

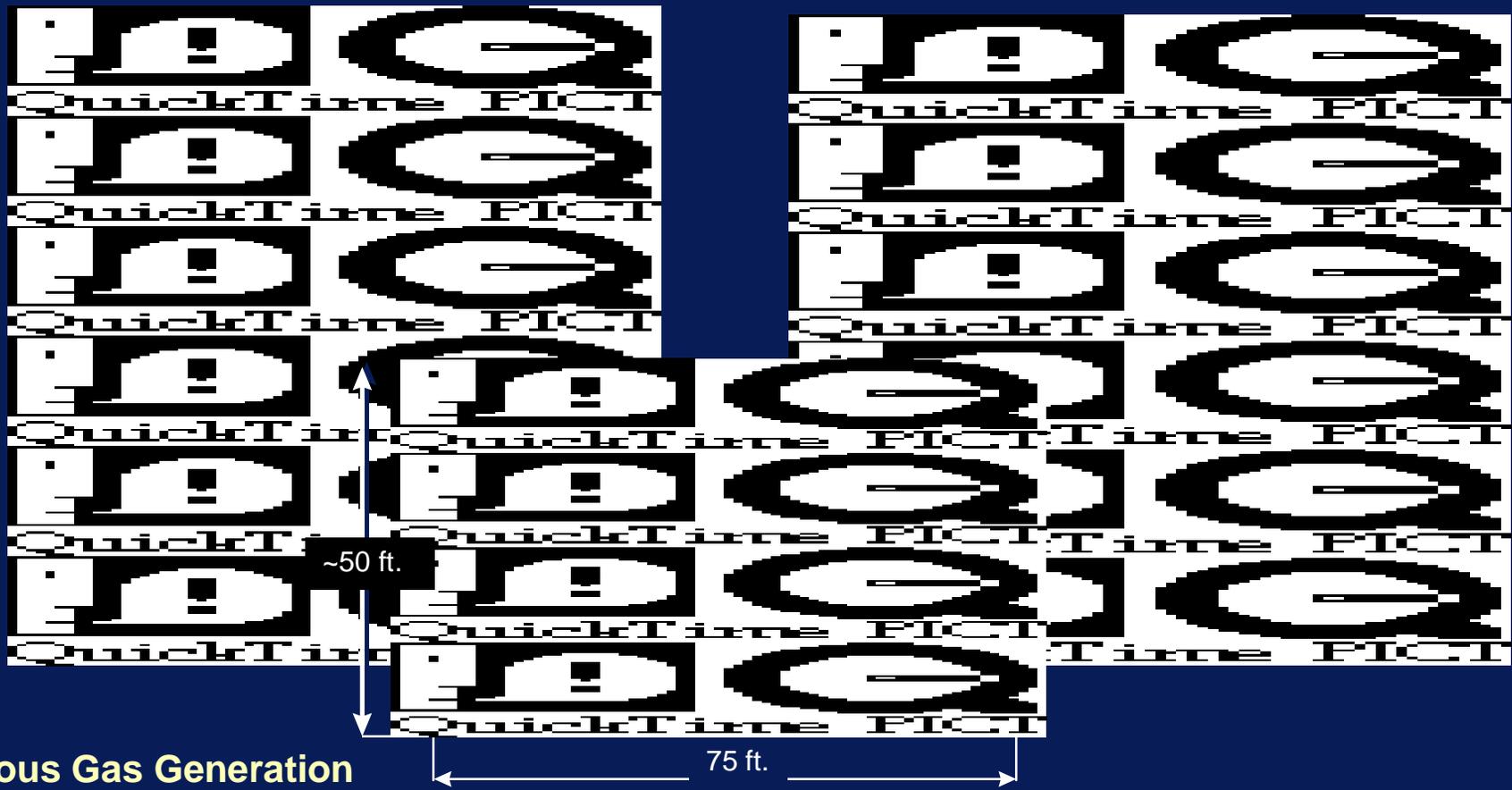
# INTERFACIAL RADIOLYSIS EFFECTS IN TANK WASTE SPECIATION

*“Interfacial Radiolysis Effects in Tank Waste Speciation” (PNNL), “The NO<sub>x</sub> System in Nuclear Waste” (ANL)*

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## Hazardous Gas Generation

Mixed (radioactive/chemical) wastes in DOE underground storage tanks are complex mixtures of sludges, salt cakes, and supernatant liquids, constantly bombarded by energetic particles produced from the radioactive decay of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ .

Chemistry initiated by radiolysis of the waste leads to the production of toxic, flammable, and potentially explosive gases, such as  $\text{H}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$ .

Solution-phase radiolysis cannot account adequately for gas generation.

Interfacial radiolytic processes in multi-phase, heterogeneous systems are not understood, yet must play an important role.

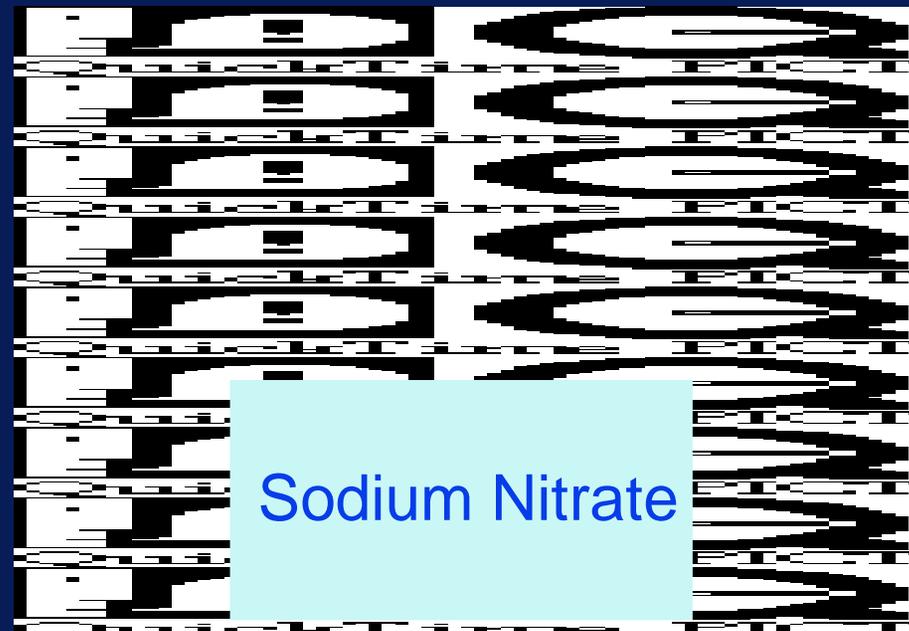
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## Primary Radiation Promotes Radiolysis via Creation of Secondary Electrons



High energy primary electrons react with matter to create thousands of low energy secondary electrons.

Secondary electrons react with solid and liquid phases to create electron-hole pairs and radicals. Reactive ions and radicals undergo redox and free radical reactions with organics to promote decomposition.

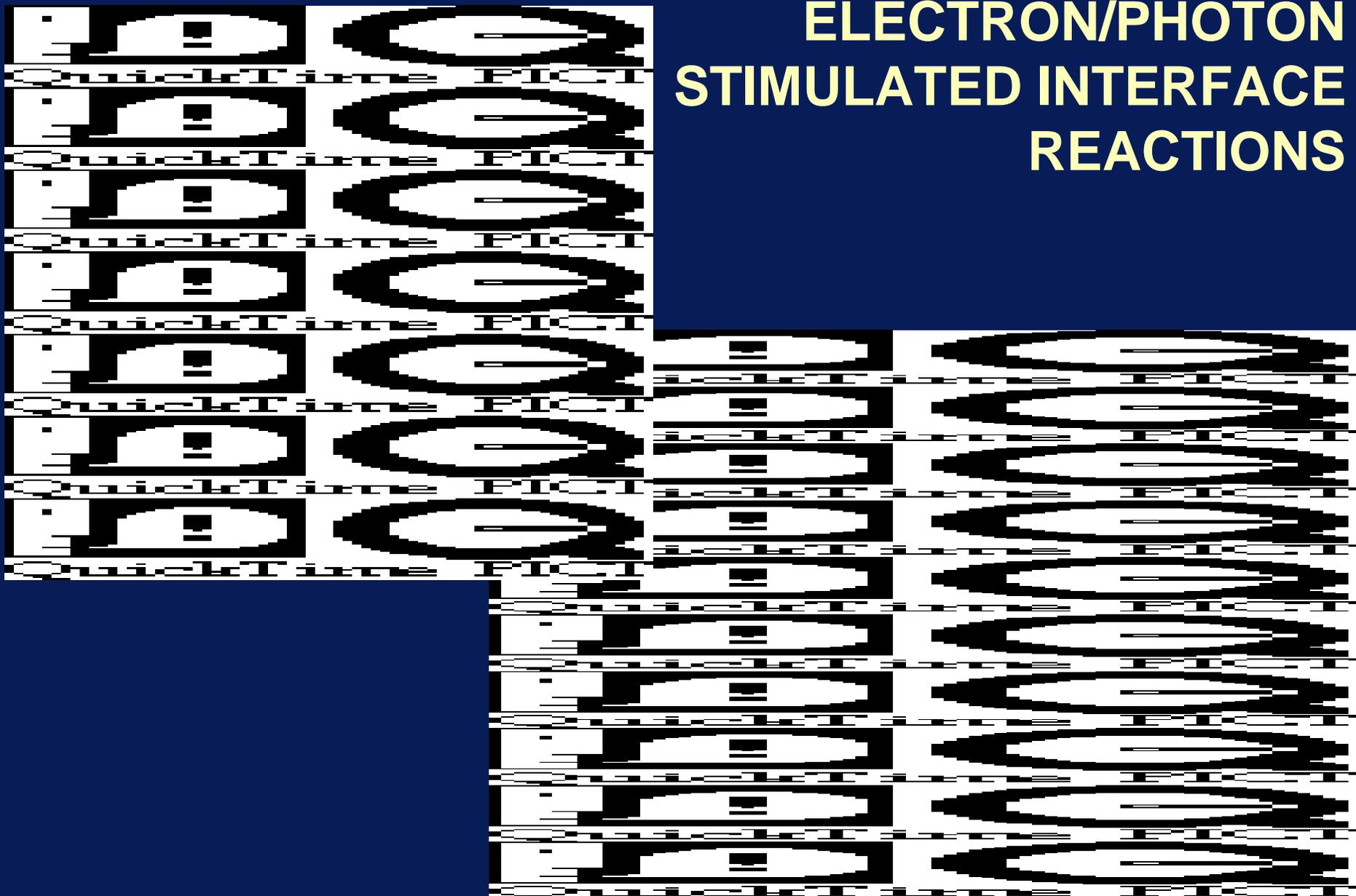


Sodium Nitrate

**Sodium nitrate ( $\text{NaNO}_3$ ) is a major solid component of the radioactive/chemical mixed wastes, and is present both as salt cake and in colloidal suspension. Experiments to date have shown that exposure of  $\text{NaNO}_3$  single crystals to low-energy (5 - 100 eV) electrons results in highly efficient destruction of the  $\text{NO}_3^-$  and the release of ionic and neutral species, predominantly the persistent radical NO**

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# ULTRAHIGH VACUUM SYSTEM FOR ELECTRON/PHOTON STIMULATED INTERFACE REACTIONS



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## EXPERIMENTAL DETAILS

Ultrahigh Vacuum (UHV): Background pressure  $10^{-10}$  Torr.

Clean or adsorbate covered (1 - 10 ML) surfaces

Yields of desorbing ions and neutrals measured **as a function of electron-energy and dose.**

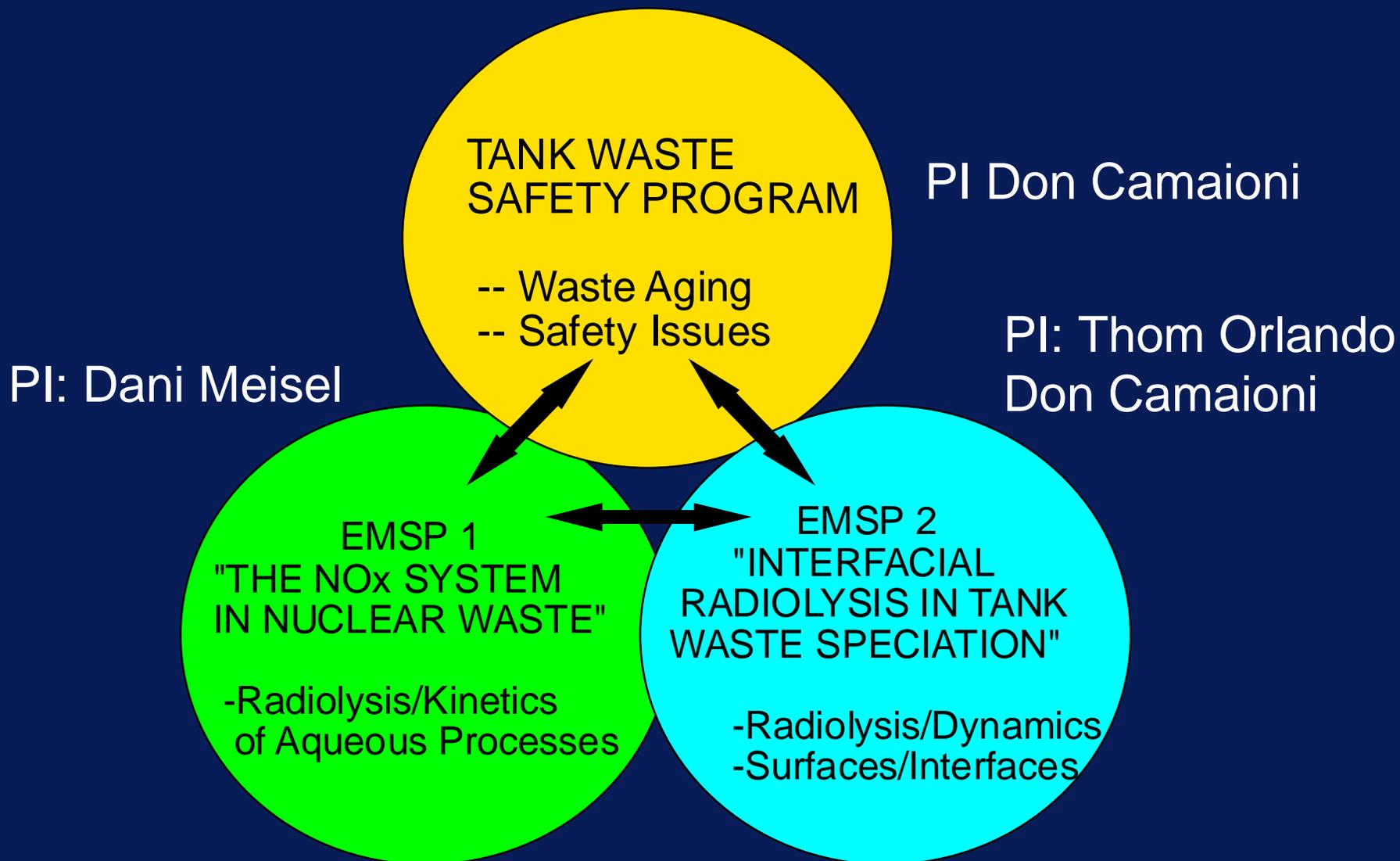
REMPI/TOF techniques used for neutral detection (pulsed technique which measures velocity distribution).

