

NO_x and Heterogeneity Effects in High Level Waste

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Abstract:

We summarize contributions from our EMSP supported research to several field-operations of the Office of Environmental Management (EM). In particular we emphasize its impact on safety programs at the Hanford and other EM sites where storage, maintenance and handling of HLW is a major mission. In recent years we were engaged in coordinated efforts to understand the chemistry initiated by radiation in HLW. Three projects of the EMSP (“The NO_x System in Nuclear Waste,” “Mechanisms and Kinetics of Organic Aging in High Level Nuclear Wastes, D. Camaioni – PI” and “Interfacial Radiolysis Effects in Tanks Waste, T. Orlando - PI”) were involved in that effort, which included a team at Argonne, later moved to the University of Notre Dame, and two teams at the Pacific Northwest National Laboratory. Much effort was invested in integrating the results of the scientific studies into the engineering operations via coordination meetings and participation in various stages of the resolution of some of the outstanding safety issues at the sites. However, in this Abstract we summarize the effort at Notre Dame. Two broad issues were identified as bottlenecks in understanding the chemistry in HLW

The heterogeneity of the systems and

The relatively poorly understood chemistry of NO_x species, rather than water degradation products.

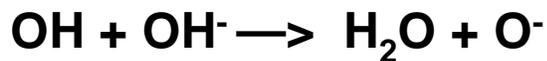
As a result of the EMSP projects mentioned above the following advancement were achieved, starting with the NO_x issue:

1. All of the initial water primary products are converted to the NO₂ or NO oxidizing species. The rates of these conversions were quantified and novel routes for the conversions outlined. Redox potentials of the relevant species were measured.
2. The hypothesis that NO₂ is the major oxidant of organic compounds in the HLW was confirmed. Relative rates, and in some cases absolute rates, of the NO₂ radical with organic substrates (mostly chelates and their degradation products) were measured. Mechanisms and rates of the reaction of relevant organic radicals with NO₂, and NO₂⁻ were collected.
3. These quantitative measurements were incorporated into a simplified computer model that describes the radiation-induced chemistry of HLW simulants and their mixtures.

Generation of NO_x Radicals:



Hydroxyl Radicals:



The basic form, O⁻:

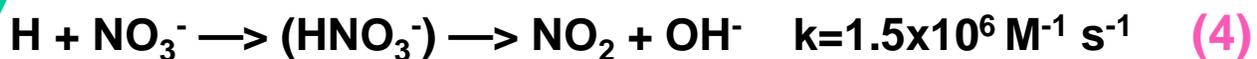


$$k=3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Hydrated Electrons:

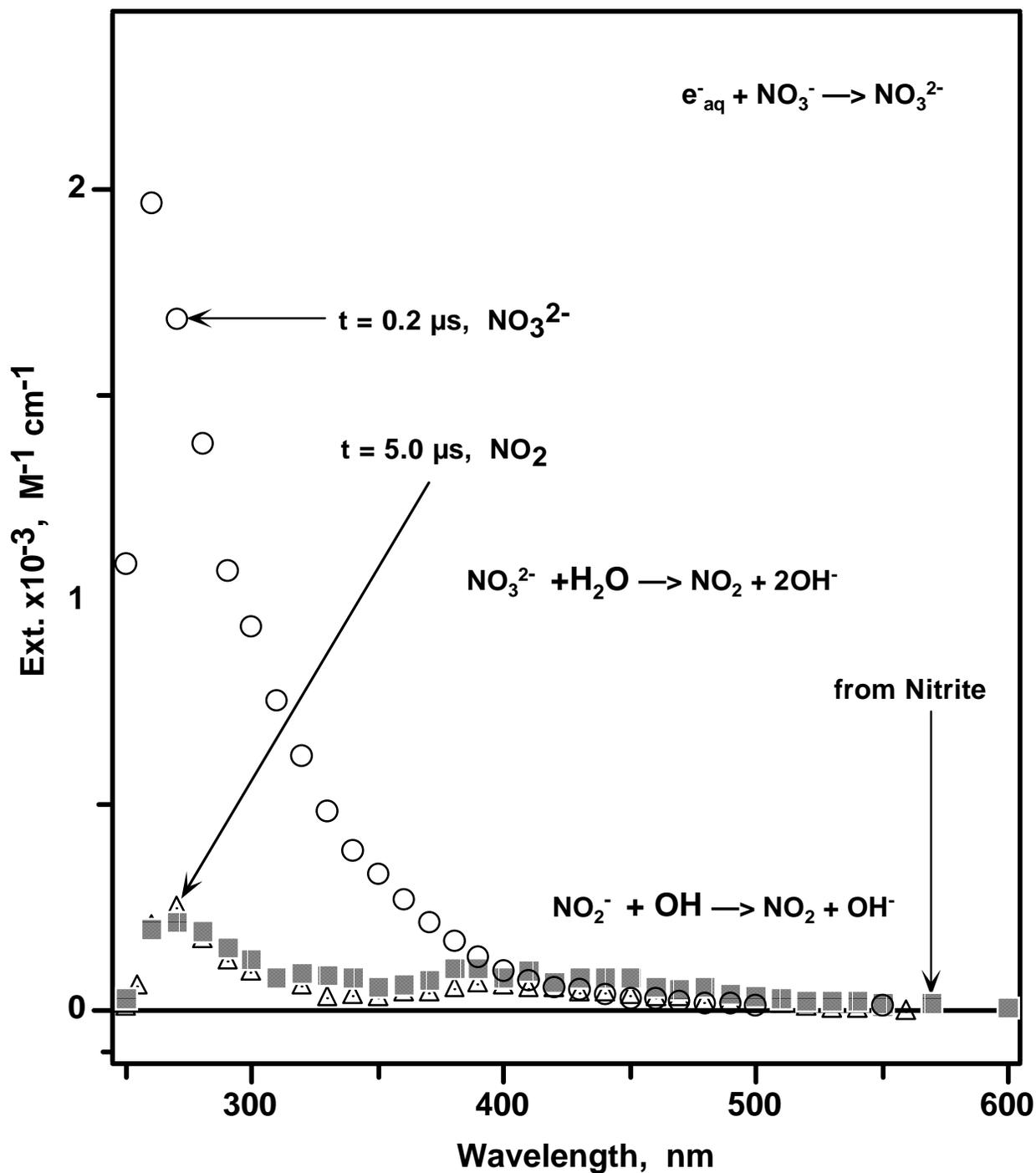


Hydrogen Atoms:



