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ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS
UNDER ULTRA-HIGH VACUUM CONDITIONS

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Jack H. Freed
Department of Chemistry
Cornell University
Ithaca, New York 14853

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Abstract

This project is directed to developing ESR for the study of surface adsorption and catalysis on clean and 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. Time resolution of the order of nanoseconds is to be introduced in the study of catalytic processes by means of Laser Time Resolved Electron-Spin Echo (ESE) Spectroscopy.

In the past year we have conducted an extensive study of the new phenomenon of surface-suppressed ESR (SSESR), in which stable paramagnetic radicals adsorbed on clean Ag or Cu surfaces have their ESR signal suppressed until several layers of molecules effectively insulate subsequent layers from the metal surface. This study employed a combination of UHV-ESR, CREMSEE, and thermal desorption techniques. A tentative model based upon transmission of the effects of the surface conduction band of the metal by the weak exchange forces between the paramagnetic species was suggested.

Experiments on a model system by means of Laser Time Resolved ESE spectroscopy were performed. In this work, a photo-induced transient electron was produced from Rb ions in non-polar medium. The spin relaxation of the transient electron was studied vs. temperature and alkali metal concentration. The transient electron is initially spin-polarized, and we have found that the degree of spin-polarization is affected by the wavelength of the irradiating light. It is suggested that such an effect would be expected from a long-lived geminate radical-pair mechanism ($\text{Rb}^\bullet + e^-$) causing the spin-polarization, with the initial separation distance affected by the energy of the photon absorbed.

In other work: an extended Hückel MO analysis of our previous $\text{O}_2^-/\text{Ti-vycor}$ study was completed; a new and improved photo-CREMSEE apparatus was completed and utilized; further analysis of our motional dynamics study of NO_2 on zeolites was carried out; and preliminary efforts directed to developing a photo-induced source of H atoms for Laser Time Resolved ESE experiments were carried out.

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- 1) Ultra-High Vacuum ESR Studies on Clean Metal Surfaces: NO_2 on Copper; M. Nilges, M. Shiotani, C.T. Yu, G. Barkley, Y. Kera, and J.H. Freed, J. Chem. Phys. 73, 588-589 (1980).
- 2) ESR Studies of O_2 Adsorbed on Ti Supported Surfaces: Analysis of Motional Dynamics, M. Shiotani, G. Moro, and J.H. Freed, J. Chem. Phys. 74, 2616-2640 (1981).
- 3) A UHV-ESR Study of the Reaction of NO_2 Adsorbed on Copper, M. Nilges, G. Barkley, M. Shiotani, and J.H. Freed, J. de Chim. Phys. (Special Issue) 78, 909-919 (1981).
- 4) ESR Studies of NO_2 Adsorbed on Surfaces: Analysis of Motional Dynamics, M. Shiotani and J.H. Freed, J. Phys. Chem. 85, 3873-3883 (1981).
- 5) UHV-ESR and CREMSEE: Two Novel Surface Techniques, M. Nilges and J.H. Freed, Chem. Phys. Letts. 82, 203-207 (1981).
- 6) Photoelectric Determination of Work Function Via CREMSEE Enhancement: Photo-CREMSEE, M. Nilges and J.H. Freed, Chem. Phys. Letts. 85, 499-504 (1982).

Manuscripts in Preparation with Support from DOE

- 7) A Molecular Orbital Study of O_2 Adsorbed on Ti Supported Surfaces, M. Shiotani, K. Tatsumi, and J.H. Freed.
- 8) Surface Suppressed ESR, G. Barkley and J.H. Freed.
- 9) Time-Resolved ESE Study of Laser-Induced Transient Electrons from Alkali Metal Atoms, U. Eliav and J.H. Freed.
- 10) An Electron-Spin Echo Study of Radicals Adsorbed on Surfaces, L.J. Schwartz, M. Shiotani, and J.H. Freed.
- 11) ESR Studies of NO_2 Adsorbed on Surfaces II: Zeolites, M. Shiotani and J.H. Freed.

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I. UHV-ESR and CREMSEE Studies

A) NO₂/Cu

We have used the NO₂/Cu system to explore and develop our UHV-ESR and CREMSEE techniques. This work has been completed. In it we have shown that 1) high-sensitivity UHV-ESR experiments may be performed on clean metal and oxide surfaces; 2) the new phenomenon of CREMSEE may be used as a sensitive indicator of surface bonding even when conventional ESR signals are absent; 3) the nature of the oxidation of Cu surfaces by NO₂ is strongly affected by presence of H₂O; 4) the reactive properties of NO₂ on supported Cu are different from those of clean metal films of Cu. This work has now appeared in an invited paper for the Special Issue of the Journal de Chimie Physique on new methods for the study of surface catalysis on metals.¹

B) Surface Suppressed ESR (SSESR)

1) Initial Results²

The special value of ESR and CREMSEE was clearly demonstrated in a study of the stable paramagnetic species DTBN [di-tertiary-butyl nitroxide] on a relatively unreactive (e.g. noble) metal surface.² This study was addressed to the question whether the DTBN would retain its paramagnetism. ESR is clearly the method of choice to resolve this hitherto unresolved question, but CREMSEE proved invaluable as well.

Initial experiments² were first 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₊ (i.e. the threshold microwave power, cf. Sect. C and refs. 1, 2) that is an order of magnitude lower than the clean Cu surface. When the DTBN is leaked in till the desired pressure at RT, a single ESR line is observed in which the ¹⁴N hyperfine structure is absent due to exchange-narrowing. 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 60 Å². Since the pressure in the UHV system must be raised to just below the vapor pressure of DTBN to see this signal, we concluded 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 about 20-30% of a monolayer coverage. At -101°C. a rigid limit spectrum is obtained with ESR parameters ($g_{\parallel} = 2.003$, $g_{\perp} = 2.007$, $A_{\parallel} = 33\text{G}$, $A_{\perp} \approx \Delta H = 6\text{G}$.) similar to DTBN in various solvents, and on silica and zeolite surfaces. Above -101°C. the lineshapes are quite temperature-dependent. Our interpretation based on computer simulation, is in terms of two components, one of which shows substantial exchange narrowing with increased T.

When experiments were performed with DTBN adsorbed on a clean Cu surface at -20°C. no ESR signals were seen.² However, the observation of a dramatic decrease in CREMSEE P_t when DTBN is leaked in at 10⁻⁸ to 10⁻⁷ torr clearly demonstrated 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 Langmuirs. After baking out the cavity at 150°C. for about 1 hr., P_t returned to almost its initial value for clean Cu, implying that the DTBN has been effectively desorbed. Similar results were obtained when clean Ag films were used, although lower temperatures were required to lead to adsorption of the DTBN.

This is the phenomenon we refer to as Surface Suppressed ESR.

2) Recent Results

This past year we have conducted a more extensive study of Surface

Suppressed ESR (SSESR). We summarize here only some of our key observations. The extensive results we have are presented in detail elsewhere.³

a) Clean Ag and Cu

Several nitroxides were adsorbed and studied on clean Ag and Cu surfaces under a range of conditions. These nitroxides are shown in Fig. 1 and will be referred to by their brief name. While DTBN is a liquid at room temperature, the others are solid at RT, but all have an appreciable vapor pressure (0.2 to 2 torr), and a characteristic mass spectrum observed with the quadrupole mass analyzer. Most important, they are all 100% paramagnetic in the bulk (i.e. each molecule exhibits an unpaired spin) and would be expected to remain paramagnetic in multilayers on the surface.

In no case does an ESR signal appear when the nitroxide is put down on the clean Ag or Cu surface until some threshold dosage, D_e is reached. However, the CREMSEE P_t drops by almost an order of magnitude before this threshold is reached. From this we may conclude that the nitroxide is adsorbing on the metal and bonding strongly enough to affect P_t . In Fig. 2 we show P_t vs. dosage for adsorption of several nitroxides on clean Ag. At some dosage, D_e (which is different for each radical), the ESR signal appears and then continues to increase with further dosage as shown in Fig. 3 for the same set of experiments as in Fig. 2. The ESR signal observed is a single exchange-narrowed line which is similar in each case. DTBN has the lowest measured D_e of 1.3kL with D_e significantly higher for the other cases (cf. Table 1). At such temperatures for a large organic molecule, monolayer coverage is expected by 1 - 10L (cf. below). This clearly implies that many layers of physisorbed nitroxide are required before the ESR signal appears. This is most graphically illustrated in the curve of P_t vs. dosage for TEMPOL in Fig. 2. There is an initial decrease in P_t , which we believe is due to

the first, or chemisorbed, layer (here the TEMPOL pressure is about 10^{-8} torr). There is no further change in P_t for several hours of dosage until the pressure is dropped substantially to about 10^{-5} torr at which time a drop in P_t is observed undoubtedly due to physisorption, which requires a higher vapor pressure, in this case, for a finite sticking coefficient. Nevertheless P_t must drop to 20% of its initial value in this case (cf. Table 1) before an ESR signal appears (i.e. $P_{t,e}/P_{t,o} = 0.20$).