Detection sensitivities of  $10^6$  molecules/cm<sup>3</sup> quantum-state.

Post irradiation thermal desorption to measure reactions at Interfaces.

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# Joint Efforts in Understanding Tank Waste Chemistry



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# PROGRAM IMPACTS

Our co-ordinated effort has incorporated fundamental data on solution and interfacial radiolysis into Hanford Tank Waste Safety Programs.

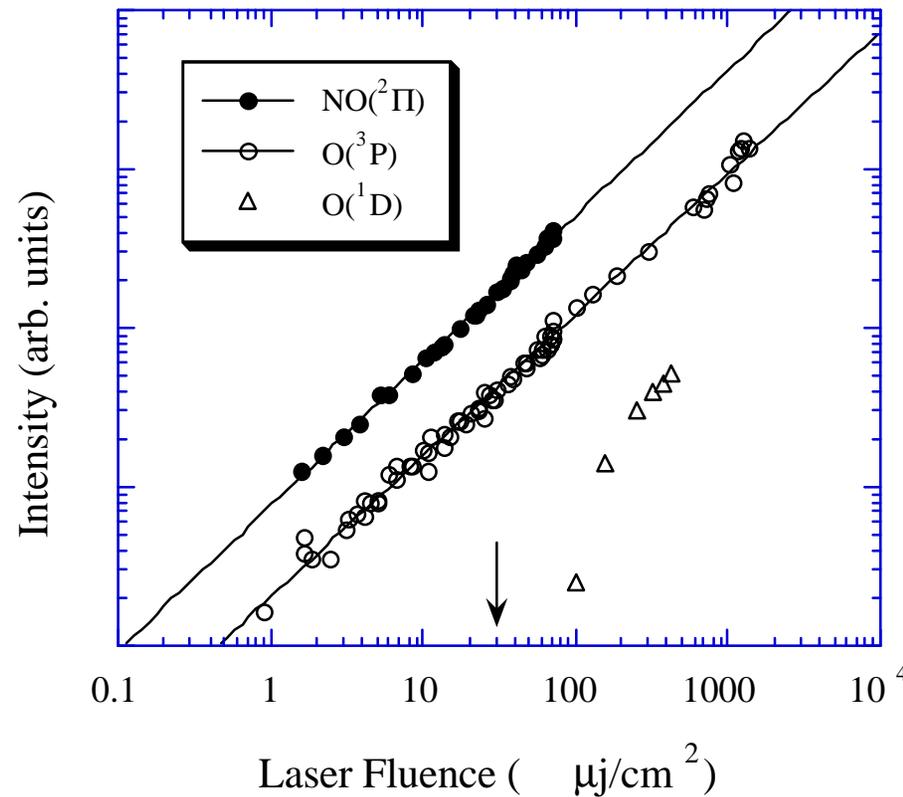
Information has been used in waste aging studies to model organic degradation. This contributes to resolution of safety Issues regarding safe interim storage of Hanford organic wastes.

These combined programs demonstrate that radiolytic processes degrade the organic complexants to products with lower energy content.

**Our work demonstrates that radiolysis of the solids is important and contributes to organic aging and the degradation of flammable and toxic gases, such as  $H_2$ ,  $NH_3$ ,  $N_2O$  and organic vapors.**

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# 6.4 eV PHOTON-STIMULATED DESORPTION (PSD) OF SODIUM NITRATE SINGLE CRYSTALS: ----FLUENCE DEPENDENCE ----



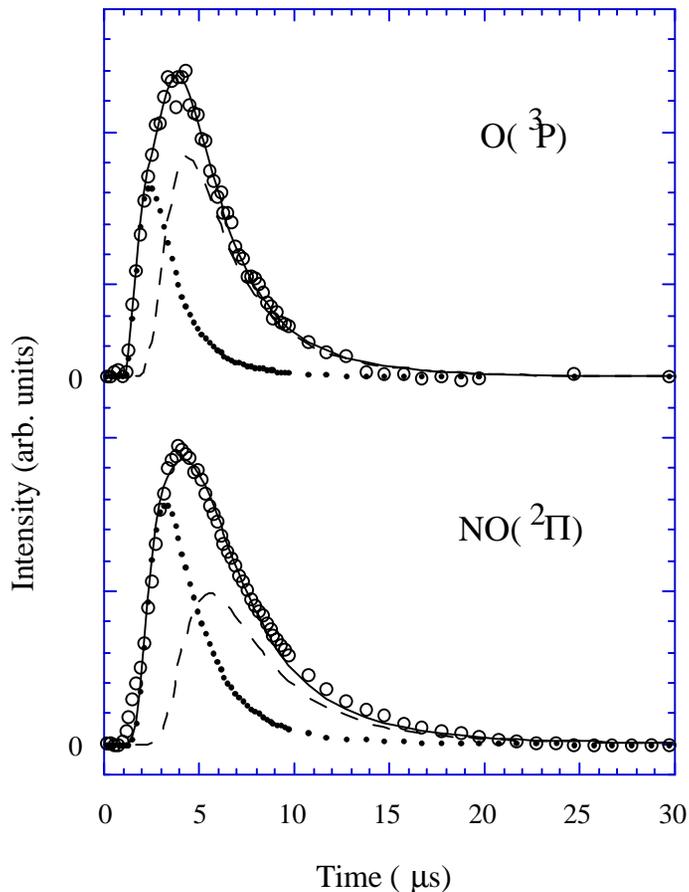
1-Photon Fluence  
Dependence

No induction time  
for desorption

NOT DEFECT  
mediated

EXCITON mediated

## 6.4 eV PSD OF NaNO<sub>3</sub> SINGLE CRYSTALS: NO (<sup>2</sup>P) AND O(<sup>3</sup>P) TOF DISTRIBUTIONS



K. Knutsen and T. M. Orlando  
Phys. Rev. B55, 13246 (1997).

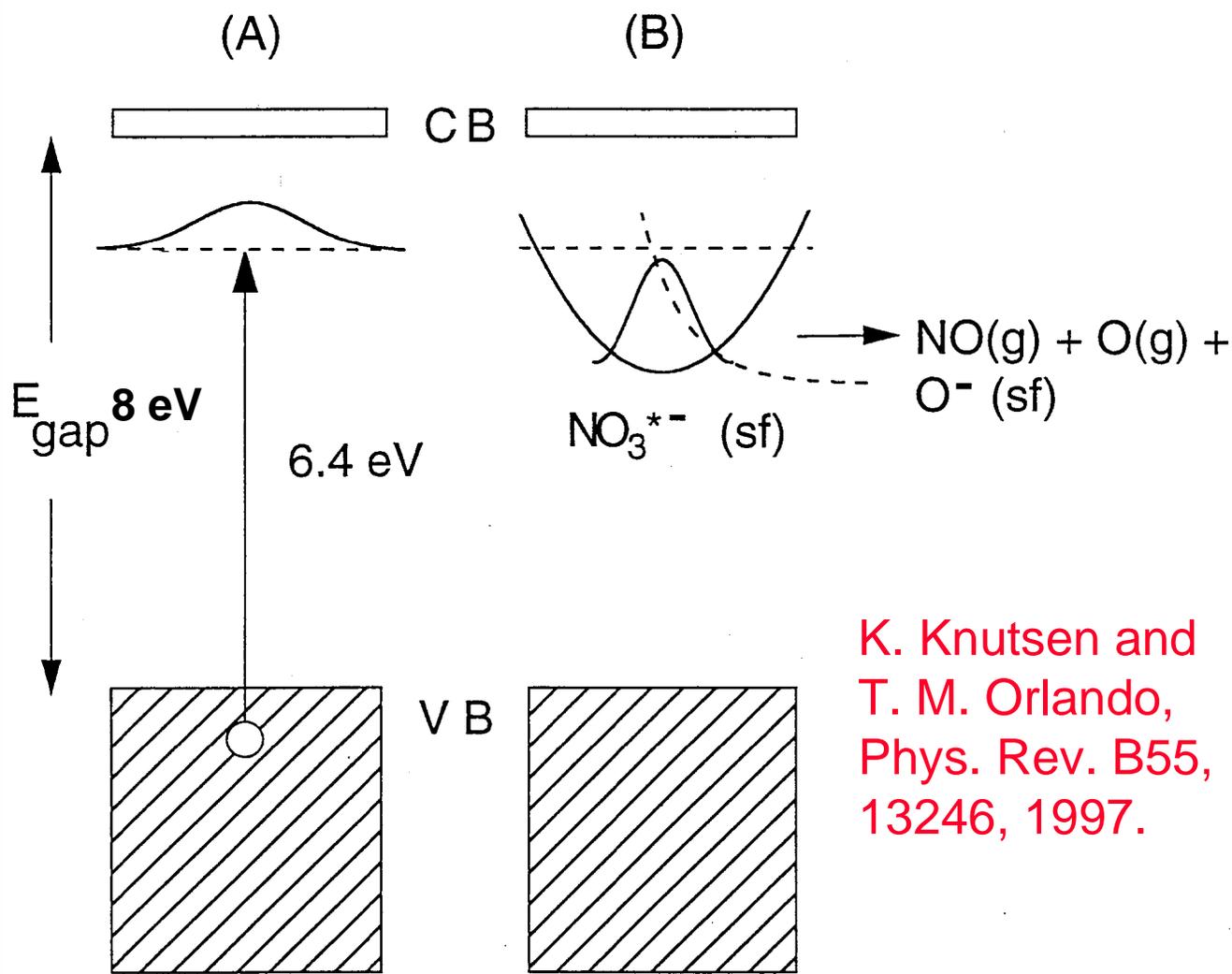
Velocity distributions  
are non-thermal.

Approximately 600 angstrom  
penetration depth.

Dissociation cross-section  
is high --  $10^{-16} \text{ cm}^2$

Some excitons must move  
to the surface.