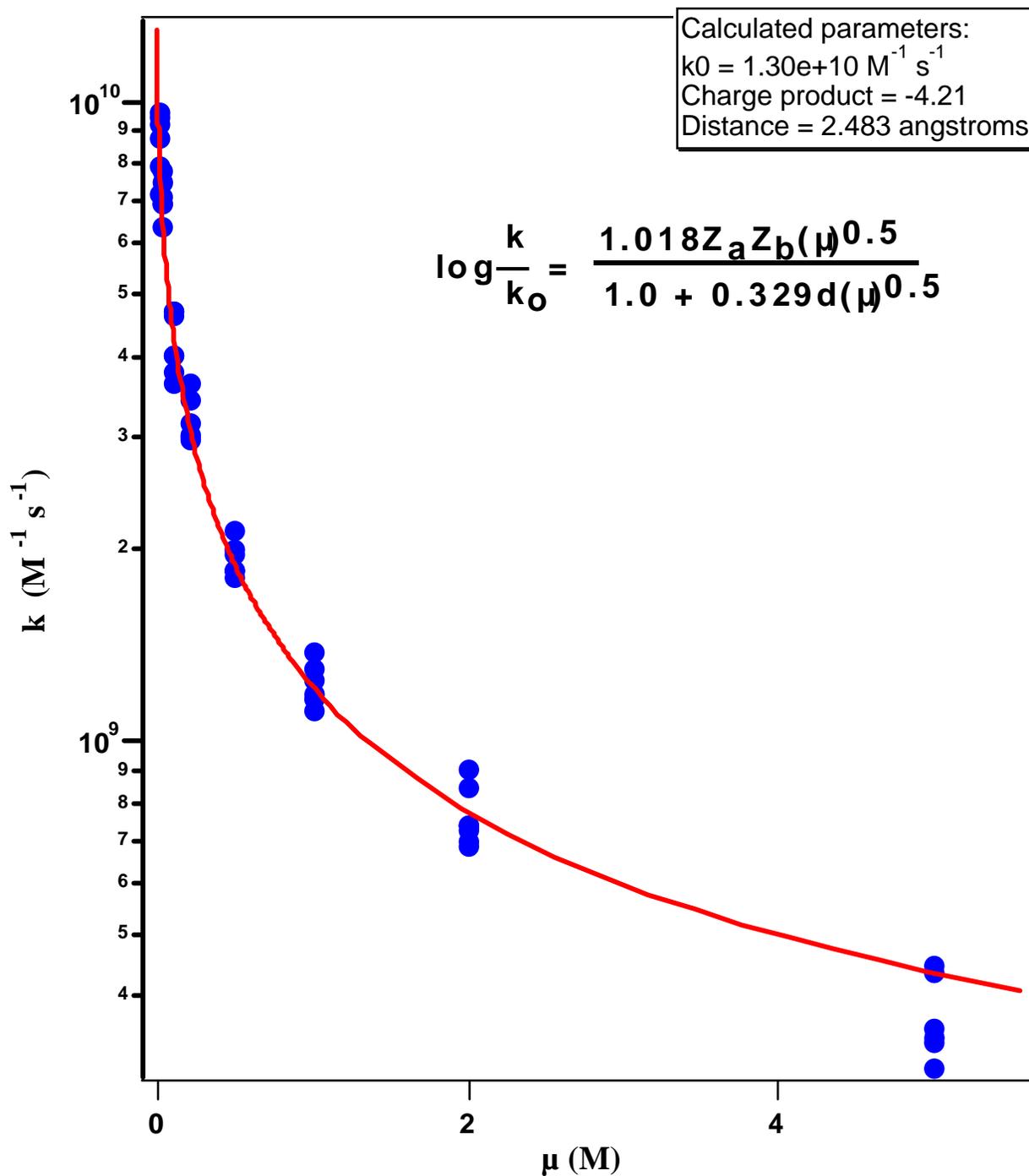
Absorption Spectra of NO_3^{2-} & NO_2

Non characteristic



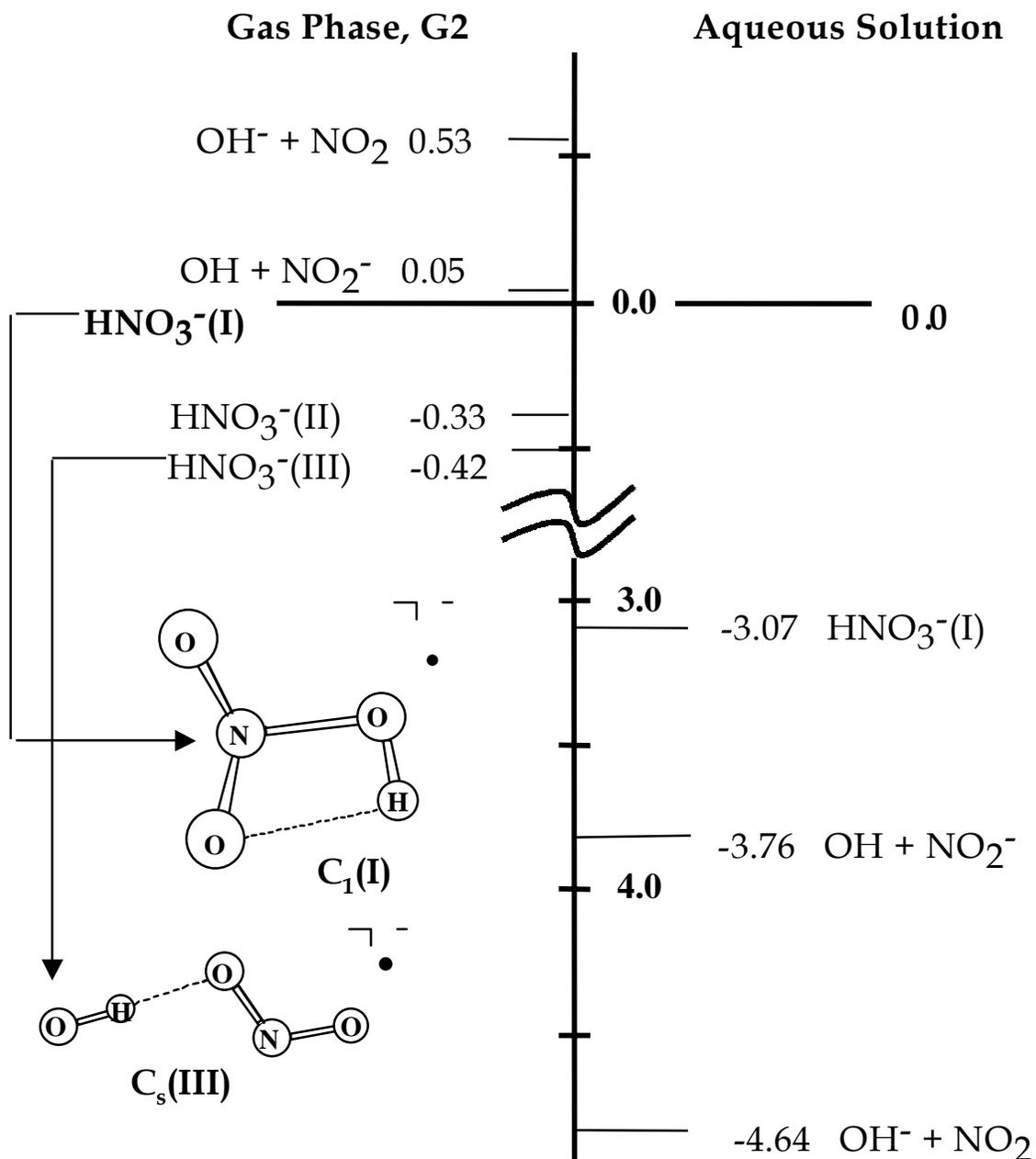
Verification of Charge on NO_3^{2-}

Ionic Strength effect on

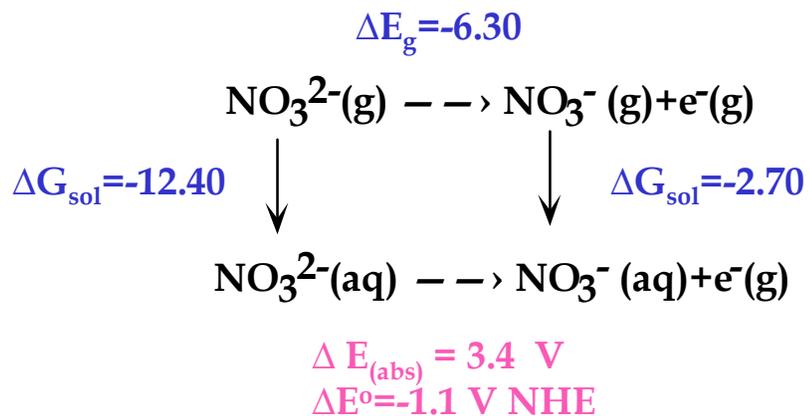


NOx Computational Estimates