The results for our experiments of nitroxides on Ag are summarized in Table 1. One may observe that the effect of performing the experiment at a higher temperature is to increase $P_{t,e}/P_{t,o}$, while a large increase in D_e is observed in cases in which higher pressures are required at higher temperatures to obtain a non-negligible sticking coefficient (e.g. TEMPONE).

Thermal desorption studies of the nitroxide can provide information on the binding of different species on the surface. We show in Fig. 4 a thermal desorption study on TEMPONE in which the ESR signal and the pressure are monitored as temperature is increased from -125°C ., the temperature at which the initial adsorption occurs. One sees a definite maximum in ESR signal intensity at -51°C . after which there is a monotonic decrease in intensity leading to a disappearance of the ESR signal at about -18°C .. When the experiment was repeated with a sample prepared at -55°C ., the desorption curve is nearly identical to the curve obtained for -125°C . (above -55°C .). The rise in pressure we observe at -95°C . does not correspond to any significant change in ESR signal or in P_t . Nevertheless, by monitoring the mass analyzer during the desorption we find that the rise in pressure is due to the nitroxide and not to any background contaminant. The pressure peak at -20°C . clearly corresponds to the species that gives rise to the ESR signal. Still P_t has not increased appreciably; this occurs slowly at a much higher temperature.

The desorption of DTBN and TEMPOL is found to be qualitatively similar to that for TEMPONE.

In a similar set of experiments for DTBN and TEMPONE on Cu the same general features were observed. In the case of Cu, however, the curves for P_t as a function of dosage are almost identical for these nitroxides as are the other parameters we measure for the adsorption process (cf. Table 2). The two nitroxides desorb at different temperatures, but again the ESR signal intensity is found to first increase with temperature and then decrease.

b) Nitroxides on Metals Pretreated with Oxygen

We originally found² that DTBN adsorbed on air-oxidized Cu (for periods of about a week) at RT gives a chemisorbed ESR signal with the conventional appearance of a nitroxide ESR pattern as noted above. We therefore undertook experiments to examine the sharp difference between results obtained with clean metal surfaces and air oxidized ones.

Experiments were performed on copper and silver pretreated with oxygen to try to form the clean insulator surface, or with wet oxygen to try to form hydroxyl groups on the surface. In every case, adsorption was performed at about -120°C . Table 3 shows the conditions of oxidation and the results. For air oxidation of copper² P_t was found to decrease by about an order of magnitude, similar to the decrease in P_t preceeding D_e for nitroxides on clean metals (cf. Tables 1 and 2). For cases 1-3 in Table 3, the decrease in P_t with clean oxygen pretreatment is small. In case 1, of Ag/O_2 , the O_2 was present during deposition of the Ag thin film, in an attempt to perform reactive evaporation. This was not effective in reducing P_t . It is unclear whether large exposures ($>10^{12}\text{L}$) of clean metal to pure oxygen will reduce P_t even if the surface oxidizes. The secondary emission yield may not change significantly for the oxide. Silver is less reactive, therefore less readily

oxidized. This is seen in the greater drop in P_t for $\text{Cu/O}_2 + \text{H}_2\text{O}$. Cases 4 and 5 are the only cases where P_t drops significantly.

We show in Figs. 5-7, the results with a copper surface that was stored under wet oxygen for one week, and which gave a large drop in P_t (case 5). Exposure to DTBN gave a further decrease in P_t as shown in Figure 5. The ESR signal (Fig. 6) appears at a dosage very near that for clean copper and DTBN. Also, the ESR signal observed is the same as that in the clean metal experiments. The ESR signal increases with temperature (Fig. 7), as in other experiments, and decreases in two steps. The disappearance of the signal is at a somewhat low temperature, -70°C .

c) TEMPONE on Silver Pretreated with Analog

As we discuss below, we believe that the many condensed layers of nitroxide insulate the subsequent layers from the metal surface. Also, the layers that are paramagnetic may interact with the earlier layers (close to the metal) by spin-exchange interactions. Therefore, we pretreated the surface with a molecule very similar to the nitroxide TEMPONE, except it is not paramagnetic. This molecule ('Analog') differs from TEMPONE only by a substitution of H for O at the nitrogen (see Fig. 1). It should be very similar to TEMPONE in its adsorption on the silver surface if adsorption is not through the N-O group.

Adsorption of Analog was performed at -120°C . as for TEMPONE. Figure 8 shows P_t as a function of dosage. The three curves are almost identical and give an indication of the reproducibility. These curves differ from that for Ag/TEMPONE in requiring larger dosage to cause P_t to drop. Progressively more Analog was put down on the surface in three runs. Table 4 lists the dosages of Analog and other details for these experiments. After some dosage, the Analog was pumped out and TEMPONE admitted. The appearance

and growth of the ESR signal was followed and the results are shown in Figure 9. For pretreatment with 1.4kL of Analog, the ESR signal appears at a much lower dosage than on clean silver (see Table 4). The Analog is effective in covering the silver surface so that TEMPONE interacts less with the metal. After pretreating the silver surface with 8.3kL of Analog, an ESR signal is observed. This is before any nitroxide is admitted. Thus, a paramagnetic species is formed on the silver surface at a low temperature from the Analog. This could be from oxidation of the nitrogen by a carbonyl of a neighboring molecule. The ESR signal increases with admission of TEMPONE. Another run was made with a higher dosage of Analog. In this run no signal was observed from Analog alone, but the signal does appear immediately with the admission of TEMPONE. [It is possible that, with the former run (8.3kL), the surface warmed up momentarily during the last part of the adsorption of the Analog, permitting the oxidation.]

The desorption data were also obtained. The curve for the 1.4kL Analog run is similar to that for Ag/TEMPONE (Fig. 3.4) in that the ESR signal intensity increases considerably with temperature, but there is the additional feature, however, of a small increase before disappearance at a much higher temperature. The curves for 8.3 and 14.5kL Analog are very similar to each other and rather different from those for lower dosages. The most notable feature here is the 5-fold increase in ESR signal intensity to nearly the original maximum intensity with further warming after the initial large decrease. Figure 3.32 shows the ESR signal and pressure as a function of temperature. The first two small peaks in pressure correspond to the initial decrease in ESR signal. The next peak corresponds to the large second increase in ESR signal intensity, and the last rise in pressure corresponds to the disappearance of ESR signal. Note that the ESR signal does not

disappear until the surface is warmed to 60°C., well above room temperature and the highest such temperature noted for any system.

d) Analysis

In no case does an ESR signal appear when the nitroxide is first put down on the clean silver or copper or on the metal pretreated with oxygen (and water). Only after some minimum dosage does an ESR signal become detectable. If the ESR signal intensity as a function of dosage is extrapolated to zero intensity, the dosage at the intercept, D_e , is greater than zero ($\sim 10^3$ - 10^5 L). The drop in P_t for dosages up to D_e indicates that the surface is affected by dosages less than D_e . Our past work has shown that P_t decreases (increases) as the work function of the surface decreases (increases). The work function decreases with adsorption of organic molecules on platinum⁴ (e.g. $\Delta\phi = -1.6\text{eV}$ for 2,6-dimethylpyridine) and thus the direction of change in P_t is consistent. It is assumed that the nitroxide is adsorbing on the metal or oxide surface and forming a surface dipole thereby lowering P_t .

Some estimate of the sticking coefficient σ would be useful. Based upon our observations, on simple models of adsorption for rare gases,⁵ and utilizing the heat of vaporization of DTBN which is 11 kcal/mole⁶ we would expect σ of order unity for the first layer on the metal.³ As the first layer begins to fill, physisorption begins to be important, for which σ should drop to some small but finite value. (Also, for conditions of our experiments we estimate that 1L of dosage would give one monolayer coverage for $\sigma = 1$.³)

In our experiments we can obtain data on σ for the physisorbed layers only when an ESR signal is observed. In particular, we can use our graphs of ESR signal vs. dosage D . The ESR signal is first converted to absolute number of spins per cm^2 of surface. This is transformed into the monolayers of detected spins, Θ using the area occupied by one nitroxide molecule⁷ [$60\text{\AA}^2$].

Then $\sigma = d\theta/dD$ (where we implicitly have used the estimate above that for $\sigma = 1$ and $D = 1L$ then $\theta = 1$). Since we are ultimately interested in σ to determine θ for the layer(s) not observed by ESR, we might use $\sigma_a \equiv d\theta/dD|_{D=D_e}$ i.e. the initial slope at D_e . These values are given in Table 5.

These results clearly suggest that the effect of the metal is to suppress ESR significantly (i.e. SSESr) beyond the first chemisorbed layer, i.e. $\theta_a > 1$. Thus, it is likely that for $D \sim D_e$ some nitroxide molecules are still experiencing SSESr and σ_a is less than the true sticking coefficient. We have therefore made a second estimate of σ : $\sigma_e = d\theta/dD|_{D \gg D_e}$, i.e. we use the slope of the (usually straight line) of ESR signal vs. D for $D \gg D_e$, and let us call the x-intercept of this line, D_x . In most cases we find $\sigma_e > \sigma_a$ as expected (cf. Table 5). If we assume that either σ_a or σ_e is a reasonable estimate for σ during adsorption after the first layer even when no ESR signal appears, then we obtain as estimates of θ , $\theta_a = \sigma_a D_e$ and $\theta_e = \sigma_e D_x$. These values are likely to be estimates of the lower limit to θ because it is possible that not all molecules are ESR observable even for $D \gg D_e$. (They will not, however, be affected by any systematic error in pressure measurement, since that cancels out in the above procedure.) Thus the values of θ_a and θ_e in Table 5 clearly demonstrate that significantly more than a monolayer coverage is required before an ESR signal is observed.