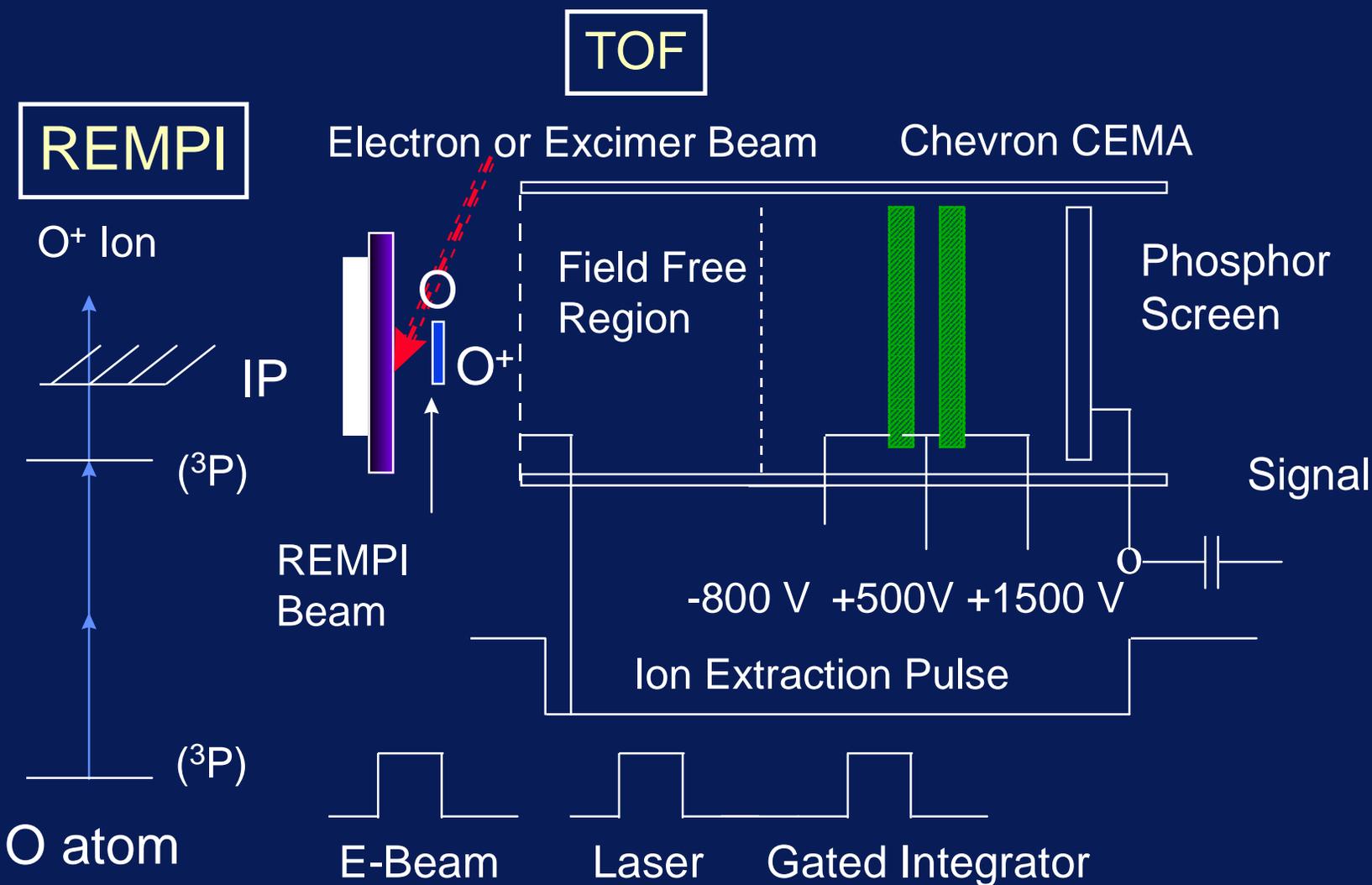
# SCHEMATIC OF THE PHOTON- AND ELECTRON-STIMULATED DESORPTION OF NO AND O FROM NaNO<sub>3</sub> CRYSTALS



(A) Exciton production via excitation of the  $\text{NO}_3^- \pi^* \leftarrow \pi$  band  
 (B) Surface exciton ( $\text{NO}_3^{*-}$ ) trapping via stabilization with respect to the bulk. The surface exciton decays to form  $\text{NO}(\text{g}) + \text{O}(\text{g}) + \text{O}^- (\text{sf})$

K. Knutsen and  
 T. M. Orlando,  
 Phys. Rev. B55,  
 13246, 1997.

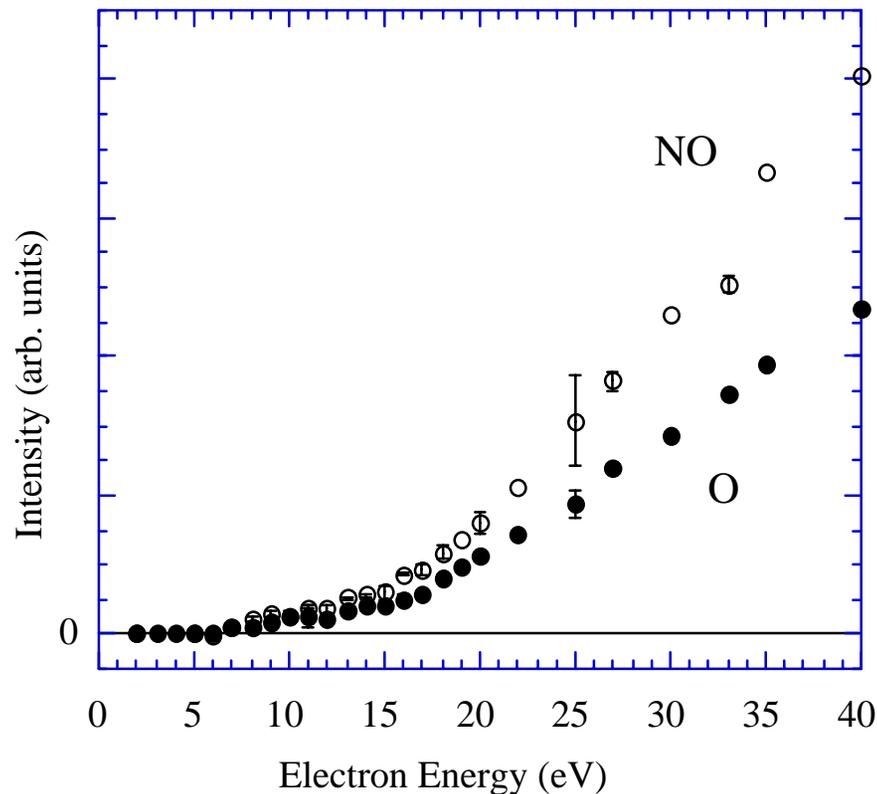
# RESONANCE ENHANCED MULTIPHOTON IONIZATION (REMPI) AND TIME-OF-FLIGHT (TOF) TECHNIQUES



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# ELECTRON STIMULATED DESORPTION (ESD) YIELDS OF NO(<sup>2</sup>Π) AND O(<sup>3</sup>P) AS A FUNCTION OF ELECTRON ENERGY

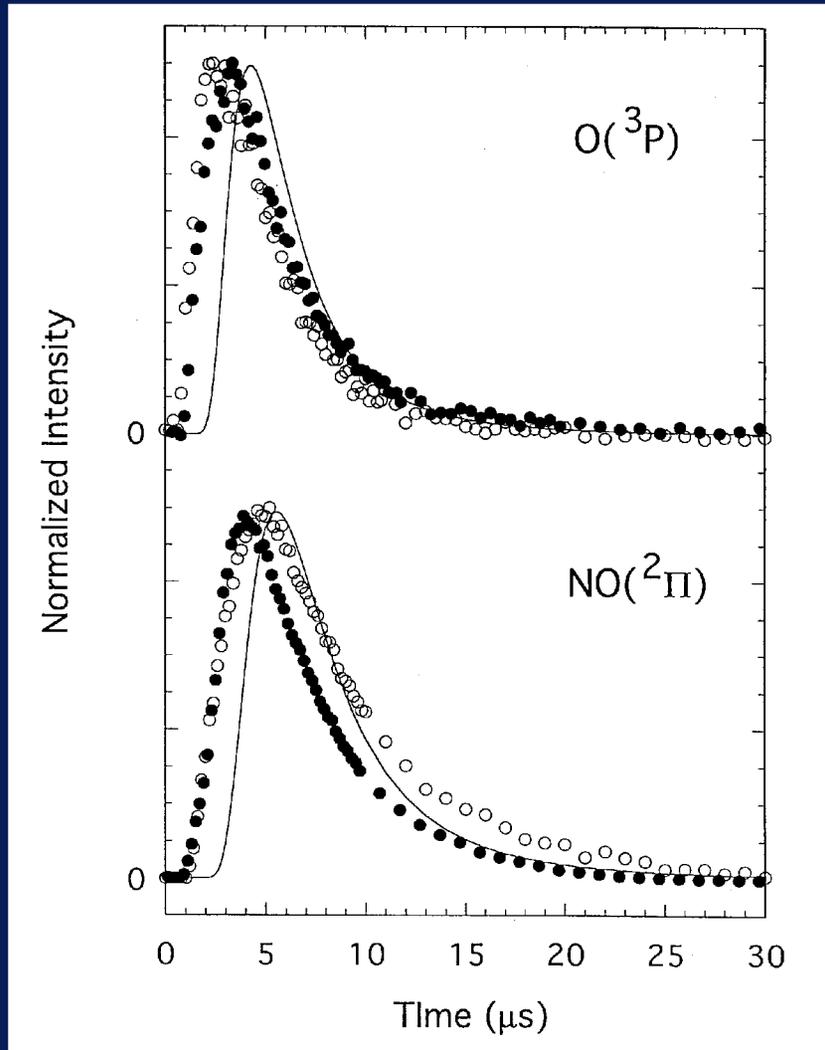
O, NO threshold data



Arrows mark the 6.4 eV photon energy, the band gap ( $E_g$ ), and twice the band-gap energy ( $2E_g$ ).

Note multiple electronic excitation channels near 25 eV!

# VELOCITY DISTRIBUTIONS FOR O ( $^3P$ ) AND NO ( $^2\Pi$ ) FROM BOTH 100 eV ESD (OPEN CIRCLES) AND 6.4 eV PSD (FILLED CIRCLES)

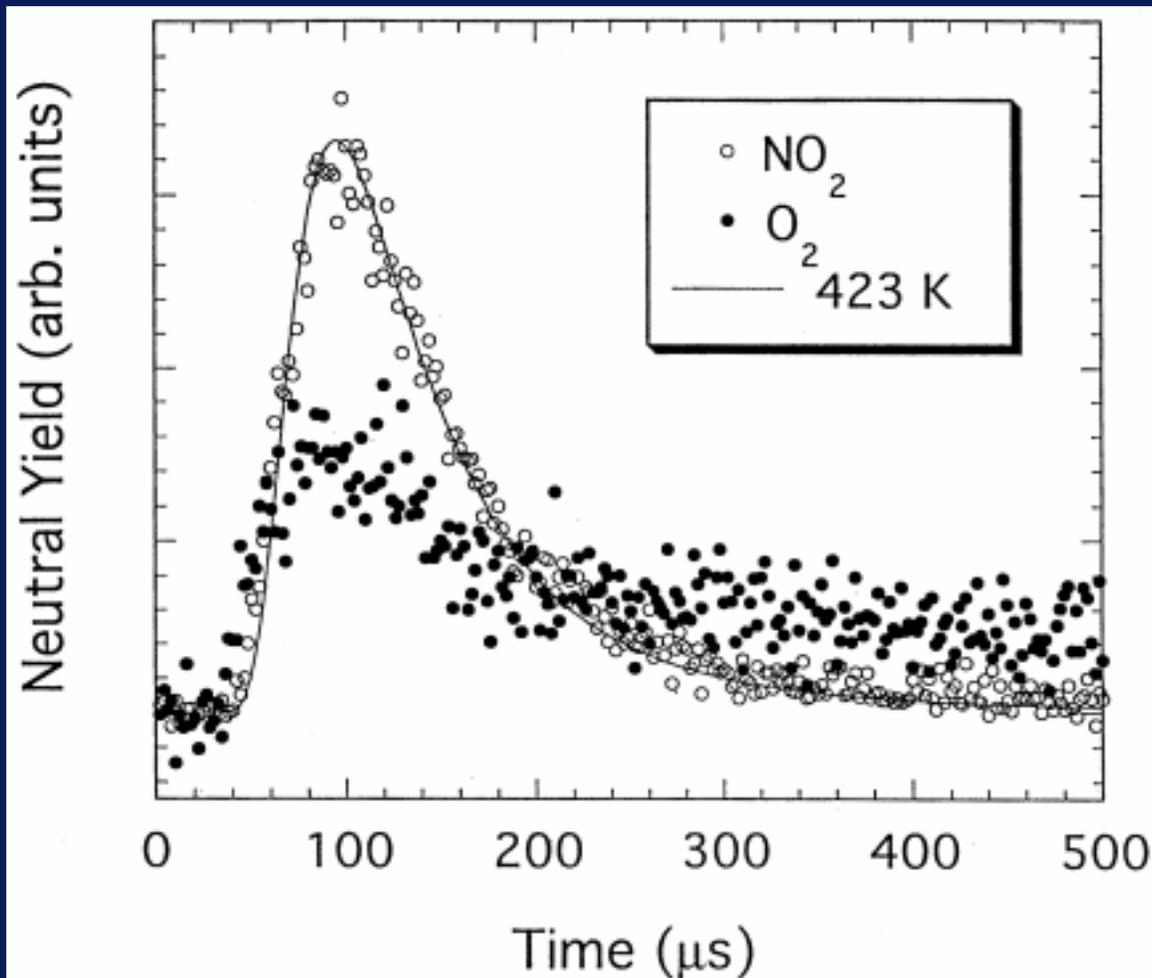


The solid lines are the calculated 423K (surface temperature) Maxwell - Boltzmann distributions.