Energies in eV

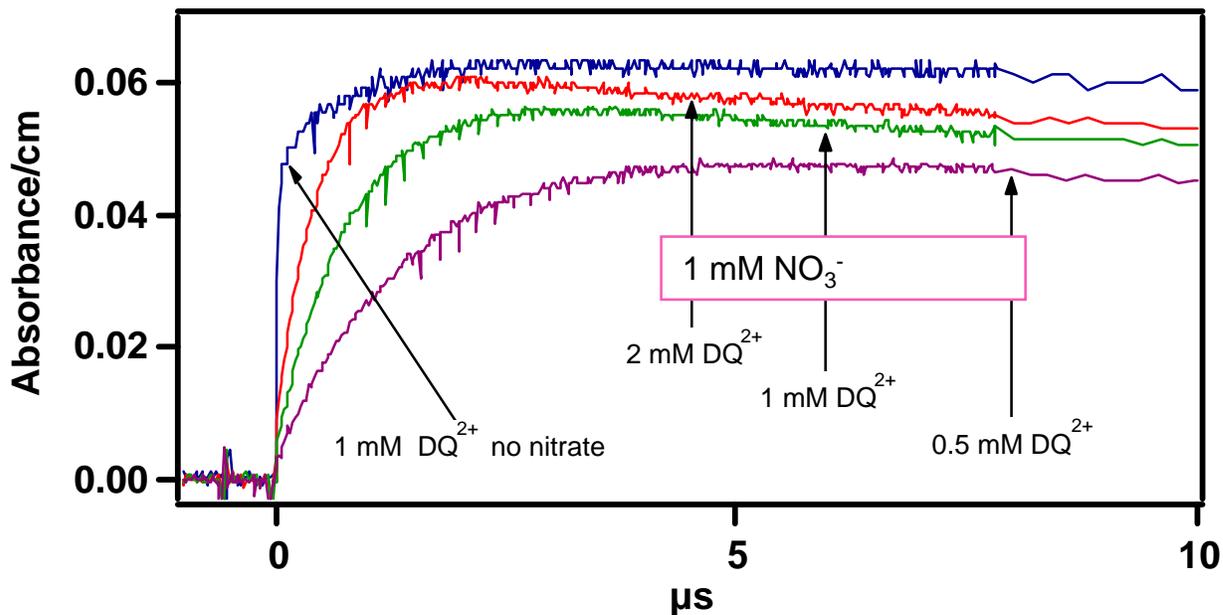
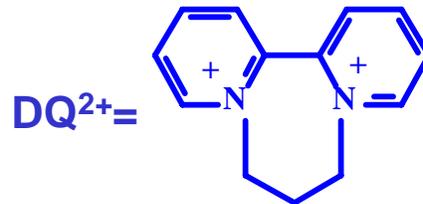


Computational Estimates of E_o



Determination of E_o ($\text{NO}_3^-/2^-$)

Kinetics:



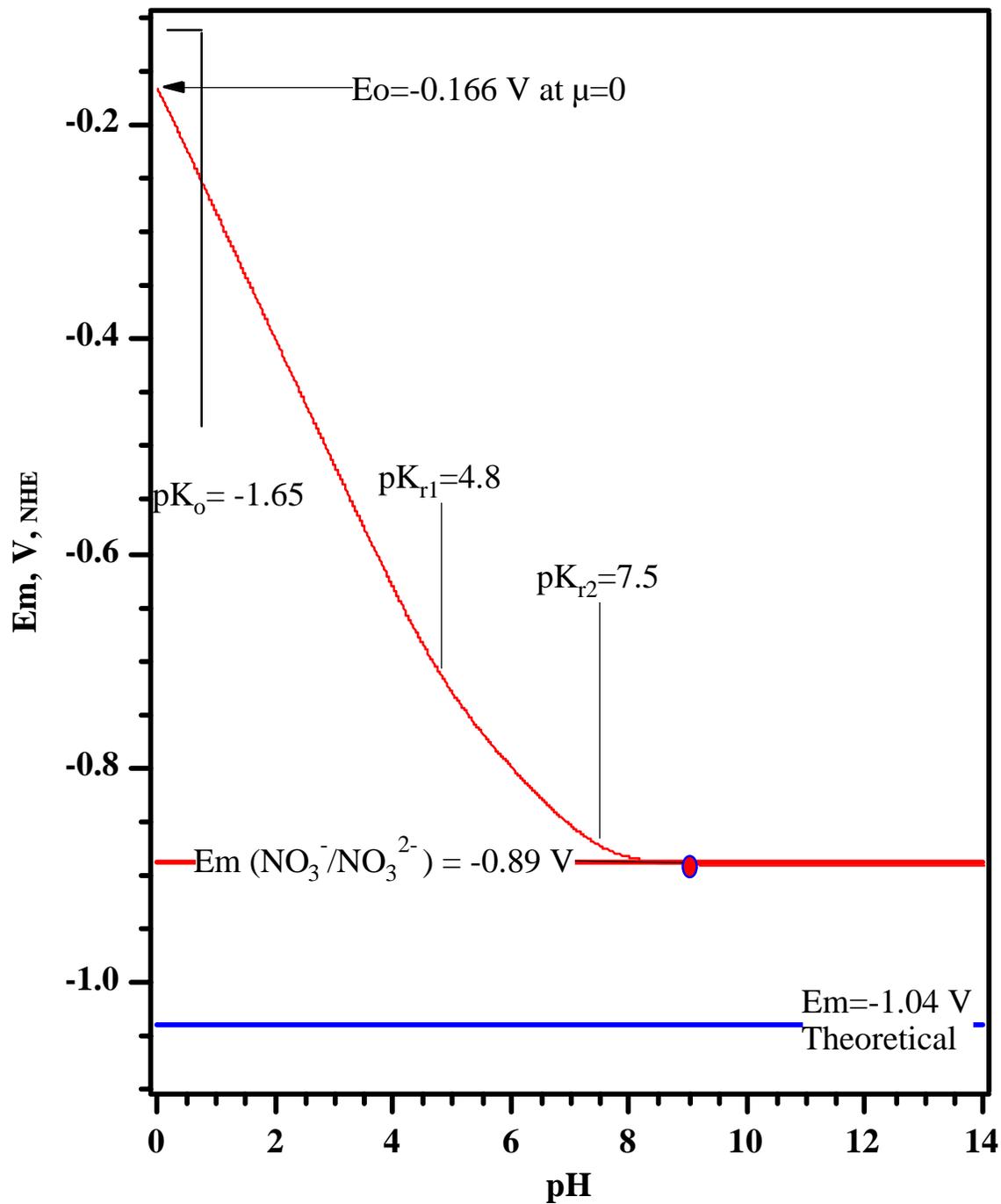
Thermodynamic Eq.:



