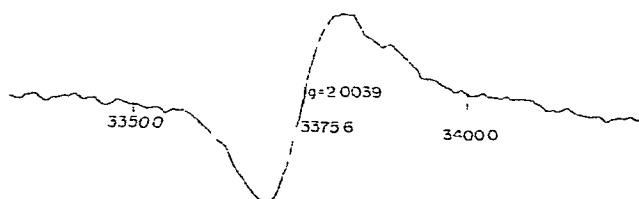


Fig. 3. Single exchange-narrowed ESR line observed below -100°C for DTBN adsorbed on Ag.

while we can semi-quantitatively explain the trends in P_t , we cannot yet produce a fully quantitative theory[‡]. In future work we plan simultaneous measurements of P_t and $\Delta\phi$.

We now return to the metal surface bonding of DTBN. The absence of an ESR signal but a large reduction in P_t can easily be explained if DTBN forms a charge transfer complex in which it donates its unpaired electron to the electron deficient metal surface. However, one typically expects only a weak ionic character [22]. Thus one might conjecture a diamagnetic bond with fractional ionic character between the O atom of the DTBN (involving indirectly the originally unpaired electron) and a surface metal atom(s). However, an alternative explanation, also consistent with our results, would be a resonance between a paramagnetic complex of DTBN chemisorbed on the surface (as for air oxidized Cu) and the charge transfer complex with the surface metal. Even with a small resonance admixture of the latter, we can expect strong enough coupling of the unpaired electron with the conduction electrons [17] of the metal, thus leading to its ESR becoming too broad to be seen [26]. In general then, the greater the overlap of the electrons on the adsorbate with electrons at the metal surface, the greater the chance for spin pairing and/or spin relaxation with the metal conduction electrons.

Although some of our interpretations are as yet somewhat speculative, it is clear that DTBN does form a substantial complex to Cu (and Ag at lower T) in which its paramagnetic resonance signal is lost, and furthermore that the interplay of UHV ESR and CREMSEE observations should prove very useful in such future studies.

Note added in proof: We have been able to use the "electron amplifier" property of CREMSEE to make an in situ measurement of the work function of the

[‡] In this context it is interesting to note, that while air oxidation of Cu and Ag causes P_t to decrease by an order of magnitude, pure O₂ on the clean Cu leaves P_t unaffected. Pure O₂ on Ag causes P_t to increase by 20%, but P_t continues to increase with time (after O₂ dosage), possibly from diffusion of O₂ into the bulk. It is known that O₂ adsorbed on Cu [24] and on Ag [25] at room temperature lead to small positive values of $\Delta\phi$, less than 1 eV. We expect that surface H₂O (or OH) groups in air oxidized surfaces are critical in lowering P_t drastically for that case.

surface by means of the photoelectric effect. Monochromatic light of variable frequency is passed through a UHV optical window into the cavity, which is operated just below P_t . When photoemission of electrons takes place, this additional electron source then induces a CREMSEE signal.

References

- [1] C.S. Fadley, in: *Electron spectroscopy: theory, techniques, and applications*, Vol. 2, eds. C.R. Brundle and A.D. Baker (Academic Press, New York, 1978).
- [2] B.S. Sexton, *J. Vacuum Sci. Technol.* 16 (1979) 1033
- [3] B.A. Morrow and L.E. Moran, *J. Catalysis* 62 (1980) 294.
- [4] T. Takenada, *Advan. Colloid Interface Sci.* 11 (1979) 291.
- [5] A.M. Bradshaw and F.M. Hoffman, *Surface Sci.* 77 (1978) 513.
- [6] T.H. Wood and M.V. Klein, *J. Vacuum Sci. Technol.* 16 (1979) 459.
- [7] B.P. Lemke and D. Haneman, *Phys. Rev. Letters* 35 (1975) 1379.
- [8] P. Svejda, *Rev. Sci. Instr.* 48 (1977) 1092.
- [9] P.A. Thomas, M.H. Brodsky, D. Kaplan and D. Lepine, *Phys. Rev. B* 18 (1978) 3059.
- [10] M. Shiotani, G. Moro and J.H. Freed, *J. Chem. Phys.* 74 (1981) 2616.
- [11] M. Nilges, M. Shiotani, C.T. Yu, G. Barkley, Y. Kera and J.H. Freed, *J. Chem. Phys.* 73 (1980) 588
- [12] M. Nilges, G. Barkley, M. Shiotani and J.H. Freed, *J. Chim. Phys. Special Issue* (1981).
- [13] D.J. Gibbons, in: *Handbook of vacuum physics*, Vol. 2, ed. A.H. Beck (Pergamon Press, New York, 1966).
- [14] A. Abragam, *Principles of nuclear magnetism* (Oxford Univ. Press, London, 1961), K.G. Mothes, E. Schutes and R.N. Schindler, *J. Phys. Chem.* 76 (1972) 3758.
- [15] L.J. Berliner, ed., *Spin labeling: theory and applications* (Academic Press, New York, 1976).
- [16] G.P. Lozos and B.M. Hoffman, *J. Phys. Chem.* 78 (1974) 2110.
- [17] D. Lubzens, M.R. Shanabarger and S. Schultz, *Phys. Rev. Letters* 29 (1972) 1387.
- [18] K.G. McKay, *Phys. Rev.* 61 (1942) 708.
- [19] L.R.G. Treloar, *Proc. Roy. Soc.* 49 (1937) 392.
- [20] K. Sixtus, *Ann. Physik* 3 (1929) 1017.
- [21] P.A. Wolff, *Phys. Rev.* 95 (1954) 56.
- [22] F.C. Tompkins, *Chemisorption of gases on metals* (Academic Press, New York, 1978).
- [23] J.L. Gland and G.A. Somorjai, *Advan. Colloid Interface Sci.* 5 (1976) 205.
- [24] T.A. Oelchar, *Surface Sci.* 27 (1971) 11.
- [25] H.A. Engelhardt and D. Menzel, *Surface Sci.* 57 (1976) 591.
- [26] P. Monod and S. Schultz, *Phys. Rev.* 173 (1968) 645; A. Raizman, J.T. Suss, D.N. Seidman, D. Saltiel and V. Zevin, *Phys. Rev. Letters* 46 (1981) 141.