The O ( $^3P$ ) and NO ( $^2\Pi$ ) velocity distributions from ESD and PSD are **similar to each other, and have non-thermal components.**

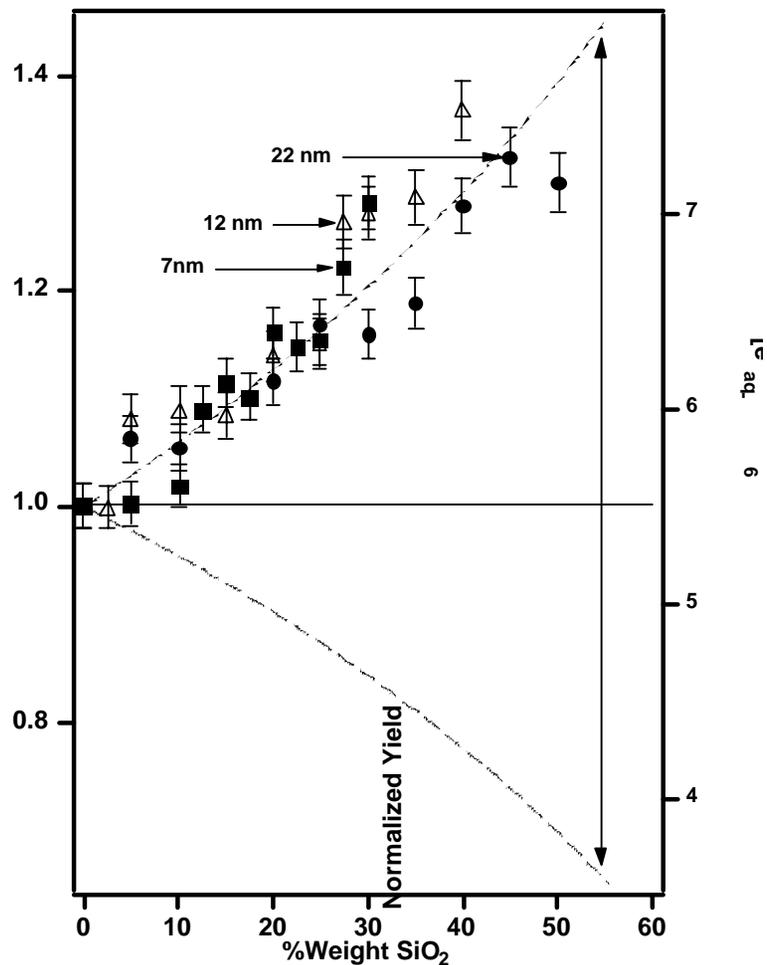
K. Knutsen and T.M. Orlando, Applied Surface Science 127-129 (1998) 1-6.

## 6.4 eV PHOTON STIMULATED PRODUCTION AND DESORPTION OF NO<sub>2</sub> AND O<sub>2</sub> FROM NaNO<sub>3</sub> SINGLE CRYSTALS



The NO<sub>2</sub> (open circles) and O<sub>2</sub> (filled circles) yields as a function of flight time to the QMS. The solid line is a 423 K (surface temperature) Maxwell - Boltzmann distribution.

# OBSERVATIONS OF SOLVATED ELECTRON PRODUCTION FROM HEAVILY LOADED SiO<sub>2</sub> SUSPENSIONS.



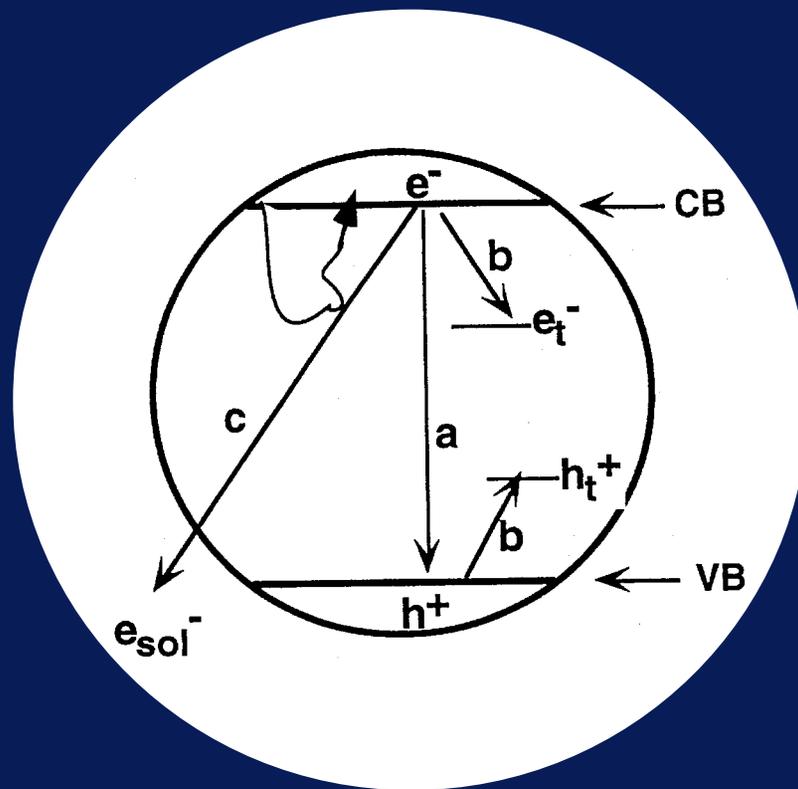
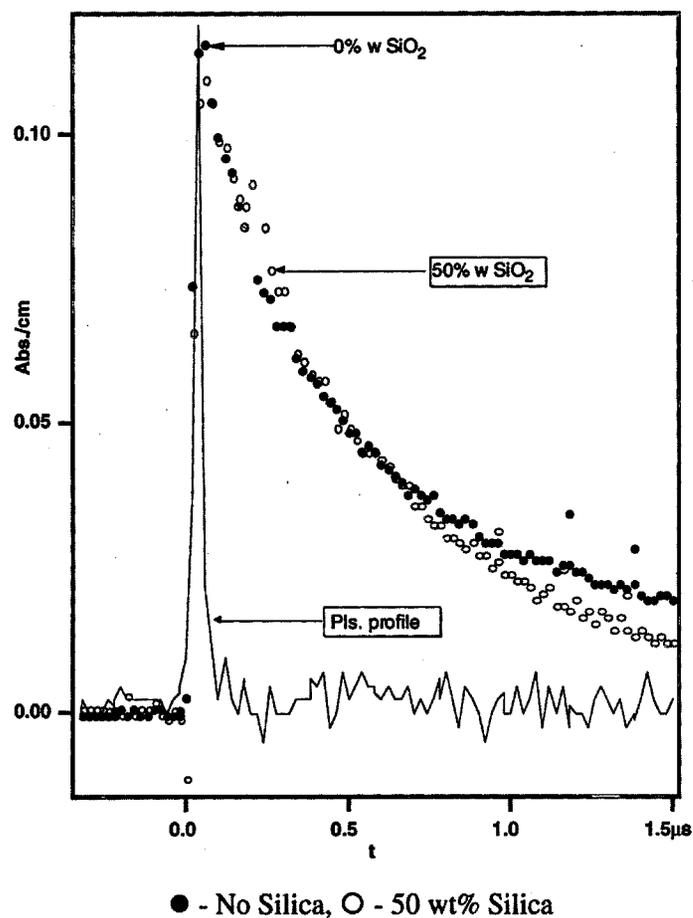
Solvated electrons produced from heavily loaded SiO<sub>2</sub>/water suspensions. The right Y-axis shows the total concentration of e<sup>-</sup><sub>aq</sub> generated in the cell. The Y-axis shows the concentration normalized to the pure water result. Lower dashed curve is the dependence of the water volume fraction on silica loading. The upper dashed curve is the dependence of the average sample density on silica loading. Data points and least-squares error estimates are shown for three particle sizes: (□) 7 nm, (△) 12 nm, and (●) 22 nm.

Argonne National Laboratory -A. Cook, T. Schatz, and D. Meisel, in press, JPC

“Interfacial Radiolysis Effects in Tank Waste Speciation” (PNNL), “The NO<sub>x</sub> System in Nuclear Waste” (ANL)

# SOLVATED ELECTRON YIELDS DURING IRRADIATION OF SiO<sub>2</sub> NANOPARTICLE SUSPENSIONS

Decay of Solvated Electrons in Suspensions of SiO<sub>2</sub> Particles



Above: Simplified diagram of the electronic structure of SiO<sub>2</sub> particles  
Left: Yield of solvated electrons in neat glycerin and in heavily loaded SiO<sub>2</sub> suspensions.

Argonne National Laboratory - A. Cook, T Schatz and D. Meisel

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# INTERFACIAL AND SOLID STATE RADIOLYSIS

Interfacial radiolysis leads to the production of non-thermal reactive species. The dominant products for  $\text{NaNO}_3$  are  $\text{O}$ ,  $\text{NO}$ , and  $\text{O}^-$ .

Exciton production, migration and decay are important.

Electron- and photon-induced processes involve the same final state, namely the  $\pi^* \leftarrow \pi$  band.

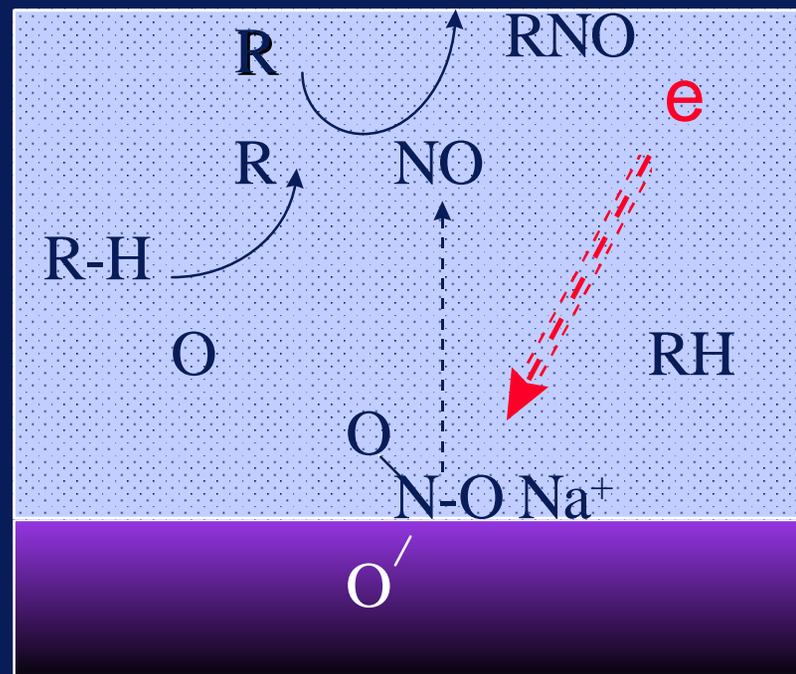
Solvated electron yields in irradiated suspensions of nanometer size particles are high. Energy originally deposited in the particles crosses the solid-liquid interface.

INTERFACIAL and SOLID-STATE RADIOLYSIS contributes to degradation of organics and production of flammable gases.

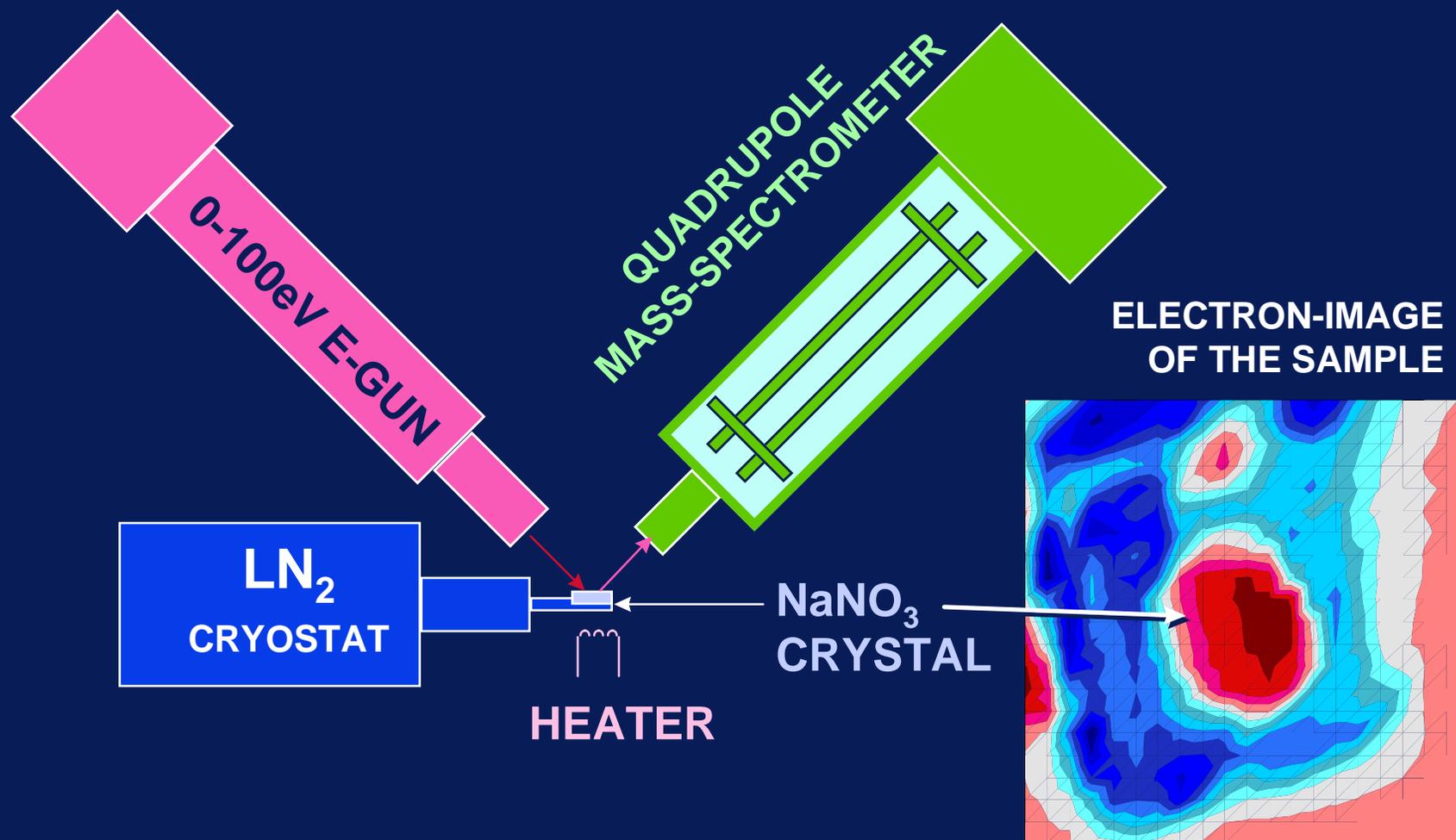
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# RADIATION-INDUCED REACTIONS AT ORGANIC/NaNO<sub>3</sub> INTERFACES

Radiolysis of NaNO<sub>3</sub> interfaces produces primarily O<sup>-</sup>, O, NO, and organic radicals. These species react and contribute to the “aging” of wastes. These radicals can also lead to the production of RNO compounds which can form N<sub>2</sub>O.



