ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS

UNDER ULTRA-HIGH VACUUM CONDITIONS

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MASTER

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ABSTRACT

This project is directed to developing ESR for the study of surface adsorption and catalysis on clean well-characterized metallic and oxide surfaces under UHV conditions and to compare the results of such studies with "real" surfaces, which are important in actual catalysis.

In the past year we have completed our first set of successful experiments with our ESR-UHV system on the NO_2/Cu system, which we previously studied by standard methods (e.g. supported surfaces). Our results showed that only in the presence of H_2O can the surface process(es) proceed that lead to stable Cu^{+2} complexes which are observable by ESR. However, by monitoring the CREMSEE (cyclotron-resonance from microwave-induced secondary electron emissions) threshold, definite evidence for the oxidation of the Cu surface by the clean NO_2 has been obtained. In real systems, as opposed to the clean surfaces prepared under UHV conditions, small amounts of H_2O are usually present. Thus, the UHV studies permitted a demonstration of the reactivity requirements. We have now performed detailed studies of the oxidation process of NO_2 on Cu. Based on our experience, we have designed and built a newer ESR-

UHV system with better expected performance.

We have completed an extensive study of motional dynamics of free radicals on supported surfaces. These include the O_2^- radical adsorbed on Ti supported on crushed vycor and NO_2 adsorbed on crushed vycor. The O_2^- is found to exhibit planar rotation about an axis perpendicular to the internuclear axis of the O_2^- and parallel to the normal to the plane. The higher temperature motion may be fit with a small activation energy of 0.5Kcal/mole, while the lower temperature motion shows interesting anomalies. The NO_2 exhibits planar-rotation at the lower temperature, but above 77°K it becomes more nearly isotropic presumably due to translational diffusion. Preliminary experiments imply that addition of acetylene increases the rate of rotational motion of the O_2^- .

Some preliminary studies leading to time-resolved UHV-ESR experiments of photo-induced catalysis have been performed with our new excimer laser.

Publications with Support from DOE Contract #DE-AC02-80ER04991.

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NO₂ on Copper by M. Nilges, M. Shiotani, C. T. Yu, G.
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- 2) ESR Studies of O₂⁻ Adsorbed on Ti Supported Surfaces:
Analysis of Motional Dynamics, M. Shiotani, G. Moro, and
J. H. Freed, J. Chem. Phys. 74 (in press, 1981).

In preparation:

- 3) ESR Studies of NO₂ Adsorbed on Surfaces: Analysis of
Motional Dynamics, M. Shiotani, G. Moro, and J. H. Freed.
- 4) ESR-UHV Studies of Heterogeneous Reactions Between NO₂
and Cu Surfaces. M. Nilges, M. Shiotani, C. T. Yu, and
J. H. Freed.
- 5) Extended Hückel Calculations of O₂⁻ Adsorbed on Ti Supported
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ESR STUDIES OF SURFACE ADSORPTION
AND CATALYSIS UNDER ULTRA-HIGH VACUUM
CONDITIONS

I. UHV-ESR Studies:

A) NO_2/Cu

In the progress report for last year¹, we described preliminary experiments on the NO_2/Cu system in our ESR-UHV system. We did not observe any ESR signals attributable to the surface reaction between NO_2 and Cu. This was compared with our successful experiments using more conventional techniques: (i.e. NO_2 on Cu supported on crushed vycor and NO_2 on Cu wire). It was postulated that the "clean" surface prepared under UHV conditions probably lacks some needed additional component(s). The component suspected was O_2 , because, when NO_2 was added into the UHV cavity, gas phase ESR signals from both NO and NO_2 were observed but not from O_2 . On the other hand, in both the Cu/Vycor and Cu metal experiments, one obtains ESR spectra from NO_2 and O_2 but not NO. In fact, in pumping the UHV system down to 10^{-7} torr, followed by heating the walls of the cavity, there is a marked increase in the peaks on the mass analyzer due to NO, N_2O , and NO_2 .

We have now completed extensive studies of these matters, which demonstrates the critical role of at least small amounts of H_2O in order to obtain positive results. A preliminary communication of our extensive results has been published.² We summarize our studies below.

When NO_2 is admitted to the UHV-ESR cavity with a fresh

Cu surface, no surface NO_2 ESR signal is observed even when the NO_2 is condensed on the surface. We attribute the absence of a surface NO_2 signal due to dimerization to N_2O_4 . Furthermore, there is no Cu^{2+} ESR signal. Even when O_2/NO_2 mixtures are used, no ESR signals are seen.

We have performed several experiments with mixtures of $\text{NO}_2\text{-H}_2\text{O}$ ranging from about 40:1 mole ratio to 1:1 mole ratio. The greater the water fraction the larger is the signal. We describe in some detail an experiment with 1:1 mole ratio. The $\text{NO}_2\text{-H}_2\text{O}$ was condensed on the Cu surface at -100°C and 0.1 torr (as the UHV pumps were gradually closed off) and no signal was observed until the cavity was warmed to -80°C when a symmetric single line with a $g=2.177$ and width of $\Delta H=100\text{G}$ appeared. This is very similar to the A-type signal we observed with the $\text{NO}_2\text{-Cu}$ wire experiment.¹

Upon further warming, this signal grows quite strong ($S/N \approx 500$) and a signal due to gas phase NO_2 is observed (cf. Fig. 1). Upon pumping, this condensed layer of $\text{NO}_2/\text{H}_2\text{O}$ an anisotropic signal is observed to develop; (Here $g_{\parallel} = 2.310$ and $g_{\perp} = 2.100$ with $g_{\text{ave}} = 2.170$), but no ^{63,65}Cu hfs is observed. This corresponds to the C-type signal we observed with the $\text{NO}_2\text{-Cu}$ wire. Finally further pumping at RT to 1×10^{-6} torr, the asymmetric signal disappears.