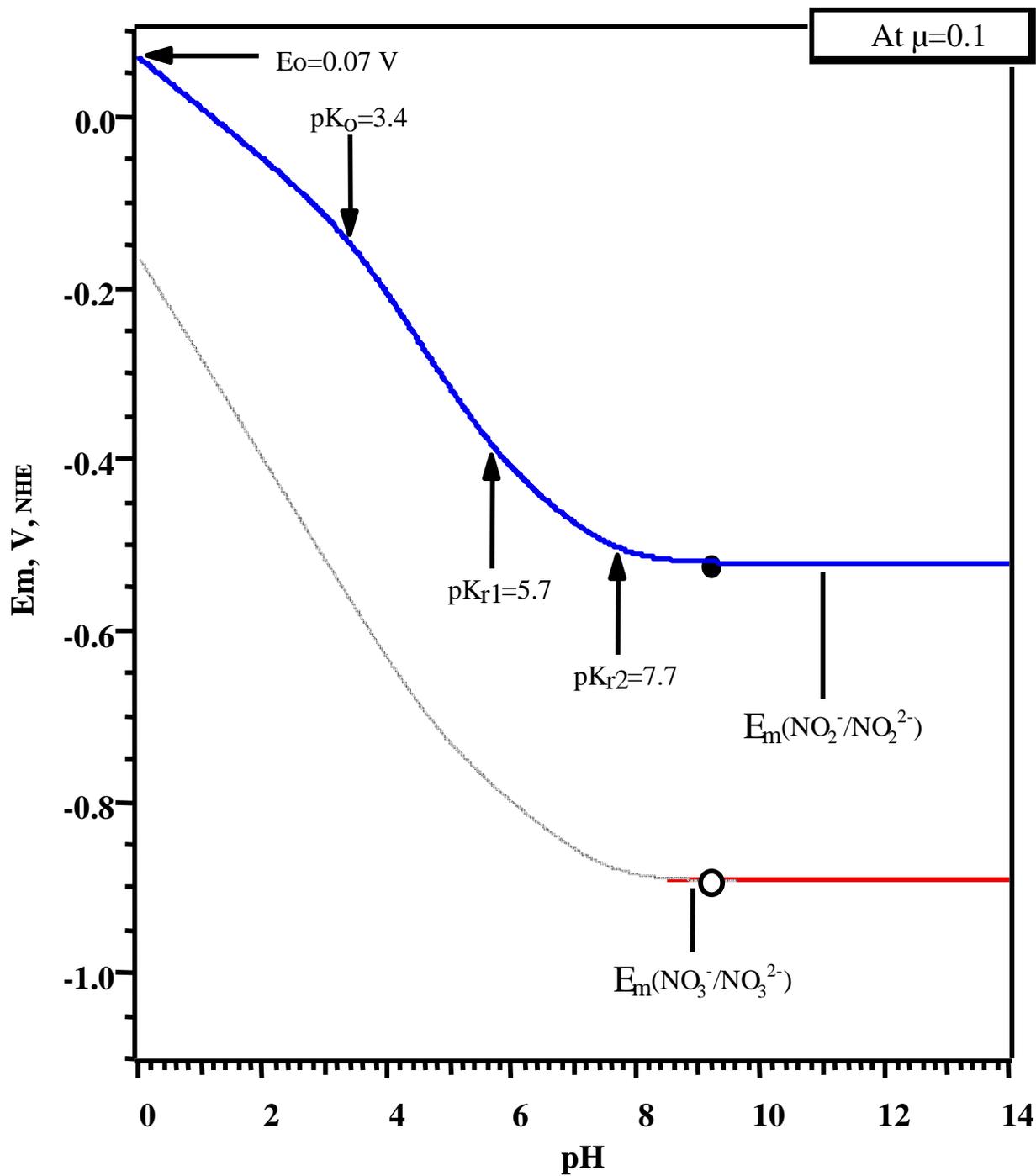
$$\Delta E = R T \ln K \Rightarrow E_o = -0.89 \text{ V}$$