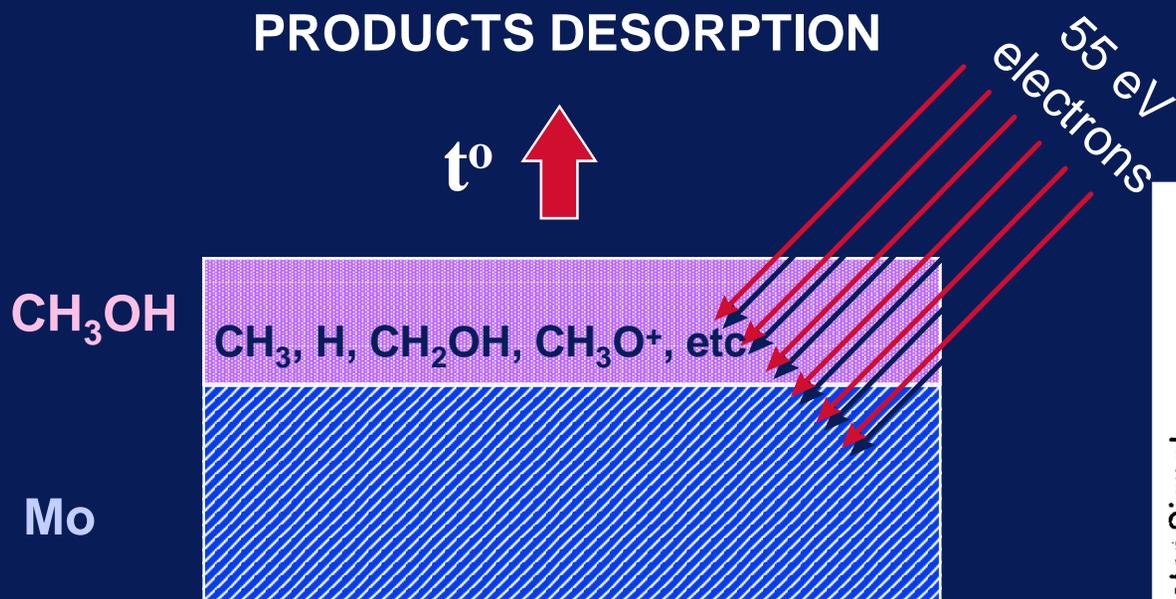
# ELECTRON IRRADIATION OF METHANOL MULTILAYERS ON $\text{NaNO}_3$ SURFACE: EXPERIMENTAL SETUP



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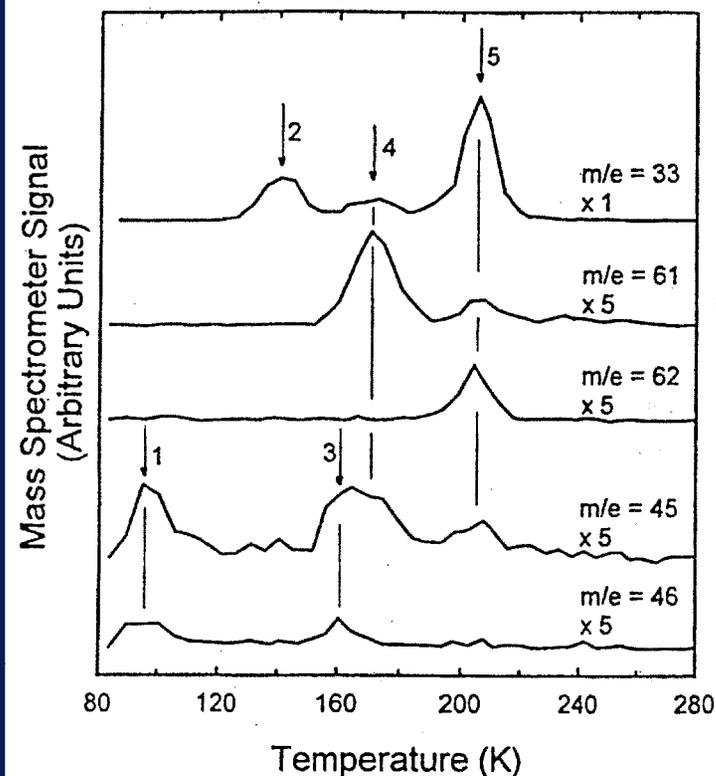
# ELECTRON IRRADIATION OF METHANOL MULTILAYERS ON METAL (Mo) SURFACE: NO INTERFACIAL REACTIONS. MOLECULAR PRODUCTS

## PRODUCTS DESORPTION



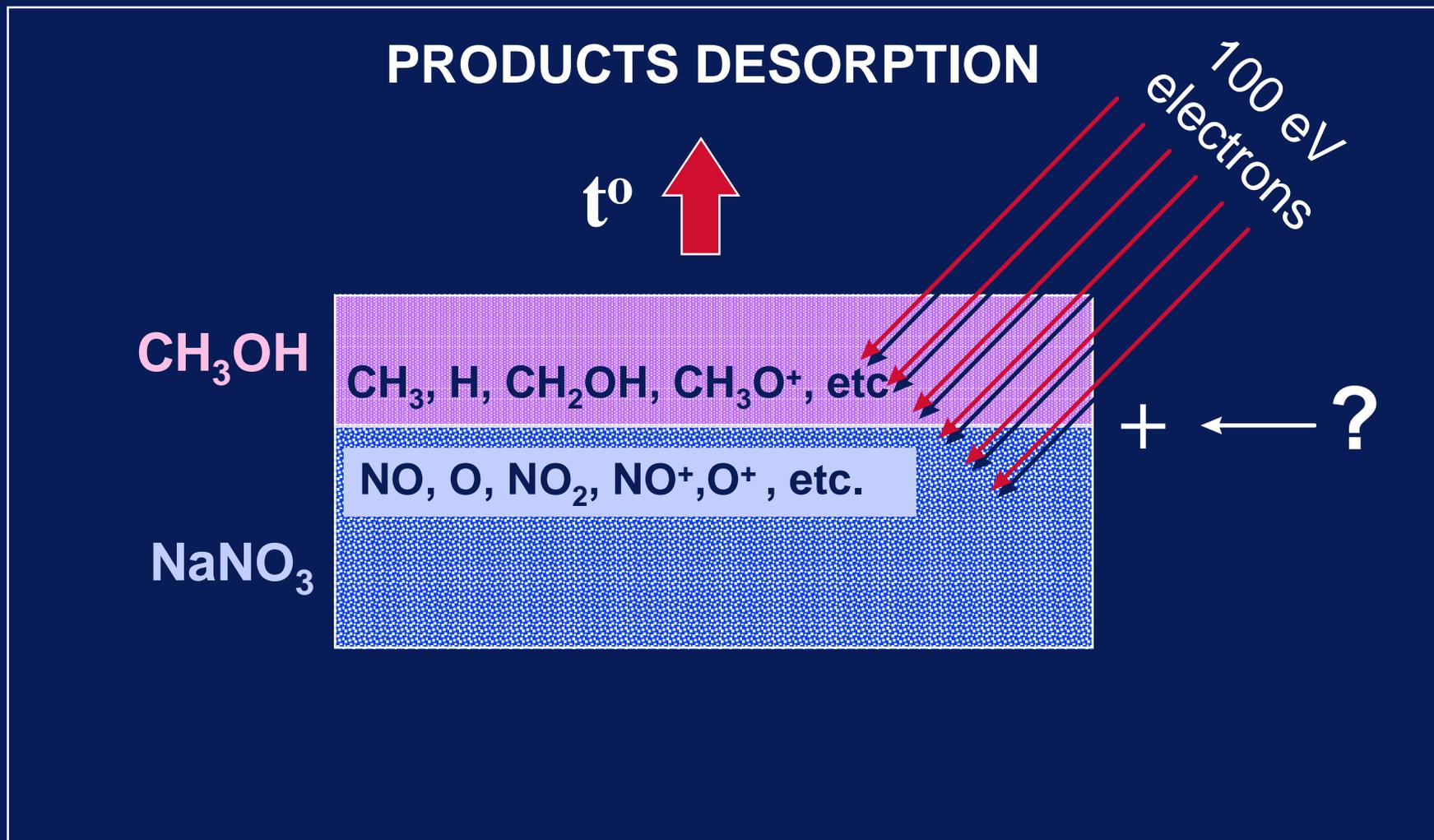
T.D.Harris et al., J.Phys.Chem., 99(23), 9530 (1995):  
Postirradiation TPD data of CH<sub>3</sub>OH multilayers on Mo  
showing several desorption features labeled by numbers:  
(1) dimethyl ether (~95K), (2) methanol (~140K),  
(3) ethanol (~160K), (4) methoxymethanol (~170K),  
and (5) ethylene glycol (~205K). 55 eV electrons.

## Identification of Methanol Radiolysis Products



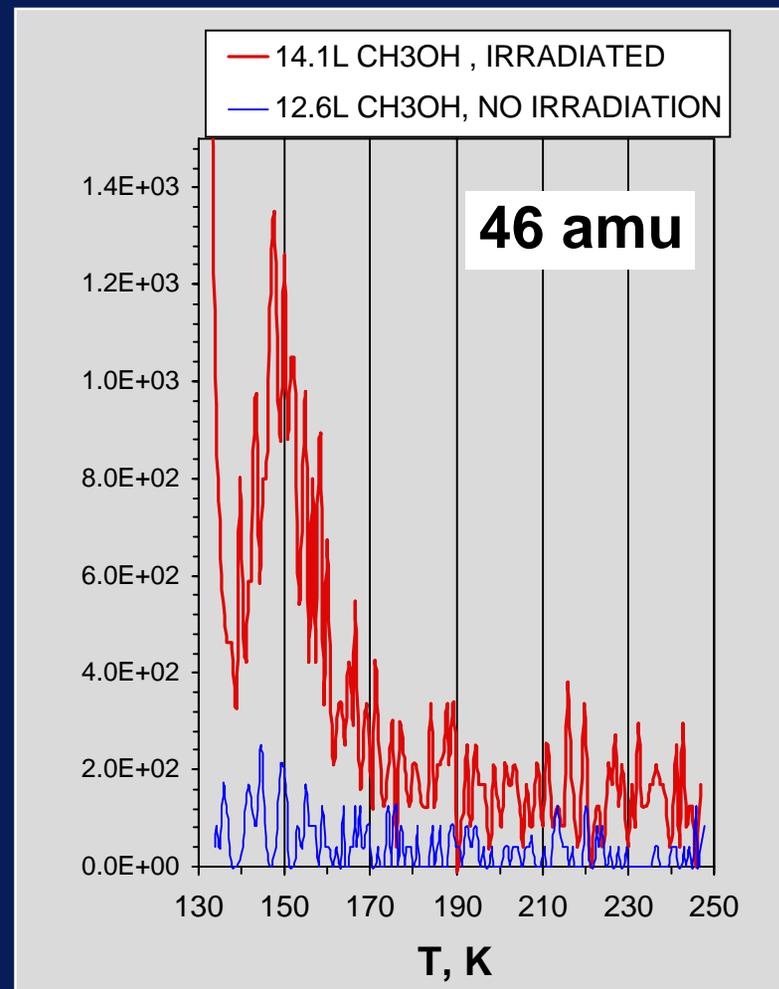
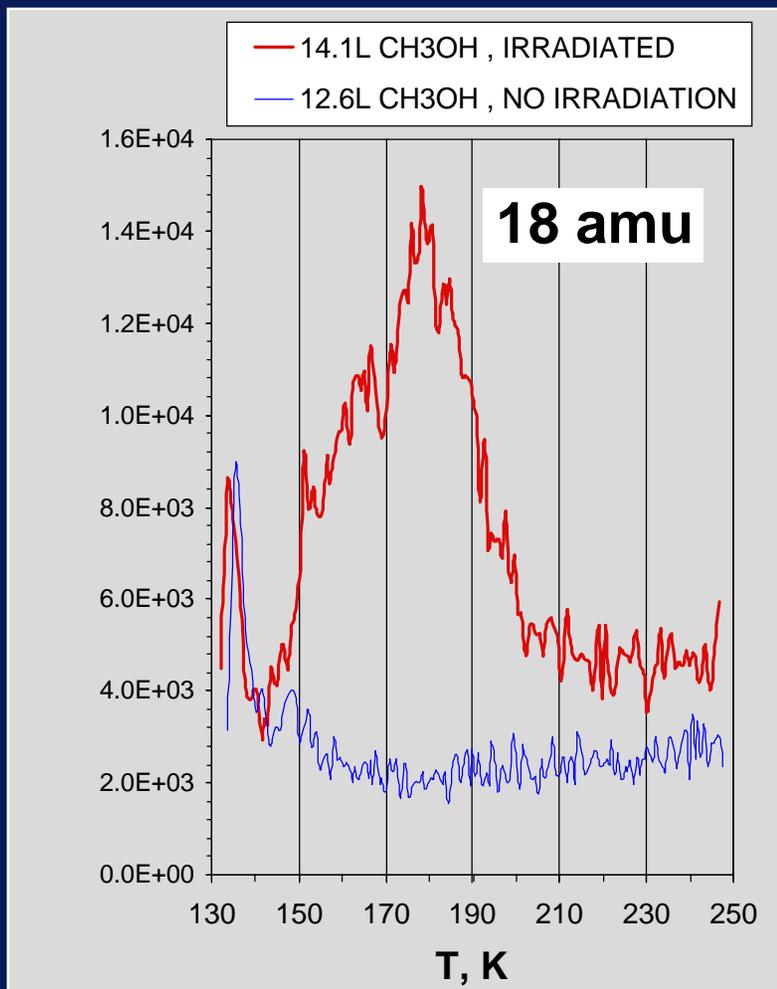
*“Interfacial Radiolysis Effects in Tank Waste Speciation” (PNNL), “The NO<sub>x</sub> System in Nuclear Waste” (ANL)*