We believe that the initial reaction of NO_2 with Cu does indeed produce a copper complex as shown by the marked decrease in the CREMSEE threshold (see below) to a value equal to that when the copper surface is oxidized upon exposure to the atmosphere. The formation of copper oxide would be as follows:

On the other hand NO_2 can dimerize and selfionize

so that

and

All the above surface reactions give NO as a product.

As noted above, we see NO when NO_2 is leaked into the cavity at pressures low enough to use the quadrupole mass analyser.

The species CuNO_3 and Cu_2O are diamagnetic, while $\text{Cu}(\text{NO}_3)_2$ and CuO are paramagnetic. However, CuO in the bulk form does not give an ESR signal,⁴ but $\text{Cu}(\text{NO}_3)_2$ isolated in rare gas matrices does give an ESR signal⁵ which is very similar to what we observe for the reaction of Cu/vycor with NO_2 .¹ We are not yet sure whether $\text{Cu}(\text{NO}_3)_2$ forms on the copper surface or even if the proper conditions have been met to form $\text{Cu}(\text{NO}_3)_2$ or whether $\text{Cu}(\text{NO}_3)_2$ when concentrated on the surface will even give an ESR signal.

The appearance of a Cu^{+2} signal when H_2O is present is due, we believe, to the formation of HNO_3 :⁶

$\text{HNO}_3/\text{H}_2\text{O}$ should readily solvate copper ions to form species of the form $[\text{Cu}(\text{H}_2\text{O})_{6-n}(\text{NO}_3)_n]^{2-n}$ which should give ESR signals (see below). The Cu^{+2} species can readily be desorbed into the

condensed layer, so further reaction of NO_2 and Cu can occur. This is consistent with our observation of a dramatic increase in ESR signal intensity as the surface is warmed.

We have found that ESR spectra of $\text{Cu}(\text{NO}_3)_2$ in frozen aqueous solutions have g values similar to those we observe in the UHV system. For example, $\text{Cu}(\text{NO}_3)_2$ in H_2O at 90°K gives a symmetric signal with $g = 2.169$ due to the octahedral $\text{Cu}(\text{H}_2\text{O})_6^{+2}$ ion, but when HNO_3 is added, an asymmetric signal with $g_{\parallel} = 2.376$ and $g_{\perp} = 2.074$ ($g = 2.175$) due to the formation of either $\text{Cu}(\text{H}_2\text{O})_4(\text{NO}_3)_2$ or $[\text{Cu}(\text{H}_2\text{O})_2(\text{NO}_3)_4]^{-2}$. While $^{63,65}\text{Cu}$ hfs is seen for dilute frozen solution, of $\text{Cu}(\text{NO}_3)_2$ and HNO_3 in H_2O , the lack of hfs in the UHV experiment is most likely due to exchange narrowing and indicates that the copper complex is rather concentrated. In fact, we observe that pure $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ shows no $^{63,65}\text{Cu}$ HFS but shows g anisotropy ($g_z = 2.335$, $g_y = 2.133$, $g_x = 2.082$, $g_{\text{ave}} = 2.183$). It should be noted that g_{ave} for the Cu^{+2} complexes observed in the UHV experiments is between 2.170 and 2.177, while for the Cu^{+2} complexes seen in frozen solution g_{ave} is between 2.169 and 2.183. These values are characteristic of Cu^{+2} coordinated by 6 oxygen atoms in an octahedral or near octahedral arrangement.

The change from a symmetric signal to an asymmetric signal in the UHV system could be attributed to the formation of a species with octahedral symmetry for which the symmetry is reduced to tetrahedral upon pumping the condensed layer off the surface. On the other hand, a Cu^{+2} ion would be expected to be rotating in the

condensed layer so as to average out any g anisotropy. Thus, pumping out this layer freezes out this rotation. However, there is no line shape change with cooling, so this is not likely. Also, if Cu^{+2} ions have random orientations with respect to adjacent Cu^{+2} ions, then both g anisotropy and Cu hfs could be exchange narrowed and not seen in the spectrum. Our results to date favor the first of these three explanations. When $\text{NO}_2/\text{H}_2\text{O}$ (10:1) is adsorbed at low enough pressures (0.5 torr, $-70^\circ\text{C}.$) so that no condensation should occur, a weak signal (S/N ≈ 5 corresponding to 10^{16} spins) at $g = 2.10$ and $\Delta H = 60 \text{ G.}$ is observed. We still have to determine whether this is an isotropic signal or just the perpendicular component of an anisotropic spectrum (i.e. a C-type spectrum), with the parallel part too weak to be observed because of low S/N. Also, we must determine when the signal first appears.