This conclusion is amplified by the observation of an increase in ESR signal as the temperature is raised, cf. Figs. 4,7,10, as though there were a phase transition which leads to an increase in number of spins which give an ESR signal.

We are inclined to regard the layers giving SSESr as performing the role of insulating the metal surface, so that further layers can give an ESR signal. This minimum insulating property, we believe is measured by $R' \equiv P_{t,e}/P_{t,o}$.

The summary in Table 5 yields an average $R' = 0.19 \pm 0.09$ for all our experiments.

Our tentative model for the phenomenon of SSESr is as follows. The first or chemisorbed nitroxide layer is interacting strongly by exchange (and other) forces with the surface conduction band of the metal. On the basis of rough order-of-magnitude estimates based on the "electronic" Korringa effect^{8,9} this coupling should lead to a $T_2 \sim T_1 \sim 10^{-11}$ sec. or a huge linewidth of 5.7kG., which would render the ESR signal unobservable. Subsequent nitroxide layers interact with the preceding layers by a weak exchange interaction $J \sim 10^{11} - 10^{12}$ sec.^{10,11} We would expect a progressively weaker transmission of the effects of the surface metal conduction band to each subsequent layer until it is ultimately no longer important to the spin properties of the layer. The effects of increasing temperature in first increasing the ESR signal (i.e. number of observable spins; cf. Figs. 4,7,10 and Table 4) might be correlated with Fig. 11 which shows a rise in ESR linewidth with temperature. (Both maxima appear at nearly the same temperature for this run.) This latter observation of linewidth variation with temperature is similar to what has been observed in pure solid samples of DTBN, where it was studied at different Zeeman frequencies.¹¹ Kreilick's¹¹ interpretation for bulk samples was in terms of changes in J and in average intermolecular separation between nitroxides taking place as a function of temperature. Such thermal effects as changes in J could very well modulate the number of surface layers which experience SSESr if our tentative model is valid. (The effective exchange interaction may also be modified by the coverage; cf. Fig. 11a.) Further work would be needed to establish this potentially important correlation.

If there is residual interaction with the surface conduction band in the observed ESR signal, then this might show up as a small shift in the

g-value from that of the pure nitroxide, and that shift might be expected to be smaller with further coverage. We have measured g-values only after significant coverage, and we observe a slight decrease in g-value (for DTBN $g = 2.0055$ vs. 2.0059 for the single crystal; for TEMPOL it is 2.0060 vs. 2.0062 and for TEMPONE it is 2.0056 vs. 2.0068). However, in our previous work² on DTBN the incipient g-value just above D_e was found to be 2.0039 , or a more significant decrease. According to our model, the g-shift would be the electron-spin equivalent of the usual nuclear Knight shift.⁹ Again further work on very accurate g shifts with coverage would be helpful.

Ultimately, experiments at 4°K and below would be very helpful, since at these low temperatures the conduction band ESR signal is narrow enough to be seen,^{9,12} and if our model of SSESr is correct, then by analogy to the study of dilute alloys in Cu,^{9,12,13} the surface nitroxides could also be visible in the ESR and show interesting effects due to their coupling to the metals. One may then deduce from such effects important properties of the dynamic electronic interactions between surface paramagnets and the surface conduction band.

Pretreated Surfaces: Results on Ag pretreated with O_2 or $\text{O}_2/\text{H}_2\text{O}$ differed little from the results on clean Ag. This may be explained by the relative inertness of Ag to oxygen adsorption, incorporation, and oxidation.^{14,15} The sticking coefficient for O_2 above 0.1 monolayer coverage is no more than 10^{-5} with 1 torr O_2 required for monolayer coverage.¹⁴ Incorporation of O_2 into the bulk is very slow,¹⁵ therefore little oxidation is expected. As a result, most metal atom sites for DTBN adsorption are still available. O_2 pretreatment has a greater effect on Cu. Adsorption of dry O_2 on Cu slightly reduces D_e and θ_e and slightly raises σ_e . Adsorption of wet oxygen prior to adsorption of nitroxides increases D_e , slightly increases

θ_e and reduces σ_e , while the increase in R' is significant. Copper is more reactive than Ag, demonstrating adsorption and incorporation of O_2 .^{16,18} For higher dosages of O_2 , the Cu surface is found to restructure such that Cu atoms are always exposed to the impinging gas.^{16,17} Thus Cu atoms are probably available at the surface to interact with the nitroxide.

These results for nitroxides adsorbed on O_2 or O_2/H_2O pretreated Cu at -120°C . are very different from those we previously obtained for DTBN adsorbed on air oxidized Cu at room temperature² and noted above. The major difference is that after evacuation of the physisorbed layer(s), a typical hyperfine structure for nitroxides was seen previously,² but not in our current experiments. Either there is some other component from air (e.g. sulfides), providing an (insulating) site that has high binding energy for the nitroxide, or else at RT, activated adsorption at sites unavailable at -120°C . becomes possible.

C) Work Function Measurements by Photo-CREMSEE

CREMSEE 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^{1,2} show that the electrons are from the surface, and the steady-state presence of free electrons (ca. 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 unity, there is electron multiplication until surface charge effects oppose further net emission of electrons (i.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_t . (Examples of this have been given above.) Similarly, the work function ϕ is modified by an adsorbed species, and this is attributed to the formation of an electrical double layer.^{5,19,20} 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 to 10 eV⁹⁻¹². However, the predicted increase in δ from this relation² shows it is much too small (only a factor of 1.6 at most) to explain the nearly order of magnitude increases in P_t . Somewhat better agreement is obtained when P_t is related to E_{pl} , the incident electron energy necessary for $\delta = 1$ (i.e. secondary electron emission yield of unity),² but further analysis is required.

We have now addressed ourselves to two matters in conjunction with this CREMSEE phenomenon. First, it is 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^{19,20} 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 photoemission²¹ (UPS)] in situ in the microwave cavity. Thus we considered how some of these measurements might be performed in conjunction with UHV-ESR and CREMSEE studies. Secondly, we studied the "electron-amplifier" and detector properties of CREMSEE. In fact, we succeeded in showing 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) by using the photoelectric effect in the presence of CREMSEE.²²

We have now completely redesigned our apparatus for photo-CREMSEE

in order to i) attain a large photon flux at the optimum surface in the ESR cavity, ii) to significantly improve light resolution; and iii) to allow for shorter λ . The photo-CREMSEE experiments are performed using the experimental arrangement in Figs. 12 & 13. Light from a PRA 150W Xenon Lamp is passed through a water IR filter and is focussed with lens 1 on the entrance slits (200 μ) of a McPherson #232 0.2 meter scanning monochromator. Light from the exit slits (200 μ) is collimated with Lens 2. Lens 3 condenses the light such that it passes through the UV grade sapphire window, reflects off the surface of the conical mirror, and is focussed onto the CREMSEE-active surface of the UHV cavity. The lenses, optical windows and monochromator are of UV grade quartz and transmitted 90% of the light at 200nm.

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. The most accurate results are obtained by keeping the microwave power below P_t . Then a stable photo-induced or "photo-CREMSEE" signal may be observed due to the photo-electric effect. We now can observe photo-CREMSEE with setting of P as low as 8mW below P_t , which is a great improvement on our original experiment.

The observed properties of this photo-CREMSEE signal are:

- 1) At a given frequency the signal height, S is proportional 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.
- 3) The signal is observed corresponding to $g = 2$ with derivative peak-to-peak width of slightly less than 0.2 G (about 170mG).
- 4) The signal has the appearance of a normal first derivative ESR signal, and its width and shape are independent of light wavelength, λ .

5) The photo-CREMSEE signal is stable, i.e. it does not add any noise above the receiver level, unlike CREMSEE^{1,2}, 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.

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, the microwave field is required to accelerate the photo-electrons to permit secondary electron emission, but the secondary electron emission yield δ is kept below what is required 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 makes photo-CREMSEE a very sensitive technique.

We have used this arrangement to measure ϕ for a clean Ag surface. 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 photo-current) per quantum of light absorbed.²³ Also $\phi_0 = \phi + \epsilon^*$, where to a first approximation ϵ^* is constant and equal to the electron energy at the Fermi level.²³ 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 $s(\nu)^{1/2}$ vs. 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 in Fig.14 for the clean Ag surface at RT, for which we find $\phi = 4.25\text{eV}$ in good agreement with non-annealed Ag films.²⁴ Our previous result for an air-oxidized Ag surface of $\phi = 4.06\text{eV}$ is quite reasonable, especially in view

of the fact that P_t for CREMSEE is decreased significantly by air oxidation.^{1,2}

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 ^{1,2} 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. Also, it appears possible to use photo-CREMSEE to perform in situ UPS²¹ in the microwave cavity. One requires a far-UV tunable source, which is swept to obtain $s(\nu)$ vs. ν . This approach is usually referred to as photo-emission total yield spectroscopy.²⁵ Then by differentiating $s(\nu)$ with respect to ν one would obtain results related to UPS.²⁵ 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. We have now obtained a GCA/McPherson Model 630 Capillary Discharge Light Source. This Hinteregger lamp can deliver VUV output down to 60nm(20.7eV) with He gas. We plan to use it as a source for performing such experiments.