# ELECTRON IRRADIATION OF METHANOL MULTILAYERS ON $\text{NaNO}_3$ SURFACE: LOOKING FOR INTERFACIAL REACTIONS



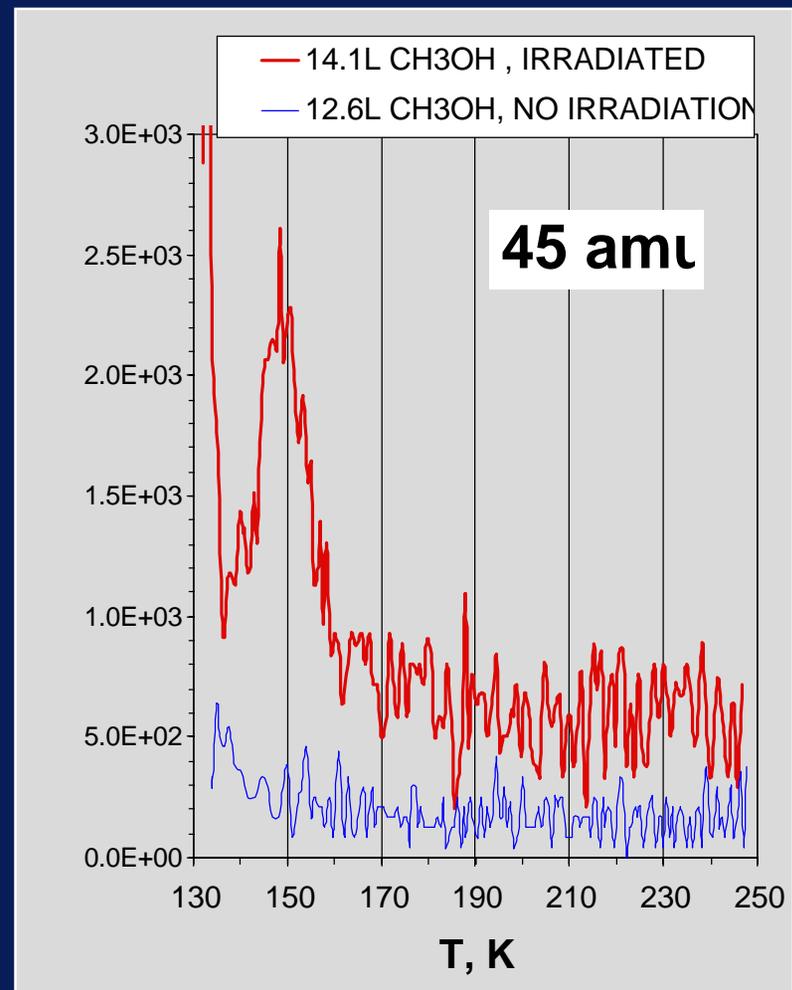
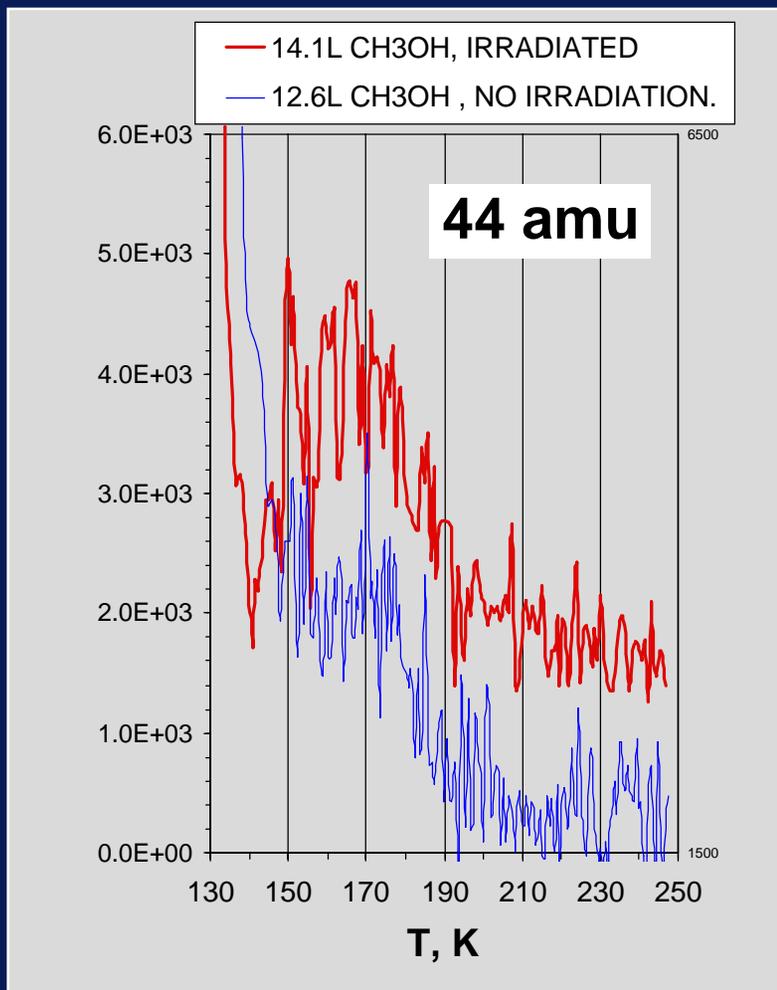
*“Interfacial Radiolysis Effects in Tank Waste Speciation” (PNNL), “The  $\text{NO}_x$  System in Nuclear Waste” (ANL)*

# EFFECT OF 100eV ELECTRON IRRADIATION ON TPD OF CH<sub>3</sub>OH FROM NaNO<sub>3</sub> SURFACE: NEW PRODUCTS - 18 amu (H<sub>2</sub>O) AND 46 amu



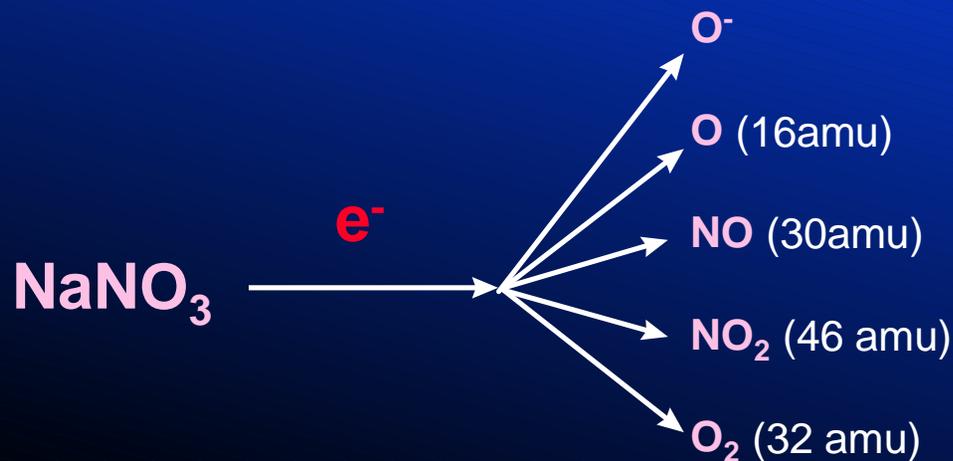
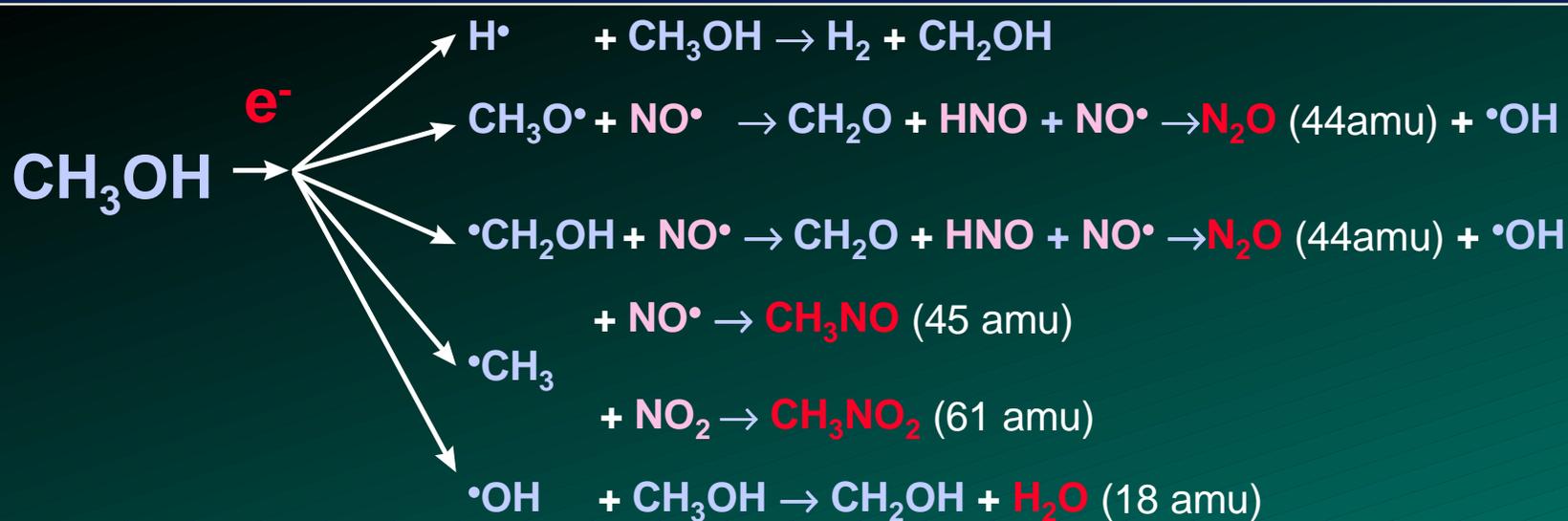
*“Interfacial Radiolysis Effects in Tank Waste Speciation” (PNNL), “The NO<sub>x</sub> System in Nuclear Waste” (ANL)*

# EFFECT OF 100eV ELECTRON IRRADIATION ON TPD OF CH<sub>3</sub>OH FROM NaNO<sub>3</sub> SURFACE: NEW PRODUCTS - 44 AND 45 amu



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# PROPOSED REACTION SCHEME FOR THE NaNO<sub>3</sub> / CH<sub>3</sub>OH OVERLAYER EXPERIMENTS



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# ELECTRON IRRADIATION OF METHANOL MULTILAYERS ON METAL(Mo) AND $\text{NaNO}_3$ SUBSTRATES:

★ DIFFERENT FEATURES

★ POSSIBLE INTERFACIAL REACTIONS

<b>~4ML <math>\text{CH}_3\text{OH}</math> on Mo @ 80K, 55eV electrons</b>	<b>~14ML <math>\text{CH}_3\text{OH}</math> on <math>\text{NaNO}_3</math> @ 134K, 100eV electrons</b>
No 18 and 44 amu products	New 18 and 44 amu products
Methanol peak @140K lower than products	Methanol peak @150K the highest
45 and 46amu peaks @ 160K(ethanol) and 205K(ethylene glycol)	45 and 46amu peaks @ 150K no ~205K peaks
61amu peak @ 170K 2 times higher than 45amu	61amu peak @ 180K 10 times lower than 45amu

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# ELECTRON-STIMULATED REACTIONS AT CH<sub>3</sub>OH/NaNO<sub>3</sub> INTERFACES

Product masses 18, 44, 45, 46 and 61 are observed as a result of electron (100 eV) irradiation of CH<sub>3</sub>OH/NaNO<sub>3</sub> interfaces.