B) NO/Cu

Although NO forms a diamagnetic cis-dimer upon adsorption on a surface, a small amount of monomer is still present.⁷ NO at pressures up to 10 torr at temperatures from -100 to -140°C showed no NO ESR signals with optimum spectrometer conditions and signal averaging, although a peculiar background signal was observed where the NO signal was expected ($g = 2.006$; $\Delta H = 30\text{G}.$). Microwave and modulation fields were approximately 90° out of phase, and the ESR signal showed an unusual phase variation as a function of temperature. The signal was unchanged upon oxidation and reduction of the Cu surface, thus indicating that the signal is due to impurities within the metal surface.

c) Di-tertiary-Butyl Nitroxide on Cu

ESR signals were observed for the stable free radical di-tert butyl nitroxide (DTBN) both physisorbed and chemisorbed on an oxidized copper surface. While most nitroxides are non-volatile, DTBN is a liquid with a vapor pressure of 1 torr, so that upon proper purification it can be leaked into the UHV system in the gas phase.

Figure 2a shows the spectra for physisorbed DTBN at RT. Note that for physisorption to occur the UHV pump must be valved off and pressures increased to just below the vapor pressure of the adsorbate. The observed single, exchange-narrowed, symmetric line with $\Delta H = 9G$ is expected for a magnetically concentrated monolayer. We observe a similar signal is observed for pure liquid DTBN. We have estimated the spin concentration observed for maximum coverage ($\theta=1$) to be on the order of 10^{14} spins/cm². Because of the large size of the DTBN molecule, the number of molecules for $\theta = 1$ will be less than the number of surface atoms (1×10^{15} /cm²) and is estimated from the density of liquid DTBN to be 2×10^{14} spins/cm².

Note in figure 2a, that while a symmetric signal is observed for all pressures, a change in lineshape is observed, between 500 and 700 mtorr. and may be due to a change in exchange and/or motion on the surface.

A weak anisotropic signal is observed for pressures below 20 mtorr.. The strength and shape of the signal is independent of pressure for a range of 50 mtorr. to 1×10^{-7} torr., indicating that this is a chemisorbed species. Double integration of both chemisorbed and physisorbed signals, show that the maximum coverage for chemisorption at RT is 10-20% and increases slightly as the temperature is lower. Figure 2b, shows the temperature dependence

of the chemisorbed signal as a function of temperature at 10^{-7} torr.. The ESR spectrum at -100°C is characteristic of a spectrum of randomly oriented rigid or near rigid DTBN molecules; observed ESR parameters are $g_{\parallel} = 2.003$, $g_{\perp} = 2.007$, $A_{\parallel} = 33\text{G}$, $A_{\perp} \approx \Delta H = 6\text{G}$. and are characteristic of DTBN.⁸ We attribute the temperature dependence of the spectra in figure 2b to an increase in motion on the surface, although these spectra are not exactly typical of slowly tumbling nitroxides in solution.⁹ This difference may be due to exchange interactions and/or a distribution of rotational correlation times, τ_R ,¹⁰ i.e., rotational motion may be site dependent.

D) CREMSEE (Cyclotron Resonance from Microwave-Induced Secondary Electron Emissions)

In our previous progress report¹ we discussed the electron cyclotron resonance signal (CREMSEE) that is observed in our UHV-ESR cavities at pressures less than 10^{-2} torr. The signal is intense, because electric dipole transitions are usually 10^4 times as strong as magnetic dipole transitions. Also, it shows an extremely non-linear microwave-power dependence, which can be characterized by a threshold power level (P_t) below which no signal is observed.

We have now found that the application of a dc electric field can greatly suppress the CREMSEE threshold.² Thus, in an experiment in which the end-plate of the ESR-UHV cavity was biased by 50V, P_t was increased by a factor of 9. Our new cavity designs allow for more effective electric field biasing to suppress CREMSEE (see below).

We have also found that by using the TE₁₁₂ mode instead of the primary TE₀₁₁ cavity mode, the threshold is 12db higher. This is because the TE₁₁₂ mode has a much weaker microwave $\vec{E}$ component perpendicular to the dc magnetic field (and the transition moment is proportional to E_1).

Perhaps most important, we have found that measurements of P_t can be used effectively in conjunction with our ESR studies to characterize the surface processes occurring. Thus (for the TE₀₁₁ mode) a freshly prepared Cu surface gives the maximum P_t of 18mW (incident on the cavity), while if an exposed Cu surface is

baked out in H_2 at $200^\circ C$ then it gives a P_t up to 8mW. After a freshly prepared Cu surface is either exposed to air or to 10^{-3} torr NO_2 , P_t is reduced to 2mW (or less) (cf. above discussion)).

We have considered these observations in the light of what is known about secondary electron emissions.¹¹ Our observed CREMSEE linewidth of 10G corresponds to ca. a 3×10^{-8} sec (lifetime for the cyclotron electron) or ca 300 microwave periods.¹² For 1mW of microwave power uniformly distributed in the cavity, 500eV could be absorbed in this time period. (Since $\vec{E}$ is not uniform in the ESR cavity, it is somewhat harder to calculate the energy absorbed, but it should be somewhat less). For electrons incident on a Cu surface with energy greater than 150eV, the secondary electron emission coefficient (S_e) will be greater than unity, i.e. on the average, more electrons will be emitted than absorbed, so that electron multiplication can occur. It is known that S_e is much larger for CuO than for Cu and this correlates with our observations of P_t vs. oxidation of the cavity walls.