Redox Potential of $\text{NO}_3^-/2^-$

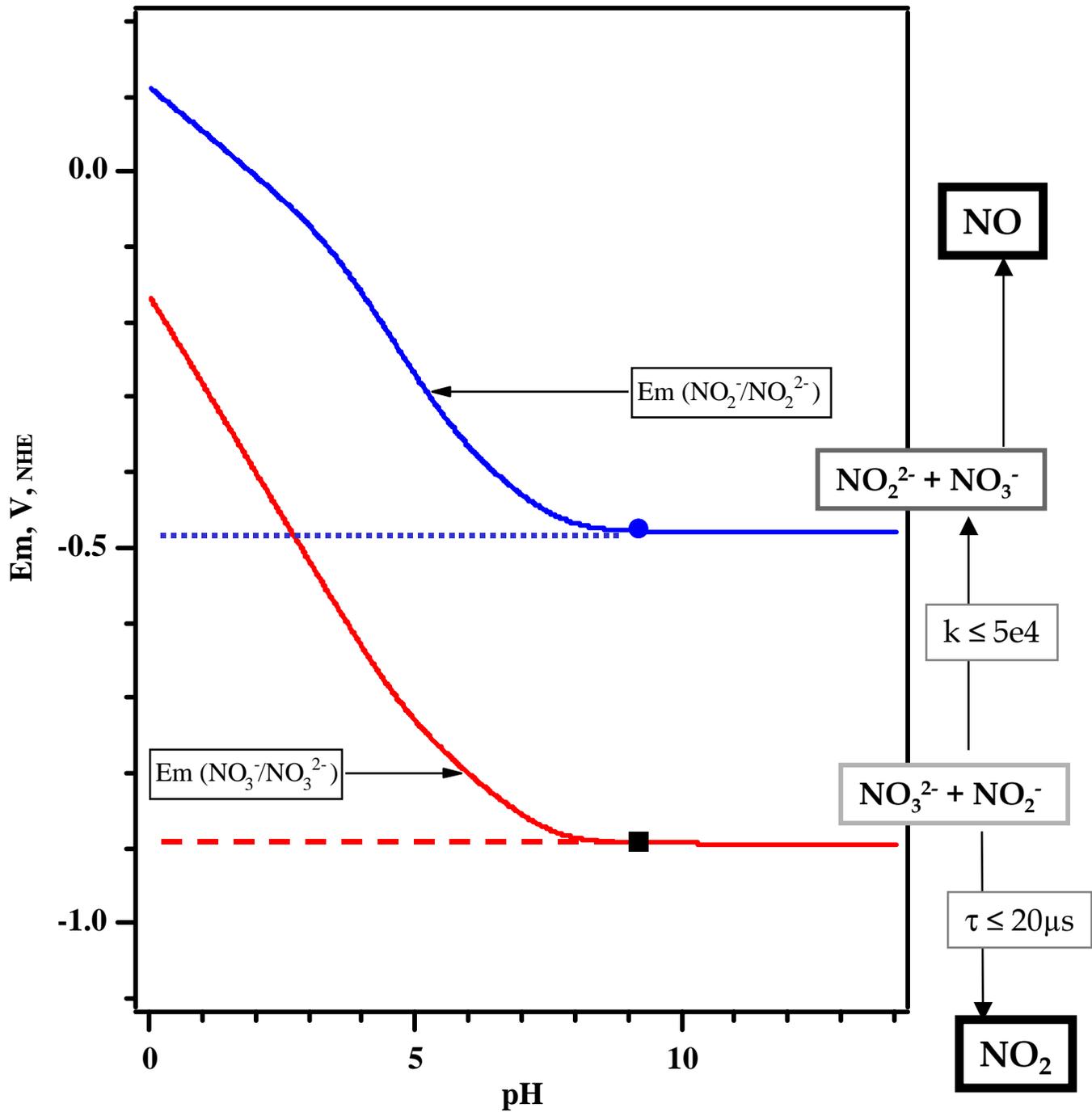
Is it pH dependent?