D) : Metal Oxide Surfaces: MgO

One of our objectives for UHV-ESR is to prepare clean and well-characterized oxide surfaces which can serve as supports for metal atoms. This would permit us to study well defined "catalytic" systems. Thus, we have performed a variety of preliminary experiments on Mg and MgO.²⁶

A new UHV arrangement for clean metal and metal oxide samples was developed for the Mg and MgO work. This arrangement can be used for all materials with low evaporation temperature. This is a quartz tube arrangement based on a design of Svejda's which he used for powders²⁷ (cf. Fig. 15). The advantages of this arrangement are a) use of a commercial wide access cavity

with its optimum sensitivity and modulation field; b) ease and range of temperature control up to 1200° to bake the sample, and down to liquid nitrogen cooling of the sample; c) sample position in center of cavity with higher microwave and modulation fields. The chief disadvantage is the small sample size. Still, sensitivity could be at least comparable to UHV cavity designs. It is not certain that evaporations can be as easily controlled in this arrangement as in the UHV cavity. Also pumping efficiency is reduced by the narrow tubing, and it is not useful for performing CREMSEE. In our future work on Mg/MgO we shall be comparing this design with our standard UHV-ESR methods.

II. Radical Dynamics on Surfaces

A) NO₂ on Vycor vs. Zeolites

In our extensive study of the motional dynamics of NO₂ adsorbed on crushed vycor glass²⁸, it was found that for NO₂ motion on the vycor surface:

- 1) at 4.8°K, NO₂ still shows residual motional effects; 2) below 77°K the rotational motion of NO₂ is axially symmetric about the y-axis (i.e. parallel to the O-O internuclear axis) such that $N \equiv R_{\parallel}/R_{\perp} \approx 10$. The parallel component of the diffusion tensor, $R_{\parallel}$ increases with temperature, e.g. $R_{\parallel} = 5 \times 10^5$ and $1 \times 10^7 \text{ sec}^{-1}$ at 4.8°K respectively (based on a Brownian diffusion model) with a very low "activation energy" of ca. 50 cal/mole; 3) above 77°K, $R_{\perp}$ increases with temperature so that almost isotropic rotational diffusion is estimated at 185°K; (i.e. $R_{\parallel} = 1 \times 10^7 \text{ sec}^{-1}$ and $N = 1.3$), presumably due to a translational diffusion mechanism with an "activation energy" of ca. 500 cal/mole; 4) There are discrepancies between the observed and calculated lineshapes especially for $T \lesssim 77^\circ\text{K}$. None of the models of Brownian vs. Jump diffusion used could improve the agreement. The

observed discrepancies are similar to those observed previously in our study of the motional dynamics of O_2^- on supported surfaces.²⁹ A quantum mechanical analysis of the 4.8°K spectrum implies either a renormalized moment of inertia for NO_2 that is orders of magnitude greater than that in the gas phase and/or a strong orientation-dependent interaction potential with the surface. In either case it appears that the y-axis should be parallel to the surface. Additional line broadening probably due to an exchange process modulated by translational diffusion rapidly increases with temperature above 77°K, even though the NO_2 surface concentration decreases with increasing temperature.

Utilizing our careful study of the NO_2 /Vycor system as a basis, we initiated a more extensive study of NO_2 with different types of zeolites. We have, so far, studied NO_2 on three different zeolites: 1) Zeolon (a mordenite) with composition $Na_{8.7}[(AlO_2)_{8.7}(SiO_2)_{39.3}]24H_2O$; 2) 13X(Na^+) a Fajassite with composition $Na_{86}(AlO_2)_{86}(SiO_2)_{106} \cdot 264H_2O$; and 3) NaY a Fajassite with composition $Na_{56}(AlO_3)_{56}(SiO_2)_{136} \cdot 250H_2O$.

We find that the zeolon results are well-fitted by rigid-limit simulations from 4.5°-77°K and substantial motional effects begin only above 100°K. The motion is anisotropic, but becomes isotropic at a little spectral change from the rigid limit till about 100°K. The high temperature spectra are readily fit with a model of nearly isotropic Brownian diffusion and activation energy of 1.4kcal/mole, but the lower temperature spectra are more difficult to fit by our standard models. We have been exploring a new model we call the "microscopic-order macroscopic disorder" model. It assumes that there is an orienting potential against which the NO_2 rotates relative to the surface, but the zeolites are polycrystalline, so there is macroscopic randomness to the orientations of the various micro-surfaces.

This model shows some of the features of the $\text{NO}_2/\text{13X}(\text{Na}^+)$ spectra, but we have a long way to go to obtain good simulations. We have had better success with the NO_2/NaY system (cf. Fig. 16). This requires a model of substantial anisotropic rotation about the NO_2/NaY axis even at 4.8K with the motion becoming more isotropic above 77°K (cf. Fig. 17). This is qualitatively similar to the results with NO_2/Vycor except that $\tau_{R\parallel}$ is much faster for NO_2/NaY at the low temperatures implying nearly free rotation of the NO_2 about its y axes.

We believe that at this stage of our efforts, we can distinguish unique and different features for NO_2 motions on the different zeolites, which must be due to the manner in which the NO_2 interacts with the different structural features of the zeolites, and we plan further work on these systems.

B) O_2^- on Supported Surfaces: MO Theory

Transition metal complexes of the superoxide O_2^- and the peroxide O_2^{2-} are of both chemical and biochemical interest.³⁰ We have already studied by ESR, the molecular dynamics of O_2^- adsorbed on Ti supported porous Vycor glass.²¹ We have now completed an extended Hückel MO analysis that derives from our interpretation of the ESR spectra. We examined by MO theory:

- 1) the spin densities on the $^{17}\text{O}_2^-$ nuclei; 2) the g-tensor; and 3) the barrier to rotation of O_2^- . We had previously found that O_2^- engages in nearly free planar rotation about the axis perpendicular to the molecular axis of O_2^- and parallel to the normal to the surface.²⁹

We took as a reasonable assumption that the Ti atom is surrounded by oxygen atoms of the SiO_2 system leaving one coordination site open, which will allow Ti to interact with O_2 (cf. Fig. 18). On the basis of our experimental evidence,²⁹ we expect the oxidation state of Ti to be +3 before O_2

is introduced. Fig. 18 shows our model of the active Ti site used for the calculations. We fixed the Ti-O distances based upon previous estimates,³² but we allowed the angles α and β to vary (cf. Fig. 18) between the two limits of O_2 lying parallel to the surface ($\alpha = 20.8^\circ$, $\beta = 69.2^\circ$) and O_2 perpendicular to the surface ($\alpha = 0^\circ$, $\beta = 180^\circ$). Also the position r of the Ti ion above the surface was optimized, (i.e. in the parallel configuration $r_{opt} = 0.2\text{\AA}$ while for the perpendicular one it is $0.0\text{\AA}$). Our analysis is in many ways similar to a more general energy diagram discussed for coordination modes of diatomic molecules in transition metal complexes.³³ The optimized potential energy curve for this cooperative co-ordinate is shown in Fig. 19. These are minima for both limiting structures, but the ESR results rule out the perpendicular configuration. [This raises the interesting question whether both species exist, but only the parallel configuration can be seen by ESR, or else whether the extended Hückel MO calculations are too crude to distinguish the true minimum.]

The molecular orbitals of the two extreme geometries are shown in the form of an interaction diagram between the $(TiO_5)^{7-}$ and O_2 orbitals in Fig. 20. The behavior of the b_1 level is the major factor of the potential maximum present in Fig. 19 for the kinked structure. As α decreases and β increases, the b_1 ($\pi_1^* + xz$) orbital is first destabilized and then drops in energy to become one of the e orbitals of the C_{4v} symmetry (or perpendicular) geometry.

Our observation of two ^{17}O hfs. of $A_{11} = 74.8G$ and A'_{11} of $80.3G$ corresponds to spin densities of $0.37e$ and $0.39e$ respectively and is consistent with the parallel or C_{2v} symmetry, but with a small tilt, i.e. $\theta \neq 0$.²⁹ Our results of spin density vs. θ are shown in Fig. 21. They confirm that only a small tilt angle θ would be consistent with our observed small difference

in observed spin densities. (Although there is not good quantitative agreement between the MO result and experiment, one may expect the trends to be more meaningful.) The minor tilting from C_{2v} symmetry probably implies a small detail in the surface complex not embodied in the MO calculation. It does appear safe to say that an unpaired electron resides in the a' orbital (a_2 in C_{2v} symmetry), i.e. in the $O_2 \pi_{11}^*$ orbital.