E) ESR-UHV Cavity Sensitivity

We have considered in some detail the "practical" cavity sensitivity, i.e. the S/N achievable under actual operating conditions. Our sensitivity determination with calibrated samples leads to a minimum spin detectability of 2×10^{12} spins/G. (i.e. $S/N = 1$), which is in good agreement with theoretical predictions for our cavity design with spins at the wall surface. Given our active

region of the cavity of about 50cm^2 and 10^{15} atoms/ cm^2 on the surface we obtain:

$$S/N \approx 2 \times 10^4 \text{ RC } \frac{\Delta H_m}{\Delta H^2} F$$

Where R is the surface roughness coefficient, which should range from 10-100 for a freshly evaporated metal film, C is the fraction of a monolayer of radical species and can be greater than unity for more than a monolayer coverage, ΔH_m is the magnetic field modulation amplitude in G. (about 3G. maximum for our systems) while ΔH is the derivative ESR linewidth in G. This expression is applicable for $\Delta H_m < \Delta H$. F is the fraction of spins contributing to the particular derivative ESR line and is ≤ 1 ; e.g. for three equal hyperfine lines characteristic of gaseous NO_2 above several torr., $F = 1/3$; while for an asymmetric g-tensor the fraction of spins contributing to the most intense peak yields an $F \cong (\Delta H / \sqrt{\Delta H^2 + (H_{\parallel} - H_{\perp})^2})^{1/2}$ where $H_{\parallel}$ and $H_{\perp}$ are the field positions of the parallel and perpendicular components respectively. This expression emphasizes the reduced S/N for broad-asymmetric solid-like signals that are observed on surfaces due to the factor $\frac{\Delta H_m}{\Delta H^2} F$.

We have found that our stainless-steel (SS) ESR cavities have a large and very broad background signal with a maximum at 500G and $\Delta H > 1,000\text{G}$. Our tests have shown that it is due to surface treatment of the SS cavity walls. Annealing the cavity before copper plating decreases the background signal intensity but does not remove it completely. This sloping baseline inter-

feres with signal averaging required to improve S/N. The original SS is nonferromagnetic but abrading the surface produces ferromagnetic sites. Our newer cavities constructed from Ti (see below) should eliminate this problem.

II. DYNAMICS OF RADICALS ON SURFACES

We have completed extensive studies on the rotational motions of simple free radicals adsorbed on surfaces. A particularly detailed study was on the O_2^- radical adsorbed on Ti supported on crushed vycor surfaces.¹³ This O_2^- radical readily forms by UV assistance and only in the presence of partially reduced Ti on the surface. The basic MO theory for describing the surface splitting of the O_2^- energy levels, which gives rise to the observed g-tensor, and the orientation of the O_2^- orbitals is shown in Fig. 3. We obtained very well-resolved temperature-dependent lineshapes over the range of 4°K to above room-temperature (cf. Fig. 4.) These spectra could only be fit to a model of planar rotation about an axis perpendicular to the internuclear axis of the O_2^- radical and parallel to the normal to the plane. Below 15°K, the spectra are time-independent (cf. Fig. 5), but they still show slow-motional characteristics. We interpret this as due to coherent quantum-mechanical averaging but of an incipient nature. For example, one model we considered is that of nearly free quantum planar rotation but with a "renormalized" moment of inertia $\tilde{I}$ that must be at least three orders of magnitude smaller than I , in order to be consistent with the spectrum, and probably due to the fact that, as the O_2^- rotates in a plane above the

surface, there is a surface countercharge polarization which must be dragged around.

The possibility of a low barrier to rotation is consistent with extended Hückel calculations we have performed for this system in conjunction with Roald Hoffman's group.¹⁴ The basic interaction diagram of O_2 interacting with a supported surface Ti (in the form of a TiO_5 complex) is shown in Fig. 6, while the calculated spin densities are shown in Fig. 7. They are consistent with our observations of O^{17} labelled O_2^- (cf. Fig. 8) suggesting a small asymmetry for the two oxygens relative to the Ti, possibly due to a tilt of the O_2^- internuclear axis. The dependence of electronic energy of the O_2 -Ti system with respect to rotation angle β and angle of tilt α is shown in Fig. 9. We find that for $\alpha > 15^\circ$ there is only a very weak dependence of the energy on β . We do find that the higher temperature motion may be fit with a small activation energy of 0.5 kcal/mole independent of the precise model used (cf. Fig. 5).

However, we find that none of our "standard" models of Brownian, various type of jump, or simple free diffusion really adequately fit the higher temperature lineshapes. We have conjectured that (1) there may still be residual quantum effects and/or (2) corrections must be made for a modest (but definitely not very large) -- and probably four-fold -- barrier; and/or (3) the surface drag effect of the charge polarization may require that we use a model of a slowly relaxing local structure.⁹ The main point at present really is the very great sensitivity of the

spectral simulations to the model for this very well-resolved experimental set of spectra and their unusual characteristics which warrant further investigation.