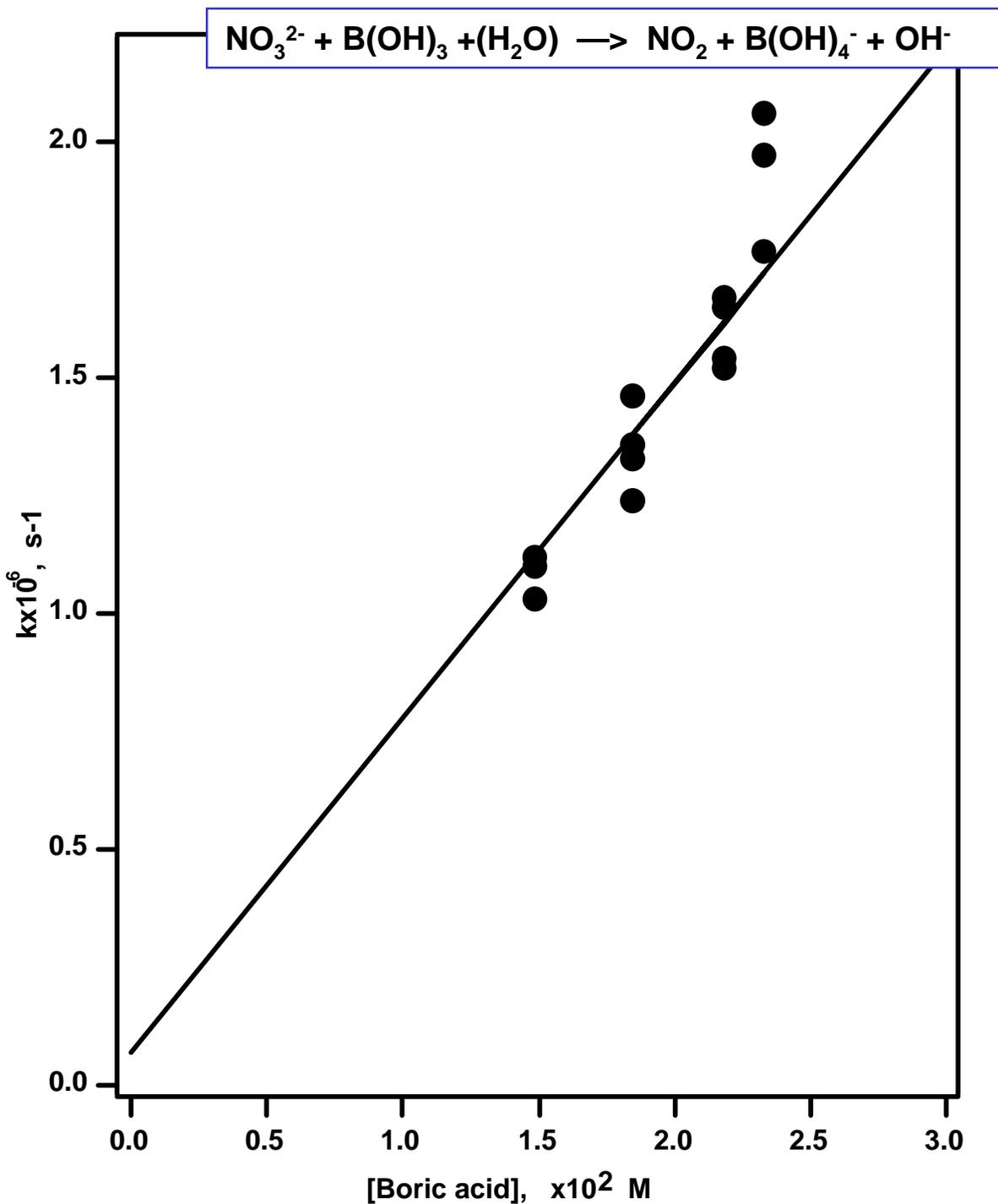
Redox Potential of $\text{NO}_2^-/2^-$



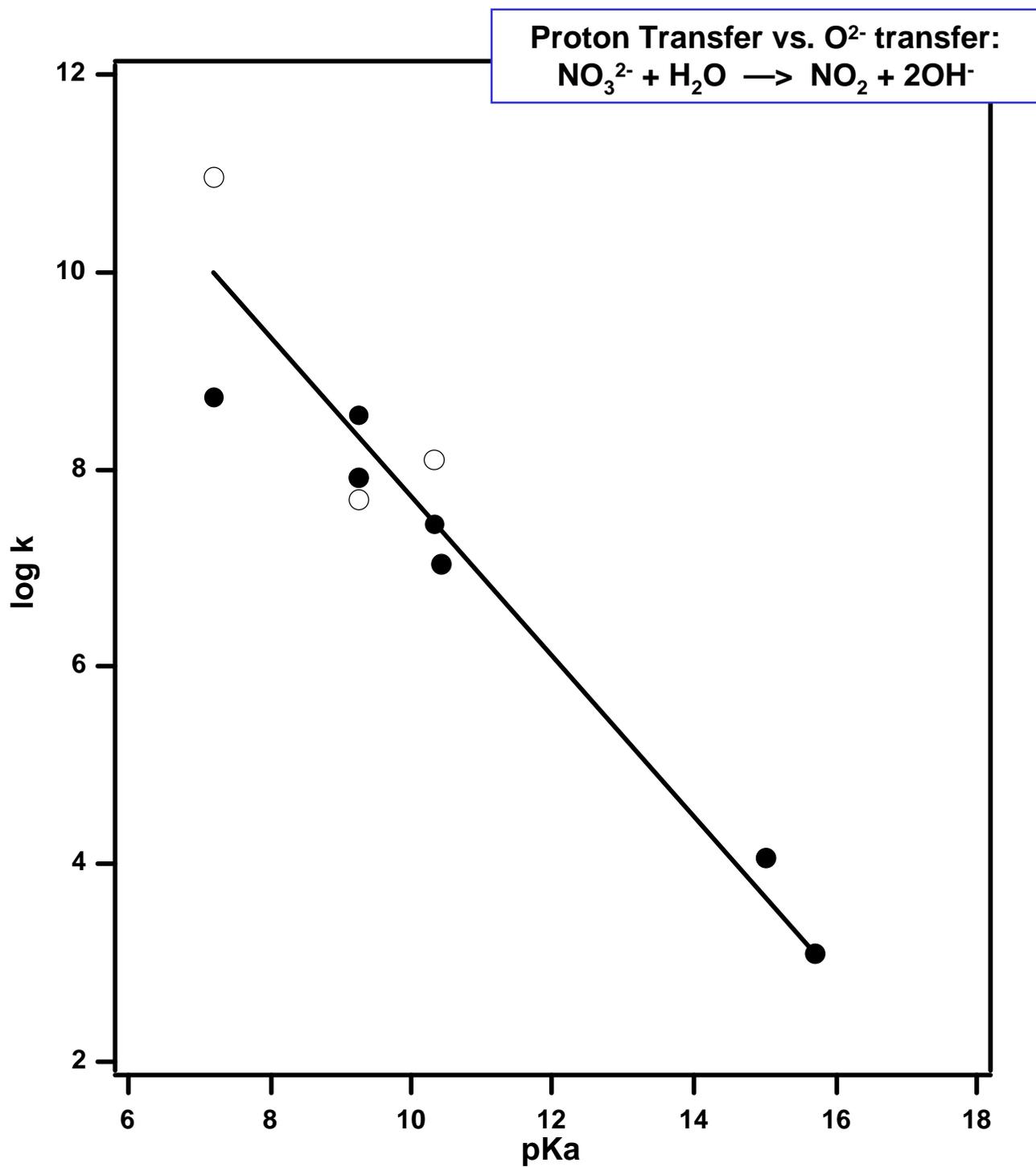
Implications of E_o in Nitrate/Nitrite Mixtures



Reaction of NO_3^{2-} with General Acids



Free Energy Correlation for NO_3^{2-} w / General Acids



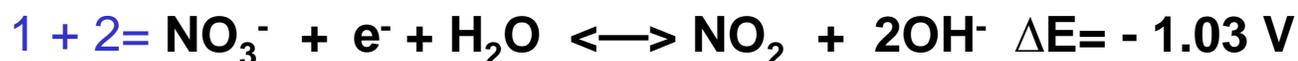
If NO_3^{2-} dissociates directly to NO_2 then E_0 is not pH dependent.

Reaction of NO_2 with oxide ions (O^{2-})?

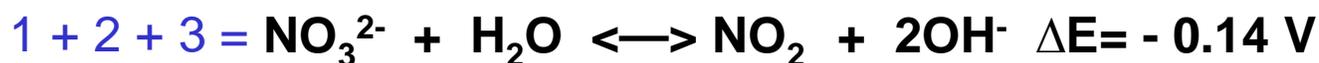
$\text{NO}_3^- / \text{NO}_2^-$ Redox potential of nitrate / nitrite:



$\text{NO}_2^- / \text{NO}_2$ one e- redox potential of nitrate

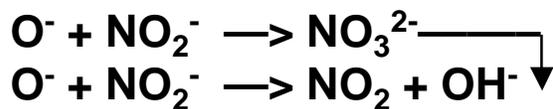
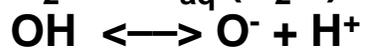
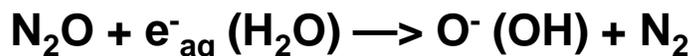
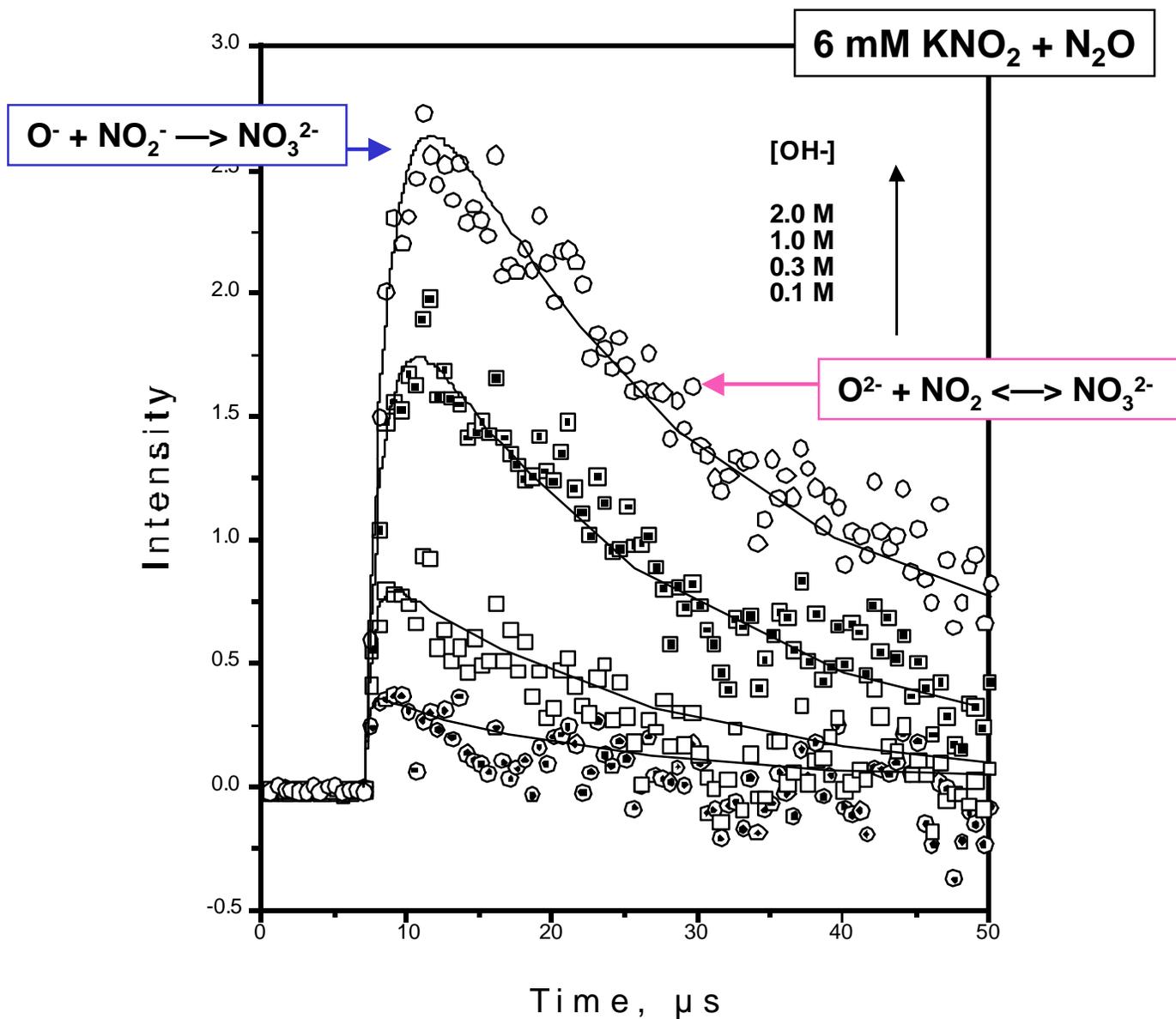