We have studied the rotational barrier of O_2 as a function of ψ (cf. Fig. 18) for small tilts. Thus for values of $\theta = 0^\circ, 9^\circ$, and 8° we obtain barriers of 0.062, 0.045, and 0.027 eV respectively. The energy maximum comes at the eclipsed conformations. All are fairly small, consistent with the experimental estimate²⁹ of 0.022 eV (i.e. the activation energy for rotation).

The g-tensor components may be analyzed according to the theory of Känzig and Cohen,³⁴ which however is a crystal field theory, and yields an empirical crystal field parameter. Given our MO theory it was possible to perform a full MO analysis of the g-tensor according to the appropriate second-order perturbation theory.^{35a} We calculated the g-tensor as a function of tilt angle (cf. Table 6). Our best agreement with experiment is for $\theta = 0^\circ$, but we predict a g_{xx} that is too high. The contribution to g_{xx} comes mostly from the $1b_1 \rightarrow a_2$ (cf. Fig. 20) excitation with a calculated excitation energy of 0.359 eV. It is likely that the extended Hückel method underestimates the $1b_1 \rightarrow a_2$ separation. But we tried varying parameters so as to enlarge the energy separation to improve agreement. We did this by 1) lowering the Ti xz orbital energy and by 2) shortening the Ti- O_2 distance. These changes do indeed bring g_{xx} into closer agreement with experiment (cf. Table 6) but we have no further justification for these changes.

In general, we conclude that the extended Hückel results supply a basis for understanding our ESR experiments in terms of the electronic

structure of the complex, even though it cannot be expected to be quantitative.

III. Time-Resolved Photo-Induced ESE Studies of Catalysis

Another major objective of ours 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. The most effective method is to use electron spin echoes (ESE) in conjunction with a pulsed laser source. This can deliver time resolution of the order of 10-20 nsec. We have concentrated these past two years on developing this method, which we believe will have important future potential. Our successful experiments have been performed on a "model system" with which Dr. Uzi Eliav, who is conducting these experiments, was very familiar.

A) Rb. in Non-Polar Medium: Transient "Solvated" Photo-electron

During the early 1970's it was established that alkali anions are present in ether and certain amine solutions of alkali metals. The major facts that lead to this conclusion are as follows: a metal-dependent absorption peak is observed in the region of $680 \mu\text{m} \geq \lambda \leq 1040 \mu\text{m}$. ($\lambda_{\text{Na}}^- = 680 \mu\text{m}$, $\lambda_{\text{K}}^- = 800 \mu\text{m}$, $\lambda_{\text{Rb}}^- = 980 \mu\text{m}$, $\lambda_{\text{Cs}}^- = 1040 \mu\text{m}$ for THF at room temperature.) An oscillator strength of 2 was measured for these peaks. The conductivity is not compatible with the mobility of the solvated electron but rather with that of alkali anions. The most significant evidence was obtained from NMR studies.^{35b} Comparison of a solution that contained only alkali cations (i.e. NaI) with that of metal solutions reveals a new narrow line whose chemical shift and line width are almost independent of the solvent, i.e. the alkali nuclei are screened by two s type electrons. In recent years an extensive study of photoionization products of the alkali anions has been carried out.

It was found that one obtains the following species: solvated electron: e^-_{solv} ; an ion pair of alkali cation and an electron without a solvent molecule separating them: denoted by $\dot{M}$, and another ion pair where the ions are kept apart by dicyclohexyl 18-crown-6: denoted by $M\text{Cr}^+$:e. Crown is added to stabilize the cations thereby enhancing the equilibrium concentration in solution. The above two species of ion pair were found to be efficient reducing agents. One could obtain benzene anions even for concentrations of 0.2 μM benzene and 0.2 μM reducing agents.³⁶ It is the high reactivity and simple structure of the parent compound (2 electrons in the ns orbital) that make the alkali anions $n = 2, 3, 4, 5$ an object of interest in studies of catalytic chemical reductions, as well as physical phenomena such as electron spin polarization.³⁷ It is important to note that the initial large non-Boltzmannian electron spin polarizations that are often observed^{38,39} greatly enhance the ESR signal, thus making this work more feasible.

Our main goal is to investigate how the anions and their photoionization products change their symmetry properties and therefore catalytic activity as a result of adsorption on surfaces such as silica. It was therefore useful to start our studies in a medium that is not expected to change the spherical symmetry of the alkali anions, i.e. an inert liquid medium such as THF.

In these initial experiments we believe we have demonstrated the great potential of the time-resolved ESE technique for this project. We have studied this past year: a) photoionization and the subsequent observation of spin polarized electrons, and b) concentration effects on the chemical rate processes.

As already noted, the photoelectrons obtained by photoionization are spin polarized. This phenomenon is quite sensitive to the symmetry of the

radical pair involved and to the (fluctuating) distance between them.³⁷ Optical studies⁴⁰ of the dependence of the absorption peak of Rb^- on temperature and solvent indicate that a model of charge transfer to solvent (with the solvated electron in an orbit near the Rb atom) may explain the spectrum. This has prompted us to consider a radical-pair cage reaction mechanism³⁷ for the polarization of the spin of the electron. Such a mechanism should be sensitive to the initial separation distance of the radical pair which in turn should depend on the wavelength of the exciting radiation (e.g. the extra energy would be used to increase the "orbiting radius" of the electron about a Rb in the solvent cage.^{40b}

We show in Fig. 22 our sophisticated experimental arrangement required to perform time-resolved photo-induced ESE. Our Lambda Physik Dye Laser was pumped with the XeCl line of our Lambda Physik Excimer Laser. This enabled us to probe the "blue tail" of the absorption peak (i.e. λ shorter than λ_{max}). The initial polarization is obtained by performing a rapid two pulse 90° - 180° echo just after the laser pulse.

We show in Fig. 23 the dependence of the initial polarization on λ for a solution with $[\text{Rb}^-] = 8 \times 10^{-6}$ M. [Note that for our sample volume of 8×10^{-6} l. this would imply an upper limit of 8×10^{12} spins. This number is probably undetectable by spin echoes, except perhaps by very extensive signal averaging, if they had just a Boltzmann polarization. The large chemically-induced spin polarization initially present after the laser pulse is however, so large (greater than 30 times Boltzmannian) that an echo signal can be obtained from only a single pulse!] These results have been corrected for i) the wavelength dependence of the photon output of the dye laser utilizing conventional power meters; and ii) the wavelength dependence of the extinction coefficient using published values.^{36b} We have found

a linear dependence of the polarization on the light intensity indicating a single photoelectron emitted for each absorbed photon. Thus the initial "normalized" signal height is directly proportional to the initial polarization per electron, P_a . The results of two runs at two different temperatures indicated that P_a is increasing monotonically with decreasing λ (although some uncertainty exists for $T = -70^\circ\text{C}$ and short λ). A simple application of the multiple re-encounter mechanism for radical-pair polarizations would suggest that as the initial separation, r_I of the radical-pair is increased, P_a should decrease (i.e. P_a is inversely dependent on r_I ³⁶) which is contrary to observation. If instead, we consider a mechanism in which the $\text{Rb}\cdot\text{e}^-$ radical-pair remains complexed and separated at r_I until the e^- is recaptured by a Rb^+ cation, and furthermore the e^- lifetime in the radical-pair is of the order of 10^{-8} sec. or longer (and this is consistent with our experimental results, cf. below), then $P_a \approx \frac{QJ}{Q^2+J^2} \left(\frac{1}{2}\right)$ where Q is half the difference in resonance frequencies between $\text{Rb}\cdot$ and e^- , while J is twice their exchange interaction.^{36,41} If $J > Q$, then a decrease in J due to an increase in separation distance r_I (resulting from a larger energy photon being absorbed), would lead to increased polarization consistent with our observations. We have also made the preliminary observation that addition of a crown, which could separate the $\text{Rb}\cdot$ and e^- (but is also expected to reduce the hfs of the Rb'), does modify these results, but further work is necessary.

We also made extensive measurements of the signal decay times, which we nominally call T_1 , vs. $1/T$ (cf. Fig. 24). This was measured by a two-pulse 90° - 180° echo coming at a time τ after the laser pulse. This time τ was stepped out to yield the decay time T_1 (the time interval between the 90° and 180° pulse remained fixed). This signal is, in general, a composite of the true spin lattice relaxation time (call it T_1') and the rate of recombination

k due to $e^-_{\text{solv}} + \text{Rb}^+ \rightarrow \text{Rb}^\bullet$ (and also to $e^-_{\text{solv}} + \text{Rb}^\bullet \rightarrow \text{Rb}^-$). We also present (cf. Fig. 25) our results for T_M , the phase memory time, which for the fast-motional region is just the transverse spin relaxation time T_2 . It also will be affected by k (which should contribute equally to T_1 and T_2) as well as by normal T_2 -type spin-relaxation processes.³⁷ The latter are usually such that as temperature increases, T_2 increases, but at low enough temperatures one is in the slow motional region and T_M becomes more complex but may be expected to increase with decreasing T .⁴² The shortest relaxation time we have succeeded in measuring so far is ca. 50nsec for T_M when crown-ether is present.