We also note that the spectral evidence for planar rotation is consistent with the O_2^- radical remaining bound to a single Ti atom. In fact Clarkson and Kooser¹⁵ reported on O_2^- on metallic silver aggregates supported on crushed vycor. Their approximate analysis of Saturation Transfer (ST) spectra suggests that the motion is isotropic Brownian tumbling. We believe this is because the O_2^- translates on the silver surfaces, thus experiencing gradual changes in the orientation of the surface relative to the magnetic field. We estimate from their limited data an activation energy of ca. 6 Kcal/mole. Thus the nature of the motions in the two cases are quite different. We believe the differences are due to the facts that 1) we see motion for the stable but less bound Type III form of O_2^- (determined by g-values) while the motion on Ag/vycor was for the more stable Type I form of O_2^- ; and 2) the Ti/vycor samples contain only small amounts of Ti (0.2wt%) in which the partially reduced Ti atoms are complexed into the silica structure (cf. Figs. 6 and 9) and relatively far apart while the Ag/vycor contains "pools" of Ag metal on the surface. Thus the O_2^- (III) may rotate with respect to a fixed Ti site while the O_2^- (I) may migrate (along with its positive countercharge) on the Ag surface.

We also wish to note that our comparative study of this O_2^- /Ti-vycor system under UHV conditions (i.e. $P < 10^{-9}$ torr) showed that these conditions do not affect the nature of the site nor the molecular motion of surface O_2^- , i.e., the O_2^- (III) is strongly adsorbed on the surface.

In order to examine the chemical reactivity of O_2^- (III), the C_2H_4 gases were introduced to the O_2^- (III) sample prepared under UHV conditions. Although no change on O_2^- (III) lineshape was detected at RT after admission of $P \approx 0.5$ torr C_2H_4 , when the sample was cooled below $-140^\circ C$, the spectrum showed a different lineshape from the O_2^- (III), which resembles an additional broadening of the outer regions of the spectrum. Upon warming the sample above $-140^\circ C$, the original spectrum of O_2^- (III) reappeared. However, when the O_2^- (III) sample was kept under 0.5 torr C_2H_4 pressure at RT overnight, the O_2^- (III) signal almost completely decayed without giving any new ESR signal. The above results indicate that the O_2^- (III) might be weakly interacting with C_2H_4 at temperatures below about $-140^\circ C$ but reacting with C_2H_4 slowly at RT.

In our study of slow-motional spectra of NO_2 adsorbed on just the crushed vycor surface,¹⁶ we find that at the lower temperatures the motion is also of the planar-rotation type (cf. Fig. 10) presumably with the NO_2 at a single surface site, but above $77^\circ K$ the motion becomes more nearly isotropic, presumably because the NO_2 (cf. Fig. 11) translates and thus samples different orientations of the surface. Below $77^\circ K$ we again found that our "standard" set of models did not adequately predict the experimental lineshapes, and here the discrepancy becomes greater with decreasing temperature. (cf. Fig. 11a). (Even at $4^\circ K$ the spectrum appears to be temperature-dependent.)

We now have preliminary results with our new Electron-Spin Echo (ESE) spectrometer on relaxation times of O_2^- (III) on Ti-vycor and NO_2 on Vycor. These results (cf. Fig. 12) are consistent with

1) Most of the low temperature cw widths are due to inhomogeneous broadening, 2) For $T > 20\text{K}$ the ESE relaxation time T_M monitors the motional dynamics. This latter is consistent with our recent study of ESE T_M 's in isotropic liquids¹⁷ showing that T_M should be a direct measure of the rotational correlation time, so we are exploring this further. Also, the techniques we are developing will be needed for our planned studies of time-resolved laser-induced desorption and catalysis (see below).

III) UHV/ESR Instrumentation

We have designed and built a second UHV system for our ESR studies. This includes many improvements designed to yield a cleaner, faster pumping, lower-ultimate-pressure system and better ESR-microwave performance.

Our new UHV system (UHV II, cf. Fig. 13) has no oil pumps, so there is no contamination from oils. Rough pumping is done with a Venturi pump (to 100 torr for H_2 removal) and cryosorption pump (to 5 millitorr). After roughing, a titanium sublimation pump (460 l/s) brings the system to a safe pressure for starting the ion pump (60 l/s). Using a larger gate valve (2-1/2") and larger plumbing, we have improved the pumping speed at the cavity by a factor of ten (13 l/s).

Pressure measurement is more complete on UHV II. The roughing line and gas manifold have convectron gauges (Granville-Phillips) for 1000 torr to 1 millitorr. The main system has a .1 to 20 torr and a 1 to 1000 millitorr thermocouple gauge. A cold cathode gauge for 10^{-2} to 10^{-7} torr, and a Bayard-Alpert (nude ion gauge for 10^{-4}

to 10^{-11} torr) complete the main section. We use a capacitance manometer for calibration of our thermocouple gauges (gas dependent calibration) in the range 1 millitorr to 10 torr. Finally, a quadrupole residual gas analyzer is used for checking purity of inlet gas and leak checking.

The gas handling system on UHV II has two isolated lines that may be pumped out independently and lead to separate leak valves. There is capacity for freeze, pump, thaw or molecular sieve purification of gases.

A new evaporation unit was developed to allow separate evaporation of two different metals and independent lead-in outgassing. Thermal insulation of lead-ins is accomplished by a length of larger stainless steel posts. Background pressure should introduce no more than 1 ppm impurity after purging.