$\text{NO}_3^- / \text{NO}_3^{2-}$ One e- redox potential of nitrate



Formation of NO_3^{2-} from NO_2^-

Time-resolved ESR, no NO_3^- present



Conclusions

(NO_x itself)

The one e- redox product of nitrate, NO₃²⁻,
is a strong reductant

$$E^{\circ}(\text{NO}_3^- / \text{NO}_3^{2-}) = -0.9 \text{ V}$$

$$(g=2.00458, a=43.4, w=0.2 \text{ G})$$

NO₃²⁻ and NO₂ easily interconvert

$$E^{\circ}(\text{NO}_2 / \text{NO}_2^-) = + 1.0 \text{ V}$$

NO₃²⁻ transfers O²⁻ to acids (H₂O)

HNO₃⁻ is dissociative

O⁻ adds to NO₂⁻ to give NO₃²⁻

$$E^{\circ}(\text{O}^- / \text{O}^{2-}) = + 2.5 \text{ V}$$

O²⁻ adds to NO₂ to give NO₃²⁻

Reactions of NO_2 with Organic Complexants in Water: Experimental Approach

- Use γ Source to Irradiate Alkaline NaNO_3 , NaNO_2 Solutions Containing the Complexant , or
- Contact N_2 Gas Stream Containing 10-200 ppm NO_2 With an Alkaline Aqueous Solution of the Organic Ion
- Analyze by Ion Chromatography and NMR.

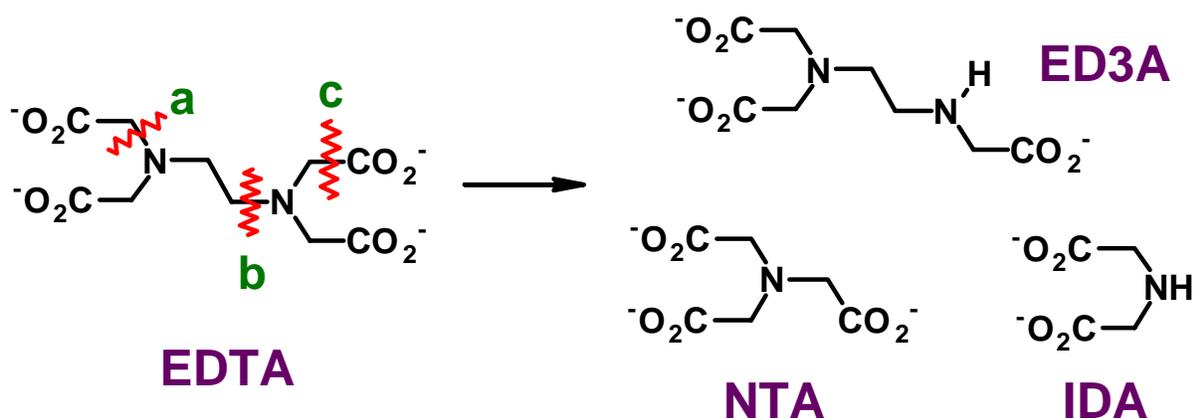


Relative Rates of Disappearance of Organic Compounds in Waste Simulants upon γ -Radiolysis

Substrate	k_{rel}
u-Ethylenediaminediacetic (EDDA)	13
s-EDDA	13
IDA	12
NTA	10
HEDTA	14
Glycine	7
Glycolate	5
EDTA	6
Formate	1 (per definition)
Citrate	0.7
Acetate	0.7

In 3.75 M NaNO₃, 1.25 M NaNO₂, 2 M NaOH and at 20°C.