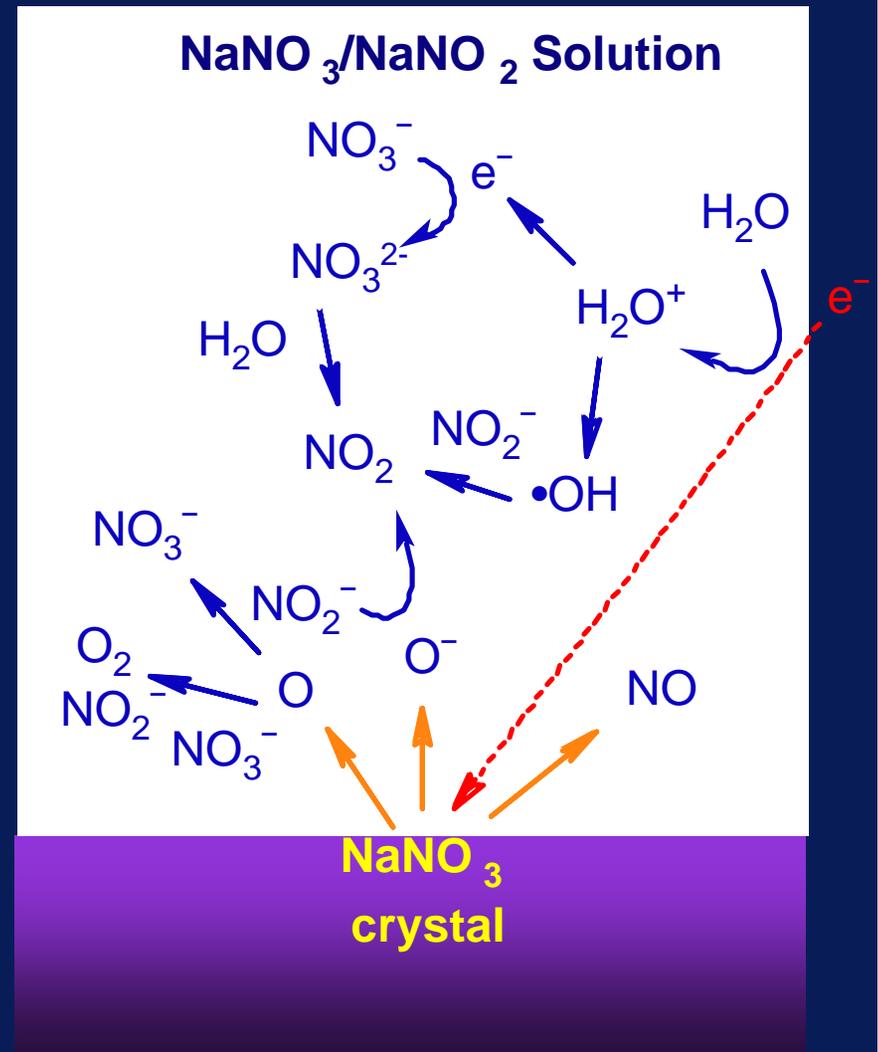
We tentatively assign these masses to H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>3</sub>NO, NO<sub>2</sub>, and CH<sub>3</sub>NO<sub>2</sub>.

We suggest that NO reactions with organic radicals produce nitrosomethane and nitromethane.

Reactions involving HNO and NO **MAY** then lead to N<sub>2</sub>O.

# RADIATION-INDUCED REACTIONS AT $\text{NaNO}_3$ CRYSTAL/SOLUTION INTERFACES

*Radiolysis of  $\text{NaNO}_3$  crystals in aqueous solution is expected to produce  $\text{NO}_x$  radicals and nitrite ions. These oxidizing species degrade organic complexants and initiate gas generation reactions. Thus, a portion of our effort examines their reactions with organic complexants to develop models for organic degradation and gas generation in tank wastes.*



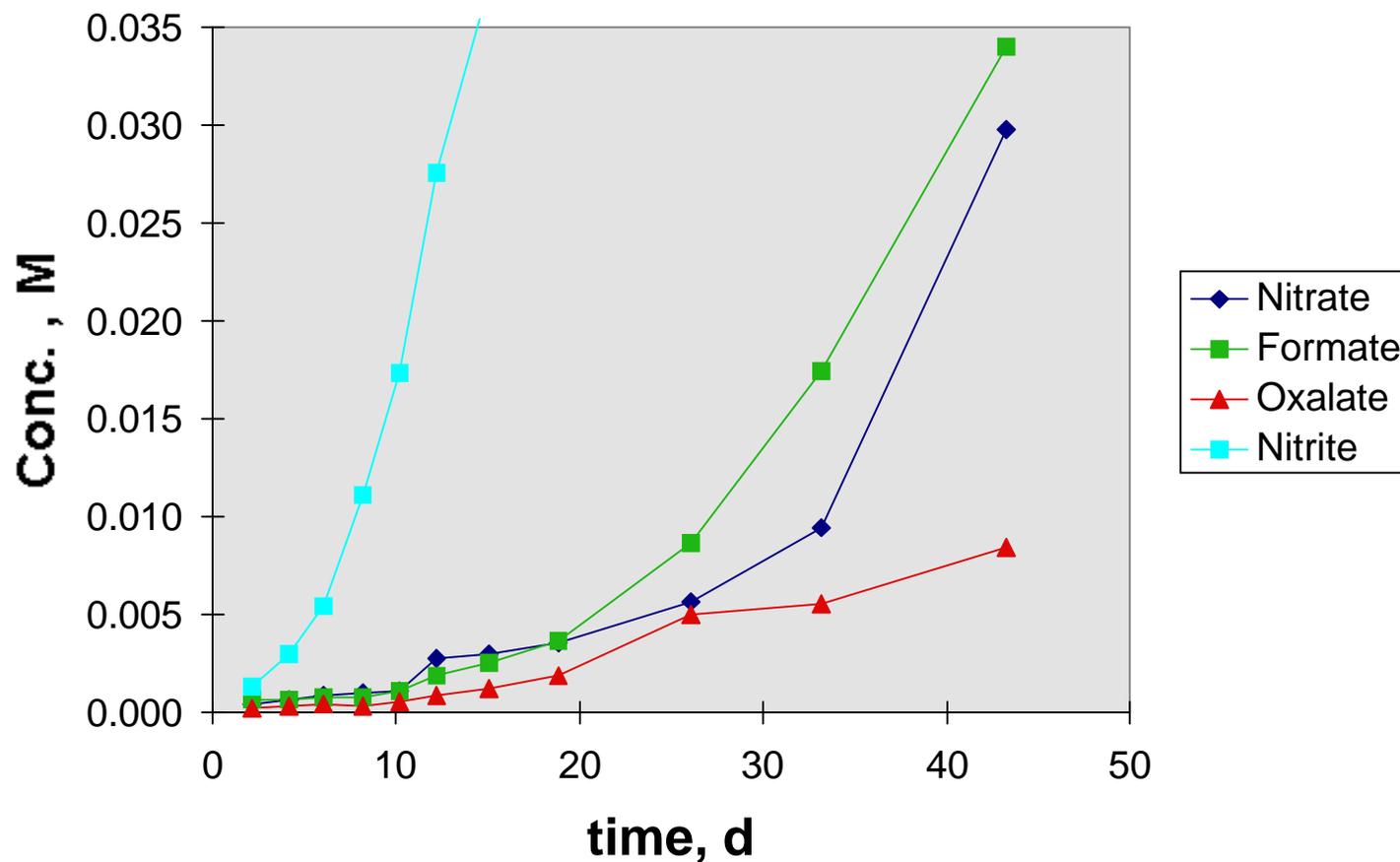
# STUDYING THE REACTIONS OF NO<sub>2</sub> WITH ORGANIC COMPLEXANTS IN SOLUTION

- *An N<sub>2</sub> gas stream containing 10 ppm NO<sub>2</sub> is bubbled through an alkaline aqueous solution of the complexant.*
- *A second approach uses a  $\gamma$  source to irradiate alkaline NaNO<sub>3</sub>, NaNO<sub>2</sub> solutions containing the complexant.*
- *The solutions are analyzed by ion chromatography and nuclear magnetic resonance spectroscopy.*



# Products vs Time of Contact with NO<sub>2</sub> Gas

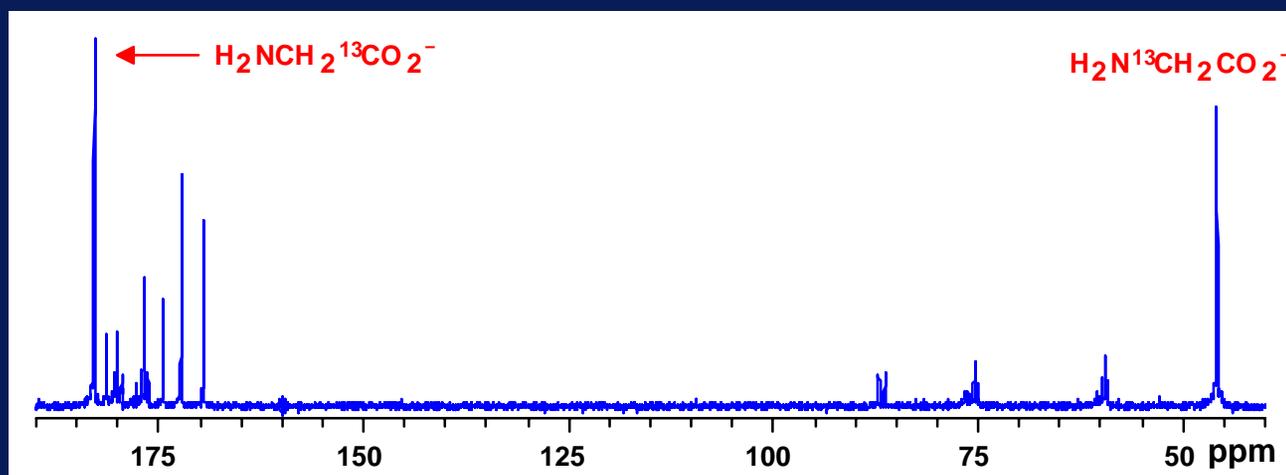
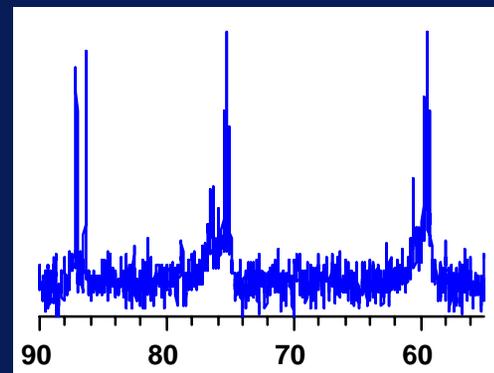
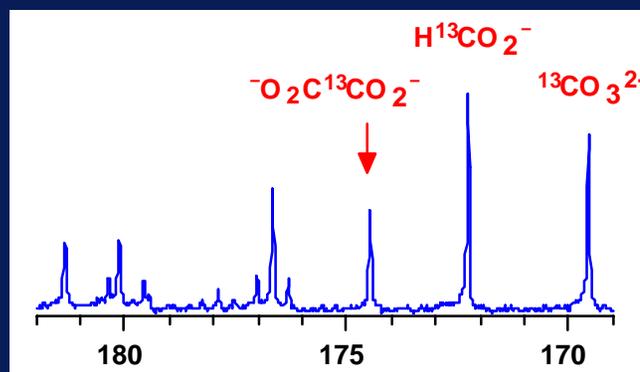
## 0.1 M Glycine in 1 M NaOH



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# REACTION OF GLYCINE WITH NO<sub>2</sub> IN ALKALINE SOLUTION

<sup>13</sup>C NMR Spectra after Contact with NO<sub>2</sub> Gas (10 ppm in N<sub>2</sub>) for 43 Days at RT

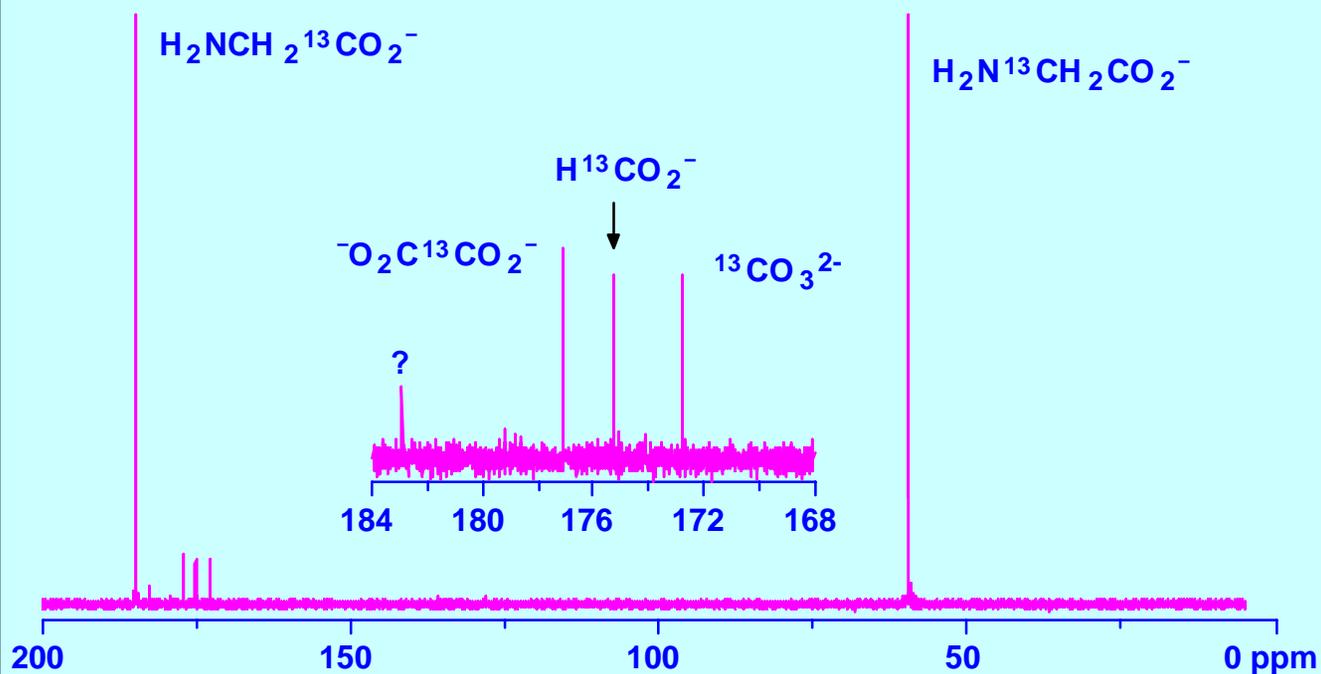


*Initial Solution: Equal Mixture of 1- and 2-Labeled Glycines (0.1 M) in 1 M NaOH*