The entire system, excluding the roughing line and gas handling system may be baked out to 180° C. Our highest vacuum is 2×10^{-10} torr.

A new ESR/UHV cavity has been designed and constructed and is now being tested, (cf. Fig. 14). This cavity is improved in five respects: better vacuum pumping conductance, better microwave coupling and adjustment, less magnetic materials to distort the static field, better vacuum seals, and improved CREMSEE reduction. The cavity is designed after the flow system cavity of Thomson et al.¹⁸ with end plates that are 80% open. This gives about 50 times the pumping conductance as compared to the old design. The microwave coupling is through an iris (opening) in

the cavity body. This excludes cables that give reflections and attenuations greater than those of waveguides. Also, the coupling may be adjusted by a iris adjust screw even while the cavity interior is under vacuum. Finally, material selection was important. Previous designs used stainless steel. Residual magnetism from machining could not be annealed out, and, thus, caused magnetic field distortion. Yet, a low conductivity material is needed so that the 100kHz field modulation would not be attenuated too much. The only usable metal we found was titanium which is much less magnetic¹⁹ but has almost the same conductivity.¹⁹ It also has the benefit of a thermal expansion coefficient much nearer that of our ceramics than stainless steel. We overcame difficulties in joining titanium (to titanium, to stainless, to ceramic), and difficulties in plating titanium, with results better than commercial procedures.

The vacuum seals to the other parts of the system are improved. The cavity is built on commercial (ConFlat) 2-3/4" flanges using crushed copper seals. These have no permeation or low temperature failure as our previous Viton seals had. Thus, our ultimate pressure is lower and lower temperatures may be used.

Finally, capability for a static electric field is provided to eliminate CREMSEE. A voltage may be applied across the two isolated end plates or between end plates and side wall. This field should distort the paths of the electrons, raising the power threshold (P_t).

The result is a new microwave cavity better designed for UHV experiments.

New High-Vacuum System

We have constructed a new low-cost, high-performance high-vacuum system (ultimate pressure 2×10^{-8} torr) to upgrade the vacuum condition of our previous high-vacuum experiments (10^{-6} torr). This system consists of two pump units.

(1) Regular glass vacuum system with gas handling manifold, made of non-greased Teflon stopcocks and valves, is used for purifying gases and evacuating sample chamber before starting the ion-pump. (2) Sample vacuum chamber, which can be sealed off from the glass system by a stainless-steel high conductance bellows sealed angle valve from VACO Co., is equipped with a stainless steel-glass hybrid plumbing with stainless steel flanges and valves replacing glass ball joints and Teflon stopcocks. We use a Perkin-Elmer 20^{sec.} l_A ion pump to achieve good high-vacuum. Before adding gas into the sample chamber, we can seal off the ion pump by a high-conductance stainless-steel butterfly valve. With such vacuum, our future experiments on supported catalyst surfaces will have at least two orders of magnitude better vacuum than was claimed by most of the other groups.

IV (Time-Resolved) Photo-Induced Desorption and Catalysis:

Preliminary Experiments

During the past year we have begun preliminary experiments, the ultimate objective of which is to perform Time-Resolved ESR experiments in which various photo-induced surface processes may be studied in the time domain to measure rapid kinetic processes. Our initial objectives have been to 1) explore potential systems of interest by more conventional CW techniques to see which might

be good candidates for the time-resolved study and 2) to develop the basic time resolved photo-ESR techniques to be appropriate for gas-metal (or metal oxide) interactions.

We summarize below some of our preliminary results.

We have prepared TiO_2 thin films deposited on a quartz rod substrate, which could fit into a conventional ESR sample tube, by a chemical vapor deposition technique as described by Hardee and Bard.²⁰ We have observed an O_2^- signal generated by UV irradiation on these films ($g_1 = 2.02, g_2 = 2.009, g_3 = 2.003$). It is very similar to the type III signal observed on Ti/Vycor samples¹³ and those reported by C. Naccache et. al on TiO_2 powder samples.²¹

In future work we plan to study this and related systems by time-resolved ESR techniques (see below).

MoS_2 powder

Polycrystalline MoS_2 powder samples were given to us by Professor Sienko and were heat-treated under vacuum as follows:

<u>Sample</u>	<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Time (hr)</u>	<u>Pressure (torr)</u>
1	150	1	10^{-4}
2	300	2	10^{-4}
3	450	2	10^{-4}
4	560	2	10^{-4}

Only sample (4) showed a strong ESR signal ($g = 2.002 \Delta H = 1.8\text{G}$) after baking. This signal broadened and weakened as the amount of oxygen gas leaked in increased. After evacuating O_2 , this signal was restored to its original intensity and linewidth.

This observation suggests that the signal may arise from paramagnetic centers on the surface (those in the bulk would not be affected by the gas). The origin of this signal is not clear yet, but the appearance of this signal may be linked to the activation process of this catalyst, normally done at 600°C. It is believed that the incompletely coordinated metal ions exposed on the surface as a consequence of desorption of sulfur atoms in vacuum are the most likely sites of catalytic activity. Therefore, this sharp signal may tentatively be assigned as an F-center signal.

ESR signals of hydrogen atoms have been observed at 77°K in $\text{H}_2\text{O(g)}$ -exposed sample (2) after UV irradiation. MoS_2 , which forms layer crystals with a band gap 1.4 eV., has been used as a semiconductor electrode for solar photoelectrolysis purposes.²² We will continue to study the kinetics of the formation of H atoms and other radicals with Time-resolved ESR techniques (see below).