The following trends are clear from Figs. 24 and 25. At $[\text{Rb}^\bullet] < 10^{-2} \text{M}$, T_1 and T_2 both increase with temperature and $T_1 > T_2$, which suggests a fairly slow motional process. Also T_2 is decreasing with increasing $[\text{Rb}^\bullet]$, while T_1 is unaffected by changing $[\text{Rb}^\bullet]$ at the lowest concentrations, but it does increase for $[\text{Rb}^\bullet] > 10^{-4} \text{M}$ at the lower temperatures. At very high concentrations T_2 decreases with decreasing temperature, while T_1 is much longer than T_2 .

These trends are entirely different from what has been observed for solvated electrons in polar solvents,⁴³ which are more stable than the transient electrons we observe in non-polar solvent. There is some evidence that the lifetime of the electrons we observe is longer than the T_1 's and T_2 's we observe,³⁶ so we look to spin relaxation processes to interpret our data.

In dilute polar solutions the mechanism for T_1 and T_2 is usually taken as modulation of isotropic hyperfine interactions between the unpaired electron and (solvent) nuclei which are encompassed in its orbital (e.g. Rb nuclei or solvent protons in our case).⁴³ We would require $\omega_0^2 \tau_c^2 > 1$ where ω_0 is the resonant frequency and τ_c is the relaxation time for the modulation process in order to have $T_2 < T_1$ for our most dilute case of

$[\text{Rb}^-] = 8 \times 10^6 \text{ M}$. As the temperature decreases, we find that T_1/T_2 becomes larger, as is consistent with $\omega_0^2 \tau_c^2 \gg 1$ and τ_c increasing with decreasing temperature. The increase in T_2 with decrease in temperature is inconsistent with such a mechanism, unless we allow the hfs, A_1 to decrease with temperature. Alkali metal atoms in solution do indeed exhibit significant decreases in A_1 with decrease in temperature,⁴⁴ and we might assume it is also true for a solvated electron and a Rb^+ atom with which it has a residual small A_1 .

The significant decrease in T_2 but no initial change in T_1 with increasing alkali ion concentration might possibly reflect lifetime uncertainty line broadening from the process:

the rate of which might be enhanced in the presence of crown:

This process would not be a T_1 process if there is no additional electron-spin flip probability during the lifetime of the Rb^- species, and this may be questionable.

The value of time resolved ESE to photo-induced processes of importance to catalysis should be clear from this study. However, it pointed up some experimental difficulties. In particular, fast acquisition of data would make studies like the present one less time consuming and more feasible. The major inhibiting factor is the low repetition rate of the laser (30-50pps) combined with a single two pulse echo after each laser pulse. In order to overcome this problem we realized that one must obtain the maximum data after each laser pulse. This may be done by resorting to multi-pulse sequences such as modified Carr-Purcell sequences, which are commonly used in NMR spectroscopy,⁴⁵ but have not to our knowledge previously been used

in ESE. We have undertaken to develop the appropriate methods, and we show in Fig. 26 initial results with a standard sample of irradiated quartz (yielding trapped electrons) with very long $T_M = 7.5\mu\text{sec}$. We have also obtained results on our solvated e^- system with faster T_2 's (cf. Fig. 27), where we could monitor 3 echoes in the sequence. Our arrangement of the digital electronics is shown in Fig. 28 and it allows us to perform successive 180° pulses as fast as every 40nsec (i.e. $\tau = 20\text{nsec}$). The major problem that remains is to reduce the spectrometer dead time of 100-200nsec., and we have initiated a significant effort to accomplish this.

Nevertheless, our preliminary results with Carr-Purcell sequences have led to some interesting observations. For the irradiated quartz, the decay time from the Carr-Purcell sequence is 3 times longer than that of a simple ESE sequence. That is, the Carr-Purcell sequence is effective in partially averaging out the spin mechanism responsible for the relaxation process. There is a close analogy^{42b} between this effect and the well-known NMR technique of using Carr-Purcell sequences to measure diffusion coefficients in inhomogeneous field gradients.⁴⁵ In the present case, the source of the inhomogeneity is in the local fields, ΔH_ℓ , to which the spins are subjected within the sample itself (e.g. differences in g-value) which are only incipiently modulated by motions (e.g. an electron jumping between two different sites). In our study with $e_{\text{solv.}}$, the Carr-Purcell sequence (cf. Fig. 27) is consistent with the $T_M = 1.0\mu\text{sec}$. obtained from a simple ESE sequence. On this basis^{42b} we may conclude that the relaxation time τ_c for the motion leading to the observed T_M obeys $\tau_c \lesssim \tau$ and/or $(\Delta H_\ell)^{-1} \lesssim \tau$ (where $\tau = 0.5\mu\text{sec}$). (cf. ref. 42b Fig. 8Cb and Fig. 9).

B) Photo-Induced H Atoms

Recently we have performed some preliminary studies on the photo-generation of H atoms on surfaces. Our objective was to find good candidates

for study by our time-resolved methods. Initially produced H atoms in condensed media commonly show large spin polarizations (as much as 300 times greater than Boltzmann spin populations) and long T_1 's (10-20 μ sec.),⁴⁶ so their detection and study by time resolved ESE methods should be very promising. Furthermore, hydrogen is important in catalyzed reactions such as hydrogenation of CO, hydrogenation of olefins, and more recently in photogeneration of H_2 from H_2O .⁴⁷

In these preliminary experiments we used a conventional Varian E-12 ESR spectrometer filled with an optical bench, upon which is mounted a 150W Xenon Arc lamp and suitable holders for mounting lenses and Schott color glass filters. CW irradiation with the Xenon Arc lamp was used.

It was our plan, in these experiments, to utilize crushed vycor glass as the support surface, which gives good penetration of light.^{28,29} In the initial runs the vycor support alone was used. It was prepared in a quartz ESR tube by oxidation (500 torr of O_2 at 500°C. for 5 hours) followed by evacuation at 500°C. for 2 hours. After the sample tube was cooled, H_2 was added to the appropriate pressure (10 torr to 1 atm.) and the tube was sealed.

Hydrogen atoms give the distinct ESR spectrum of a doublet with a hyperfine splitting constant of approximately 500 gauss. When the system is irradiated in situ at low temperature (77K) the appearance of this doublet is almost immediate. The signal continues to gain intensity for the duration of the irradiation (1-2 hours). The signal persists and does not decay after the lamp is shut off. At temperatures above 77K (around 100K) the signal rapidly disappears indicating a small activation energy for diffusion of the hydrogen atoms on the vycor surface. The rate of radical formation is also dependent on the radiation wavelength with high frequency

light being the most efficient. The threshold is approximately 350nm (cf. Fig. 29).

The pressure of H_2 in the sample cell appears to have a surprising effect on the formation of H atoms. After an induction time (ca 30-40 minutes) the higher pressure (ca $\sim$ 200 torr) sample exhibits an increase in the rate of production of H atoms. (Perhaps adsorbed H_2 serves as an effective third body for H atom recombination, and at least at lower pressures the surface coverage of H_2 is reduced as H atoms form on the surface.)

At all pressures, the high field hyperfine line has a smaller width, hence a greater amplitude than the low field line. At high pressure (1 atm.) this difference is substantially greater than that at lower pressure (cf. Fig. 30), suggesting a pressure-induced line broadening mechanism that is dependent upon the nuclear hyperfine state. It is well-known that H atoms trapped in crystals or adsorbed on surfaces usually exhibit several different hf splittings (or a-values) and g-values corresponding to different sites, and they can be anisotropic.⁴⁸ It is known from general relaxation theory,⁴⁹ that such a difference in widths of the hf lines arises from a cross-term between the variation in the a and g values modulated by the motional process. Thus, for example, if the H atom resides at a single site, collisions with H_2 may induce oscillations about that site which modulate a and g.⁵⁰ Alternatively the collisions can induce translational motion of H atoms between different sites for which the a and g values differ.

Our results differ from most previous work⁴⁹ in the absence of any observed site splittings of the hfs, suggesting that the vycor support supplies rather uniform sites with, perhaps, only small site inhomogeneities. If we adopt the simple gas-like point of view^{51,52} that collisions of H with H_2 lead to more rapid averaging, then we would predict a decrease in

the hf-dependent line-broadening with increased pressure, which is contrary to our observations. Instead, it appears we need to adopt a modified point of view analogous to that previously used to explain gas-phase nuclear spin relaxation of atoms (as distinct from molecules).⁵¹ This point of view would include the above suggestion that the collision itself induces the important change in a and g (or their tensors) by momentarily modifying the H atom binding to the surface. In that case one predicts an increased relaxation rate with increased pressure (i.e. increased collision rate) in accordance with our observations. Further experiments are required before we can have confidence in this preliminary interpretation.

H₂/MoS₂/Vycor

In another set of experiments we interspersed polycrystalline flakes of MoS₂ (as supplied to us by Professor M.J. Sienko) into the vycor powder. MoS₂, which forms layer crystals with a band gap of 1.4eV, has been used as a semiconductor electrode for solar photoelectrolysis purposes.^{22,54} The initial results are similar to those with H₂/Pure Vycor (cf. Fig. 29). However after a short time (ca. 20 minutes) the signal levels off to a constant value. When the light is shut off, then the existing signal remains. This could indicate that the photo-activated MoS₂ is catalyzing the recombination reaction: $2H\cdot \xrightarrow[\text{MoS}_2]{h\nu} H_2$. (Kazansky⁵³ has postulated that the photoreduction of Mo⁶⁺/SiO₂ leads to H $\cdot$ formation which would be nearly the reverse process.)