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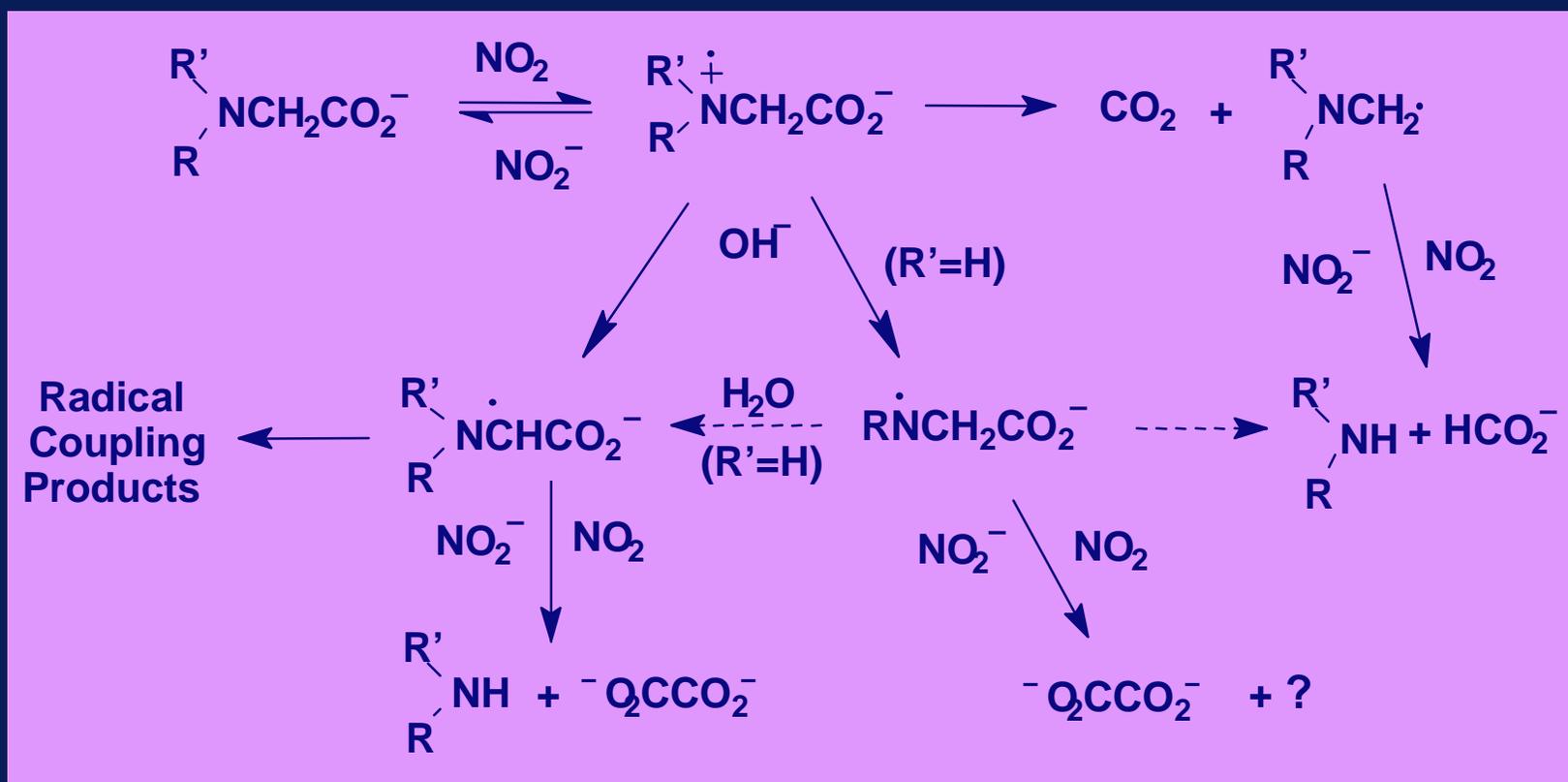
## Reaction of Glycine with $\text{NO}_2$ in Alkaline Solution

$^{13}\text{C}$  NMR Spectrum after Contact with  $\text{NO}_2$  (10 ppm in  $\text{N}_2$ ) for 24 Days



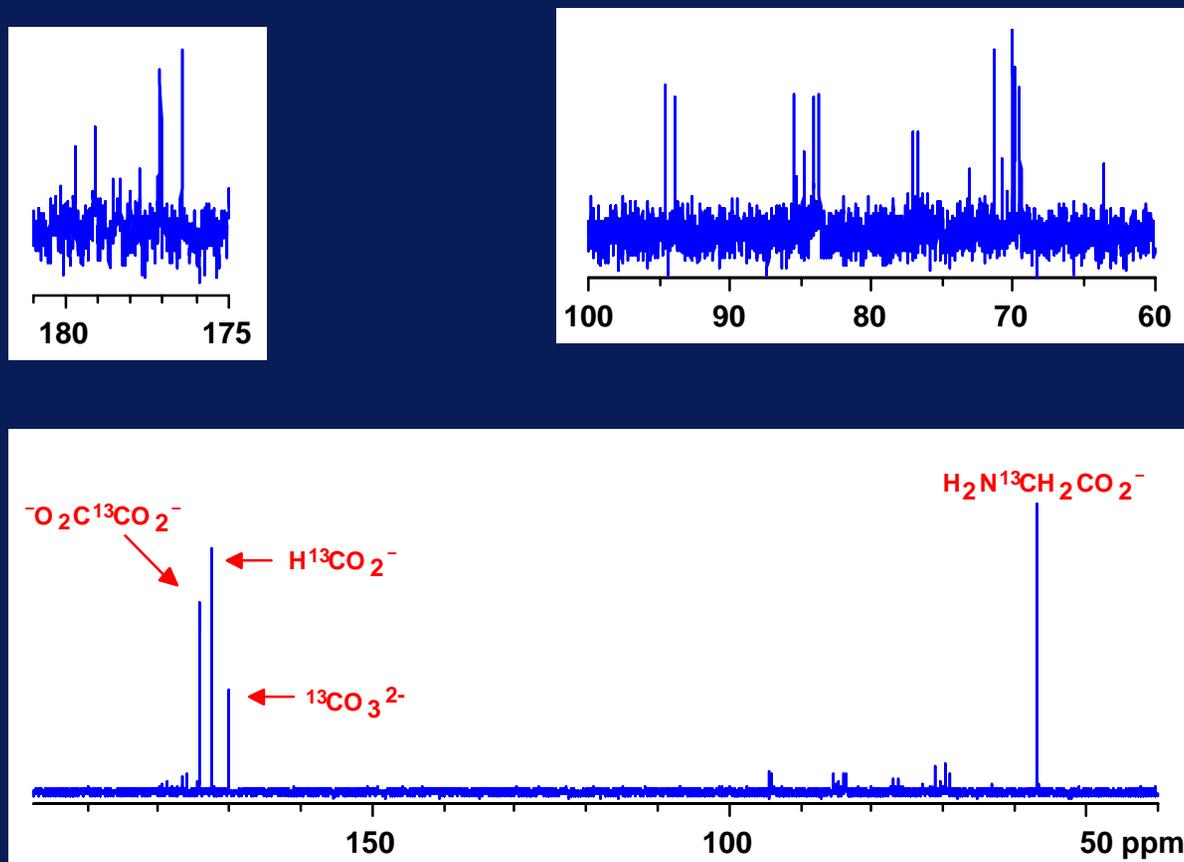
Initial solution: equal mixture of 1- and 2-labeled  $^{13}\text{C}$ -Glycines (0.1 M)  
in 1 M  $\text{NaNO}_2$  and 1 M  $\text{NaOH}$

# MECHANISM FOR OXIDATION OF AMINO-ACID COMPLEXANTS BY NO<sub>2</sub> IN ALKALINE SOLUTIONS



# $\gamma$ IRRADIATION OF GLYCINE IN ALKALINE $\text{NaNO}_3$ SOLUTION

$^{13}\text{C}$  NMR Spectra after 29 MRad Dose at 25 °C

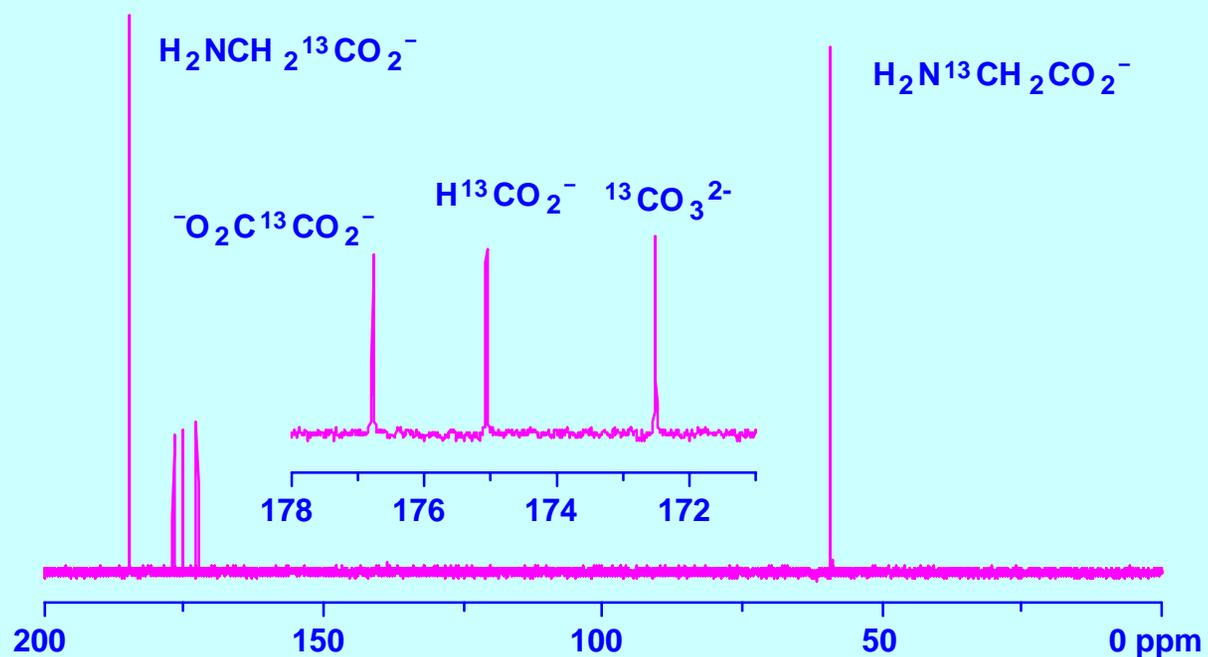


Initial Solution: 0.08 M 2-  $^{13}\text{C}$ -Glycine in 2 M  $\text{NaNO}_3$ , 2 M  $\text{NaOH}$

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## $\gamma$ Irradiation of Glycine in Alkaline Nitrate/Nitrite Solution

$^{13}\text{C}$  NMR Spectrum after 17 MRad at 25 °C



Initial solution: equal mixture of 1- and 2-labeled  $^{13}\text{C}$ -Glycines (0.08 M)  
in 2 M  $\text{NaNO}_3$ , 2 M  $\text{NaNO}_2$ , and 2 M  $\text{NaOH}$

# COMPARISON OF COMPLEXANT REACTIVITIES IN NO<sub>2</sub> CONTACT AND γ IRRADIATION EXPERIMENTS



Complexant	$k_{rel}^{(a)}$ (NO <sub>2</sub> )	$k_{rel}^{(b)}$ (γ irradiation)
$\begin{array}{c} CH_2CO_2^- \\   \\ N-CH_2CO_2^- \\   \\ CH_2CO_2^- \end{array}$	19	10
$\begin{array}{c} CH_2CO_2^- \\   \\ H-N \\   \\ CH_2CO_2^- \end{array}$	11	12
H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	4.5	7
H <sup>13</sup> CO <sub>2</sub> <sup>-</sup>	1	1

<sup>(a)</sup> From initial yields of H<sup>12</sup>CO<sub>2</sub><sup>-</sup> relative <sup>13</sup>CO<sub>3</sub><sup>2-</sup> formed after contacting alkaline solution with NO<sub>2</sub> gas.

<sup>(b)</sup> From decrease in concentration of complexant relative to yield of <sup>13</sup>CO<sub>3</sub><sup>2-</sup> after γ irradiation in 1.25 M NaNO<sub>2</sub>, 3.75 M NaNO<sub>3</sub>, 2M NaOH solutions.

## SOME FUTURE EMSP STUDIES

Methanol/ $\text{NaNO}_3$  experiments will continue with  $\text{CD}_3\text{OD}$ .

Photon and electron irradiation of aqueous solutions using novel liquid beam technology will begin.

Studies of  $\text{NO}_2$  oxidation of aminocarboxylates, glycolate and formate will be carried out in collaboration with Meisel. et. al.

Radiolysis of nanometer sized oxide particles will continue with an emphasis on the fate of the holes, also in collaboration with Meisel et. al.

The general role of radiolysis of solids and interfaces in Tank Waste Processes will be examined.

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