GeSe_x:

Professor Ruoff has supplied us with a variety of GeSe_x films. These form a class of amorphous semi-conductors. Ge-type materials tetrahedrally coordinated and rigid structure are characterized by a large density of free spins (of order 10^{19} - 10^{20} spins/cm³ with $g \approx 2.01$) and Curie-like susceptibility. When prepared in the presence of hydrogen, however, they give a very weak signal, since the hydrogen undoubtedly serves to saturate the dangling bonds which would otherwise give an ESR signal. Only the hydro-

generated material exhibits photoinduced ESR. Se-class materials exhibit two-fold coordination and a great degree of structural flexibility. They do not normally exhibit an ESR signal in the dark, but it is possible to photoinduce metastable paramagnetic centers (about 10^{17} spins/cm³, $g \approx 2.00$) by irradiating with a frequency source close to that of the band gap at low T. This signal may be thermally bleached or infrared quenched (i.e. irradiation with sub-band-gap light).

Mixed systems such as $\text{Ge}_x\text{Se}_{1-x}$ fall into either class according to the value of x , and the ESR signal can be used to distinguish between them.

These following photoinduced ESR signals have been observed:

GeSe_2 (80° deposition angle) $g_{\parallel} = 2.04$, $g_{\perp} = 2.00$ (77°K)

GeSe_3 (0° deposition angle) $g = 2.003$ (weak) (120°K)

GeSe_3 (80° deposition angle) $g = 2.001$ (weak) (120°K)

(Future experiments should be done at 4.2°K, or below 30°K, because of the thermal bleaching effect.)

Photoinduced ESR signals of H-atom have also been observed (at 77°K) in GeSe_2 films after they were exposed to water vapor. (The signal disappeared at higher temperature.) Mercury lamp was used as light source. This result does not conclusively indicate that the observed H-atoms are generated by photodecomposition of H_2O on GeSe_2 surface. There are two additional sources which could produce H-atoms by irradiation:

- 1) hydrogenated quartz¹⁹ (sample tube, film substrate) and 2) hydrogen already on the GeSe_2 (see above). The latter is not

likely given the method of preparation. Using band-gap excitation (i.e., a He-Ne gas laser, 6328Å), one can exclude the other two possibilities, since those bond breaking processes (M-H) require high energy radiation: (for quartz: $\lambda < 3200\text{Å}$)

Light Sources and Detection Equipment

We now have a 150 W Xenon Arc lamp system manufactured by Photochemical Research Associates Inc.. In conjunction with the lamp/system operated in the modulated mode (up to 5KHz) we have set up a phase-sensitive detection system to monitor slow kinetics (i.e., in the millisecond range). Also, we now have an operating Lambda Physik EMG101 Excimer Laser and the optical equipment needed for our fast-kinetics studies. Our Excimer Laser delivers high power pulses of ca. 10 nsec duration for a variety of wavelengths in the range of 157 to 351 nm. It is currently being interfaced to our electron-spin-echo spectrometer.

Initial Laser Photolysis Experiments

Photo damage on fused Silica sample tubes were also observed (KrF, ArF), but it could be saturated with a few pulses and no further transient could be seen. Our initial time-resolved experiments will be aimed at detecting transient H atom signals which are far away from these photo damage signals ($g = 2$).

Because some gases (such as N_2 ...) enhance cavity ringing, we have also performed tests on several gases which we might be using in the future surface photolysis experiments. The experimental arrangement we used in these time-resolved ESR experiments

is shown in Fig. 15.

In our initial trials of irradiating samples in situ with KrF laser pulses (249 nm) through the optical window of a Varian E-231 cavity, we observed intense noise which lasted ca. 400 μ sec. after each laser pulse. Later, we eliminated such noise by directing the laser beam through the central axis of a Varian E-235 cylindrical cavity horizontally mounted.

This observation indicates that the noise arises from the cyclotron resonance of photoelectrons from the cavity walls (and the grid of the optical window) irradiated by high energy photons, (pulse energy 250 mJ). We did not observe such noise when N₂ (337nm, 7mJ) laser pulse was used.

We have observed a variety of time-resolved signals by using the gases NH₃, O₂, NO₂, and NO. These signals are of the transient nutation type.^{24,25} The first type of signal, observed with NH₃ (5 torr) is a magnetic field-independent transient nutation with oscillation period, τ a function of microwave power ($\sim 30 \mu$ sec for 1mW incident power) as one would expect for this diamagnetic substance.²⁵ It is induced by a 2 or 3 photon process (for ArF $\lambda = 193$ nm). The second type of signal was observed for the Σ -type paramagnetic gases O₂ (3 torr), NO₂ (5 torr). An on-ESR resonance transient nutation (6287 G for O₂, 3107 G for NO₂), which is independent of microwave power, but is absent far from ESR resonance (4287 G for O₂, 6107 G for NO₂). The last type of transient nutation was exhibited by the $^2\pi$ radical NO (5 torr). It exhibits a signal similar to NH₃ for magnetic fields < 4 KG.

and >5 KG., but for $4 < H < 5$ KG, it changes over into an inverted signal. Such transient nutations arise from the laser pulse leading to an initial non-equilibrium population between two rotational type levels separated by the microwave frequency, and the resonance frequency can be tuned by the Zeeman field for the paramagnetic species.