H₂O/Vycor

When 15 torr of H₂O is placed over the vycor surface and the system is irradiated in the same manner, the formation of H $\cdot$ occurs more rapidly than from H₂. When the system was warmed until the ESR signal disappeared, and then reirradiated the signal appears even more rapidly (cf. Fig. 29).

Furthermore an additional ESR signal: a broad singlet close to $g = 2$ was observed. [It might possibly be related to a signal we previously observed for heat-treated MoS_2 ($g = 2.002$, $DH = 1.86\text{G}$).⁵⁴]

Further work is needed to improve H atom production techniques so that we can study the kinetics of photo-induced formation and reactions of $\text{H}\cdot$ by our time-resolved ESE techniques.

Table 1. SSERS Data for Nitroxides on Silver

<u>Nitroxide</u>	<u>T_{ads}</u> <u>°C</u>	<u>D_e</u> <u>kL</u>	<u>P_{t,e}</u> <u>P_{t,0}</u>	<u>D_f</u> <u>kL</u>	<u>P_{t,f}</u> <u>P_{t,0}</u>	<u>ΔD</u> <u>kL</u>
DTBN	-150	2.5	0.12	30	0.07	27.5
DTBN	-116	1.3	0.26	31	~ 0.18	29.3
TEMPONE	-125	22	0.09	58	~ 0.07	36.1
TEMPONE	-55	112	0.33	149	< 0.22	37.0
TEMPOL	-120	47	0.20	76	0.04	28.7

	<u>T_{ads}</u>	<u>T_{em}</u>	<u>T_{e1}</u>	<u>T_{e2}</u>	<u>T_{d1}</u>	<u>T_{df}</u>
DTBN	-150	-81	-80	>-66	--a	--a
DTBN	-116	--b	--b	>-61	--a	--a
TEMPONE	-125	-51	--b	-18	-95	-20
TEMPONE	-55	-55	--b	-22	--a	--a
TEMPOL	-120	~ -63	~ -53	-24	-106	-98

T_{ads} Adsorption Temp.

$$\Delta D = D_f - D_e$$

P_{t,0} P_t at 0 dosage

T_{em} Temperature of Max. ESR signal in °C.

D_e Dosage where ESR appears

T_{e1} Temperature at which ESR starts to decrease

P_{t,e} P_t where ESR first appears

T_{e2} Temperature at which ESR signal disappears

D_f Final dosage

T_{d1} Peak in pressure

P_{t,f} P_t at final dosage

T_{df} Peak in pressure

--^a not measured

--^b none observed

Table 2. SSERS Data for Nitroxides on Copper at -120°C

	$\frac{D_e}{kL}$	$\frac{P_{t,e}}{P_{t,0}}$	$\frac{D_f}{kL}$	$\frac{P_{t,f}}{P_{t,0}}$	$\frac{\Delta D}{kL}$		
DTBN	3.0	0.074	46	0.045	43		
TEMPONE	2.6	0.11	31.5	0.034	29		
	T_{em}	T_{e1}	T_{e2}	T_{d1}	T_{d2}	T_{d3}	T_{d4}
DTBN	-98	--b	-57	-81	-65		
TEMPONE	-53	-25	2	-101	-80	-55	-4

key: see Table 1

Table 3. SSERS Data for Nitroxides on Oxides at -120°C.

<u>System</u>	<u>T_{ox}</u>	<u>D_{ox}</u>	$\frac{P_{t,ox}}{P_{t,c}}$	<u>Nitroxide</u>	<u>D_e</u>
	<u>°C</u>	<u>L</u>	<u>mW</u>		<u>kL</u>
1. Ag/O ₂	117	--	--	DTBN	1.2
2. Ag/O ₂ +H ₂ O	15	10 ¹¹	0.85	DTBN	~ 2.8
3. Cu/O ₂	33	10 ⁶	0.69	TEMPONE	< 2
4. Cu/O ₂ +H ₂ O	43	10 ¹²	0.26	TEMPONE	24.8
5. Cu/O ₂ +H ₂ O	RT	10 ¹⁴	0.18	DTBN	3.3

$\frac{P_{t,e}}{P_{t,0}}$	$\frac{D_f}{kL}$	$\frac{P_{t,f}}{P_{t,0}}$	<u>T_{em}</u>	<u>T_{e1}</u>	<u>T_{e2}</u>	<u>ΔD</u>
			<u>°C</u>	<u>°C</u>	<u>°C</u>	<u>kL</u>
1. 0.21	18.2	0.075	-76	--b	-55	17
2. 0.30	22	0.17	-80	--b	-58	19
3. --a	12.3	--a	-110, -73	-35	14	10
4. 0.25	460	0.086	-90	--b	-26	435
5. 0.31	8.0	0.32	-94	-82	-70	4.7

T_{ox} Temperature of oxidation

D_{ox} Dosage of oxygen

P_{t,c} P_t of clean metal

P_{t,ox} P_t after oxygen

See also Table 1

Table 4. SSERS Data for TEMPONE on Silver Pretreated with Analog

$\frac{D_{fA}}{kL}$	$\frac{P_{t,fa}}{P_{t,c}}$	$\frac{D_{e,T}}{kL}$	$\frac{P_{t,e}}{P_{t,c}}$	$\frac{D_{fT}}{kL}$	$\frac{P_{t,f}}{P_{t,c}}$	ΔD $\frac{kL}{kL}$
0	1.0	22	.093	58	0.69	36
1.4	0.25	4.7	0.21	61	0.19	56
8.3	0.093	0	0.093	35	--a	35
14.5	0.082	0	0.082	22	--a	22

$\frac{D_{fA}}{kL}$	T_{em} °C	T_{em2}	T_{e1}	T_{e2}	T_{d1}	T_{d2}	T_{df}
0	-51		-18	--b	-95	--b	-20
1.4	-39		-20	19	--a	--a	--a
8.3	-93	17	-42	60	-84	14	>52
14.5	-105	25	--a	61	-86	25	61

$P_{t,c}$ P_t of clean metal

D_{fA} Dosage of Analog

$P_{t,fa}$ P_t after depositing Analog

See also Table 1

D_{eT} Dosage of TEMPONE when ESR appears.

D_{fT} Final Dosage of TEMPONE.

$$\Delta D = D_{fT} - D_{eT}$$

Table 5. Estimated Parameters from SSERS Data^{a,b}

System	D_e kL	σ_a 10^{-3} L ⁻¹	θ_a^{-1}	σ_e 10^{-3} L ⁻¹	θ_e^{-1}	R^c	R'^d
Ag/DTBN -150°C	2.5	1.1	2.8	1.2	5.2	.05	0.12
Ag/DTBN -116°C	1.3	1.6	2.1	1.6	2.1	0.11	.265
Ag/TEMPONE -125°C	22	0.23	5.1	1.3	47.	.025	.093
Ag/TEMPONE -55°C	112	0.55	61.	0.37	41.	.14	.329
Ag/TEMPOL	47	0.42	20.	0.15	5.9	.17	.204
Cu/DTBN	3.0	0.43	1.3	1.0	10.	.03	.074
Cu/TEMPONE	2.6	1.5	3.9	1.9	7.3	.08	.110
Ag/O ₂ /DTBN	1.2	0.90	1.1	2.3	4.4	0.14	.206
Ag/O ₂ +H ₂ O/DTBN	2.8	~ 0	~ 0	1.0	2.1	0.16	.298
Cu/O ₂ / TEMPONE	1.0	5.8	5.3	4.7	6.0	-- e	--e
Cu/O ₂ +H ₂ O/TEMPONE	24.8	0.47	12.	0.47	12.	0.18	.250
Cu/O ₂ +H ₂ O/DTBN	3.3	0.42	14.	4.2	14	0	.314
Ag/1.4kL Analog/TEMPONE	4.7	1.6	7.4	1.2	3.4	.364	.212
Ag/8.0kL Analog/TEMPONE	0	1.1	0	0.38	0	--e	.093
Ag/14.kL Analog/TEMPONE	0	0.41	0	0.72	0	--e	.080

a) All adsorptions performed at -120°C unless otherwise noted.

b) θ_a , θ_e are sticking coefficients as described in text.

c) $R = (P_{t,e} - P_{t,f}) / (P_{t,0} - P_{t,f})$

d) $R' = P_{t,e} / P_{t,0}$

e) Not measured

Table 6. Observed and Calculated g-Tensor Components for $\text{O}_2^-/\text{Ti-Vycor}$

<u>Geometry</u>		<u>g_{xx}</u>	<u>g_{yy}</u>	<u>g_{zz}</u>
Side-On	$\theta=0^\circ$	2.0718	2.0028	2.0130
Bent	$\theta=9^\circ$	2.0925	2.0028	2.0149
	$\theta=18^\circ$	2.1519	2.0031	2.0274
	$\theta=21^\circ$	2.4158	2.0035	2.1229