These results clearly show that the gases are indeed substantially photo-excited. In fact, with the intense KrF laser pulses, we can detect the ESR signal from just a single pulse. This seems encouraging for future time-resolved ESR photocatalysis experiments.

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FIGURE CAPTIONS

- Figure 1: ESR spectra (9.4GHz, TE011 mode, 15 mW, Gain 2.5×10^3) for reaction of NO_2 with copper. a) Initial condensation of $\text{NO}_2/\text{H}_2\text{O}$ mixture; surface warmed b) and c) and then cooled d) with UHV pumps closed off; e) through i) cavity pumped and warmed to remove $\text{NO}_2/\text{H}_2\text{O}$ layer.
- Figure 2a: ESR spectra (9.0 GHz, TE112 mode, 14 mW, Gain 2×10^4) of physisorbed DTBN at 26°C as a function of pressure.
- Figure 2b: ESR spectra (9.0 GHz, TE112 mode, 13 mW, Gain 2×10^5) of DTBN chemisorbed on a copper oxide surface as a function of temperature at 1×10^{-7} torr.
- Figure 3 I: Electronic energy levels of the superoxide ion O_2^- ,
II: Illustration of the molecular orbitals in which there is coincidence between the molecular coordinates and principal axes of g-tensor. In the slow motional calculations, the axis corresponding to $R_{||}$ was chosen as parallel to y-axis,
III: Illustration of the geometry showing the case in which the principal diffusion axis is not coincident with the principal axes of the O_2^- g-tensor.
- Figure 4: The best fitting theoretical spectra compared with the experimental spectra of O_2^- (III): A) 4.2K to 78.7K and weak jump diffusion; B) 104K to 149K and Browman diffusion.

Figure 5: Plot of $\tau_{R_{\parallel}}$ vs. $1/T$ for the different models: Brownian diffusion (open circles), free diffusion (open triangles, $R_{\parallel}\tau_{\parallel} = 0.1$), and jump diffusion (open squares $R_{\parallel}\tau_{\parallel} = 0.1$).

Figure 6: Interaction Diagram for O_2 and $(TiO_5)^{7-}$ used in the extended Hückel MO Calculations.

Figure 7: Spin densities for $O_2/(TiO_5)$ System Calculated from results of extended Hückel MO theory. The three cases illustrated are from left to right: symmetric complex, the O_2^- oxygens not equidistant from Ti but in plane parallel to surface, and the O_2^- axis tilted by angle $\alpha = 10^\circ$ relative to surface plane.

Figure 8: Comparison of experimental and simulated (^{17}O - ^{18}O) $^-$ spectra for 36K. The bands marked as (*) correspond to (^{17}O - ^{18}O) $^-$. There are two ^{17}O splittings: 74.9G and 80.3G. Simulation II is based on equal abundances but different linewidths (3 and 5G resp.) while III is based on a 2:1 abundance ratio but equal linewidths (3G).

Figure 9: Plot of Energy of O_2/TiO_5 system as a function of both rotation angle β and tilt angle α for one configuration.

Figure 10: Principal axes for rotation of NO_2 on the surface. The low temperature motion is predominantly a rotation about the y-axis.

Figure 11: A comparison between experimental and theoretical spectra simulated on the basis of a Brownian rotational model for NO_2 on Vycor. A) 4.8K to 42.2K; B) 77K to 185K.

Figure 12: Phase memory time, T_M measured by electron-spin-echoes for A) O_2^- /Ti-Vycor and B) NO_2 /Vycor.

Figure 13: Ultra high vacuum ESR system: (A) Roughing Line, (B) Titanium Sublimation Pump, (C) Ion Pump, (D) Cold cathode gauge, (E) Ionization gauge, (F) Quadrupole Residual Gas Analyzer, (G) Variable Leak Valves, (H) Evaporator unit, (J) Cavity (see Figure 14), (K) 12 inch magnet.

Figure 14: ESR Microwave cavity: (A) brass backup ring, (B) stainless steel knife edge, (C) medium voltage feed thru for static electric field, (D) titanium/ceramic end ring, (E) titanium walls, (F) brass/copper waveguide and flange, (G) ceramic microwave iris.

Figure 15: Arrangement for laser-induced transient-nutation ESR experiments..

Figure 1

Figure 2a

Figure 2b

A

I

II

III

Figure 3

A Weak Jump

$$(R_{||} \tau_{||} = 0.1)$$

— Exp
--- Cal

4.2 K

14.5 K

36.0 K

57.4 K

78.7 K

10 G → H

Figure 4a

Brownian Diffusion

Figure 4b

Figure 5

Interaction Diagram of O_2 and $(TiO_5)^{7-}$

Figure 6

Spin Densities

($\alpha = 10^\circ$)

Figure 7

Figure 8

Figure 9

Figure 10

A

Figure 11a

B

Figure 11b

Figure 12a

Figure 12b

Figure 13

Figure 14

Figure 15

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AA:

Enclosures:

1. Renewal Proposal (4 cys)
2. DOE Form 538 (3 cys)
3. Progress Report C00-4991-2 (5 cys)

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