Side-On ^a	-12.11	2.0718	2.0028	2.0130
$H_{ii}(\text{Ti}, 3d) \text{ (eV)};$	-13.11	2.0604	2.0028	2.0129
	-14.11	2.0517	2.0028	2.0127
	-15.11	2.0452	2.0028	2.0126

Side-On ^b	1.83	2.0718	2.0028	2.0130
$\text{Ti-O } (\text{\AA});$	1.61	2.0595	2.0032	2.0122
	1.46	2.0489	2.0038	2.0109
	1.29	2.0387	2.0042	2.0092

Observed		2.0268	2.0027	2.0092

^a $\text{Ti-O}=1.83 \text{ \AA}$

^b $H_{ii}(\text{Ti}, 3d) = -12.11 \text{ eV}$

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Figure Captions

1. Nitroxides Used, Their Structures, Descriptive Names and Brief Names.
2. CREMSEE P_t vs. Dosage in Langmuir ($= 10^{-6}$ torr. sec): Ag/DTBN, TEMPONE, and TEMPOL at -120°C . Values are normalized so that the low (zero) dosage values coincide.
3. ESR Signal vs. Dosage: Ag/DTBN, TEMPONE, and TEMPOL at -120°C . Data are scaled such that nominal signal of 100 corresponds to approximately 2.1×10^{15} spins per cm^2 or 12 layers.
4. ESR Signal and Pressure vs. Temperature: Ag/TEMPONE deposited at -125°C . ESR Signal of 200 corresponds to approximately 4.1×10^{15} spins per cm^2 or 25 layers.
5. CREMSEE P_t vs. Dosage in Langmuir: $\text{Cu}/\text{O}_2 + \text{H}_2\text{O}/\text{DTBN}$ at -120°C .
6. ESR Signal vs. Dosage: $\text{Cu}/\text{O}_2 + \text{H}_2\text{O}/\text{DTBN}$ at -120°C . ESR Signal of 1000 corresponds to approximately 3×10^{15} spins per cm^2 or 18 layers.
7. ESR Signal vs. Temperature: $\text{Cu}/\text{O}_2 + \text{H}_2\text{O}/\text{DTBN}$ deposited at -120°C .
8. CREMSEE P_t vs. Dosage: Ag/Analog/TEMPONE at -120°C . Arrows show the break between Analog and TEMPONE adsorption.
9. ESR Signal vs. Dosage: Ag/Analog/TEMPONE at -120°C . ESR Signal of 400 for the 1.4kL curve corresponds to approximately 3.8×10^{15} spins per cm^2 or 23 layers. For the other two curves, a height of 400 corresponds to approximately 1.2×10^{15} spins per cm^2 or 7 layers.
10. ESR Signal and Pressure vs. Temperature: Ag/Analog/TEMPONE deposited at -120°C . for 8.3kL Analog. ESR Signal of 800 corresponds to approximately 2.4×10^{15} spins per cm^2 or 14 layers.
11. ESR Derivative Line Width vs. ESR Signal and Temperature for 1.4kL Analog Pretreatment. Adsorption at -120°C . (a) Line width vs. ESR signal (cf. Fig. 9 caption for calibration); (b) Line width vs. temperature.

12. Photo-CREMSEE apparatus.
13. Adaptation of UHV-ESR microwave cavity and bellows for Photo-CREMSEE.
14. The factored photo-CREMSEE Signal Height raised to the half power vs. photon energy in eV for an evaporated Ag surface: $\phi = 4.25\text{eV}$.
15. Quartz Tube arrangement for UHV evaporation of metals with low evaporation temperatures.
16. Experimental ESR Spectra vs. theoretical simulations for NO_2/NaY for various temperatures. The theoretical simulations are based on a Brownian rotational diffusion model for values of $R_{\parallel}$ and $R_{\perp}$ as shown.
17. Plot of $\tau_{R_{\parallel}}$ and $\tau_{R_{\perp}}$ vs. $1/T$ for NO_2/NaY based upon Brownian rotational diffusion model.
18. Model deformation coordinate of O_2 in $\text{Ti}(\text{O}_5)\text{O}_2^{7-}$. The out-of-plane displacement of Ti, r , and the angles $\alpha, \beta, (\text{or } \theta)$ are varied simultaneously from the side-on to end-on geometries. Fixed are $\text{O}^1\text{-O}^2 = 1.3\text{\AA}$, $\text{Ti-O}_{\text{ax}} = 1.944\text{\AA}$, $\text{Ti-O}_{\text{eg}} = 1.944\text{\AA}$, and $\text{Ti-O}^1 = 1.83\text{\AA}$.
19. Potential energy curve calculated for model deformation coordinate which is specified at bottom.
20. Interaction diagrams for O_2 and $\text{Ti}(\text{O}_5)^{7-}$ fragment of the side-on geometry (to the right of the dashed line) and the end-on geometry (to the left). At the middle, the $\text{Ti}(\text{O}_5)^{7-}$ fragment for either of the two geometries carries four low-lying Ti d orbitals. Symmetry assignment of orbitals is based on the standard co-ordinate system, which retains the x-axis where the four-fold axis of $\text{Ti}(\text{O}_5)^{7-}$ used to be, though our choice of co-ordinates differs from it.
21. Variation of spin distribution at O_2^- calculated as a function of deformation.
22. Experimental arrangement for Laser-Induced Time-Resolved Electron-Spin-Echo Spectroscopy.

23. Transient photo-electron in Rb/THF. Intensity of the initially polarized ESR signal vs. exciting wavelength, λ . $[\text{Rb}^-] = 8 \times 10^{-6} \text{ M}$.
24. T_1 vs. $1/T$ for the polarized photo-electron in Rb/THF.
25. T_2 vs. $1/T$ for the polarized photo-electron in Rb/THF.
26. Both photos are ESE for an irradiated quartz sample; they show the effect of the Carr-Purcell sequence on the measured T_2 . Upper photo: Normal 90° - 180° echoes. The time τ is stepped and a sequence of echoes is obtained which are superimposed on the photo. Each division of x-axis equals $1.5\mu\text{sec}$. Lower photo: Carr-Purcell sequence with alternating phase. Each division of x-axis equals $20\mu\text{sec}$. and $2\tau = 1\mu\text{sec}$.
27. A Carr-Purcell sequence with alternating phase for the polarized photo-electron at -87°C . and $[\text{Rb}^-] = 5 \times 10^{-5} \text{ M}$. Each division of x-axis equals $0.5\mu\text{sec}$. and $2\tau = 0.9\mu\text{sec}$. The measured T_2 is consistent with $1.0\mu\text{sec}$. measured by 90° - 180° sequences.
28. Diagram of multi-pulse sequencer. An HP generator synchronizes the pulse counter, the delay-generators and the Dye-laser pumped by the excimer laser. After being triggered, the BNC delay generator No. 3 causes sequential triggering of the BNC delay generators No. 4 and No. 5. The pulse from No. 5 is fed back to the pulse counter which generates a pulse that triggers No. 4. This cycle continues until the desired number of times of triggering BNC (No. 4) is achieved. This delay generator (No. 4) is one that triggers the 180° pulse generator. The required delay between the laser and the first 90° is controlled by BNC No. 3.
29. Production of H Atoms on Vycor and MoS_2 /Vycor surfaces by light irradiation of adsorbed H_2 and H_2O at different pressures. Rate of production of H Atoms with exciting wavelength λ also shown.

30. Ratio of high field derivative amplitude to low field derivative amplitude for $H\cdot$ produced by light irradiation on Vycor surface as a function of H_2 pressure.

di-*t*-butylnitroxide

DTBN

4-hydroxy-2,2,6,6-tetramethyl-
piperidine-1-oxyl

TEMPOL

4-oxo-2,2,6,6-tetramethyl-piperidine-
1-oxyl

TEMPONE

4-oxo-2,2,6,6-tetramethyl-piperidine

Analog

CREMSEE threshold vs dosage
Ag/nitroxide -120°C

FIG. 2

Fig. 3

ESR signal and pressure vs temperature
Ag/TEMPONE -125°C

FIG 4

CREMSEE threshold vs dosage
Cu/O₂+H₂O/DTBN -120°C

FIG. 5

FIG. 6

FIG. 7

FIG. 8

Fig. 9

Fig 10

a)	Xenon Lamp	f)	Lens 3
b)	IR Filter	g)	UV Grade Sapphire Window
c)	Lens 1	h)	UHV-ESR Cavity
d)	Monochromator	i)	Magnet
e)	Lens 2	j)	Conical Mirror
		k)	Bellows

- (A) UV grade sapphire window
- (B) UHV-ESR Cavity
- (C) $\approx 140^\circ$ conical mirror
- (D) Bellows assembly
- (E) Filament

Clean Ag Surface

Fig 15

NO₂/NaY
 $\nu = 9.273 \text{ GHz}$

—Exp.
---Cal. (B.D.)

FIG. 16

FIG. 17

Fig 18

FIG. 19

Fig. 20

Fig. 21

FIG. 23

FIG. 24

FIG. 25

Fig. 26

Fig. 27

MULTI-PULSE GENERATOR

Production of H Atoms

Fig 29