Reaction Pathways and Products

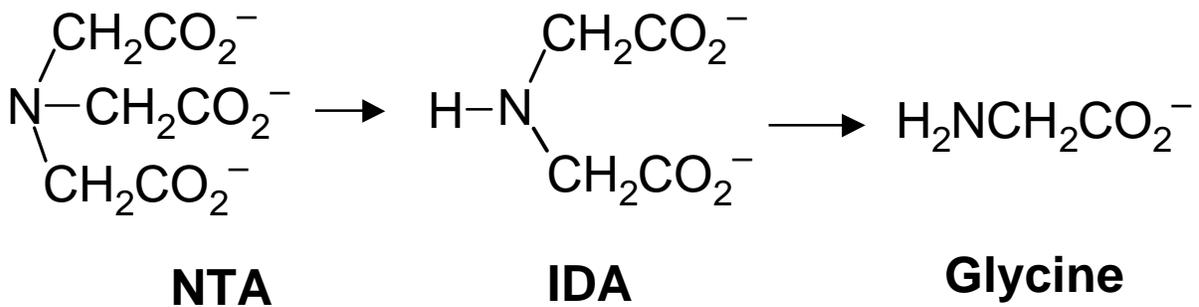
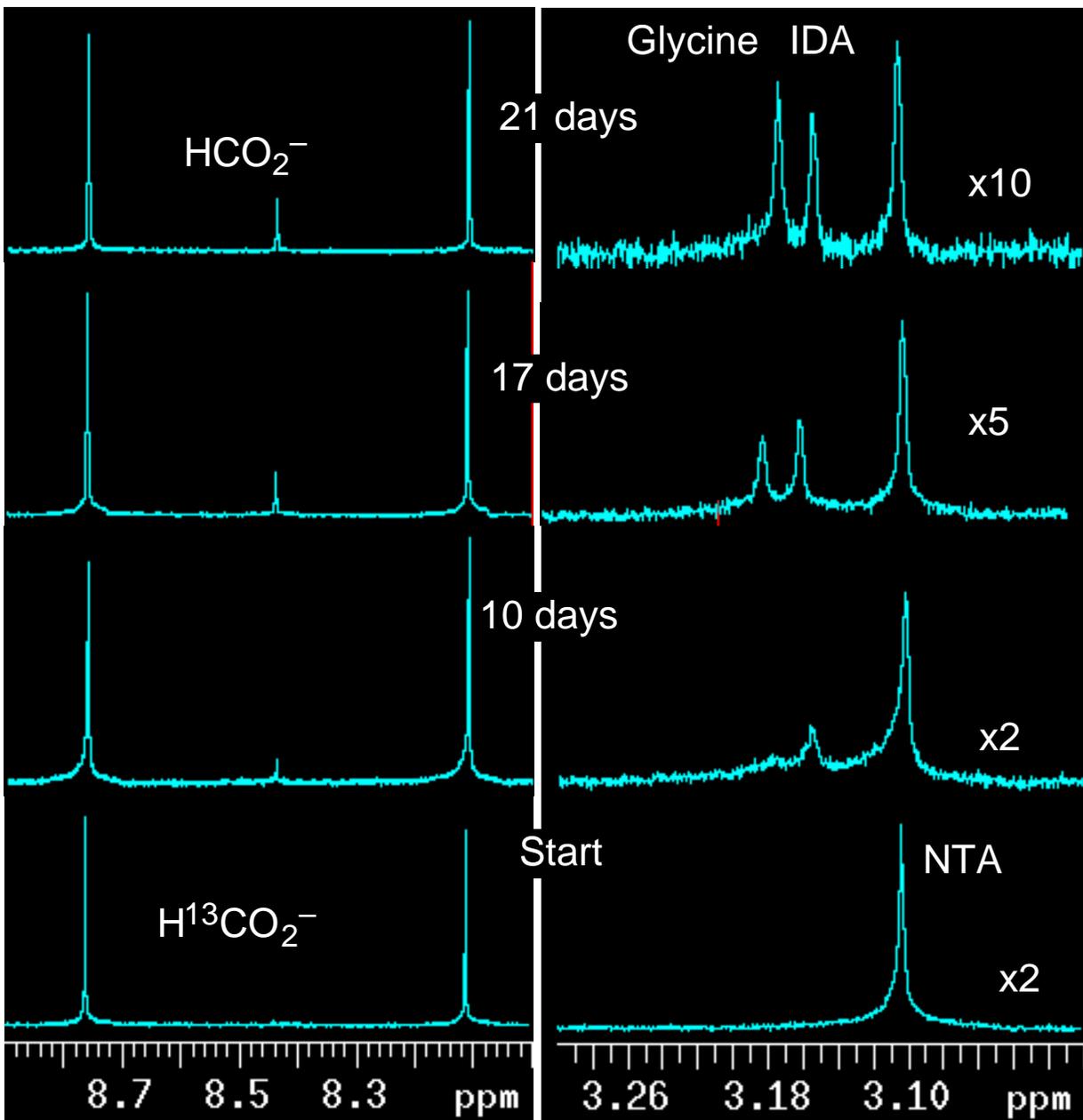


- a:** $\rightarrow \text{CO}_3^{2-} + \text{HCO}_2^- + \text{ED3A}$ “Decarboxylation” via Attack at $-\text{CO}_2^-$ or $-\text{N}<$
b: $\rightarrow \text{NTA} + \text{IDA}$ “H-abstraction” via Attack at CH_2 of $-\text{N}<$
c: $\rightarrow \text{O}_2\text{CCO}_2^- + \text{ED3A}$ “H-abstraction” via Attack at CH_2 of $-\text{N}<$

^1H NMR Spectra of NTA/Formate Solution

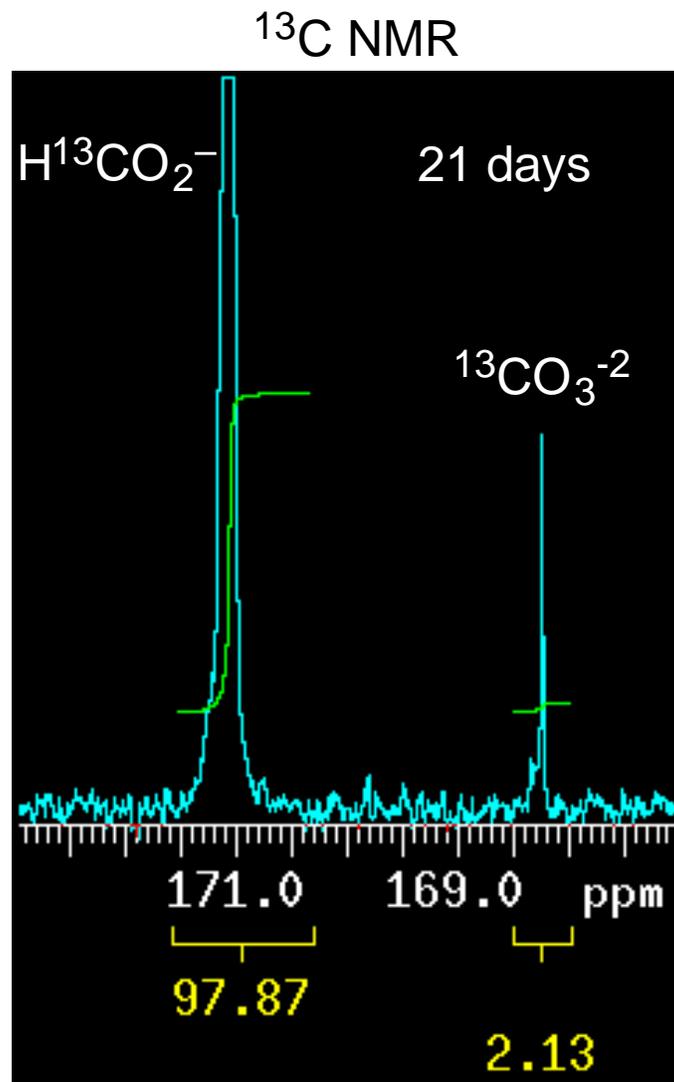
Contacted with ~ 10 ppm NO_2

0.02 M NTA, 0.2 M $\text{H}^{13}\text{CO}_2^-$, 1 M OH^- , 24 $^\circ\text{C}$



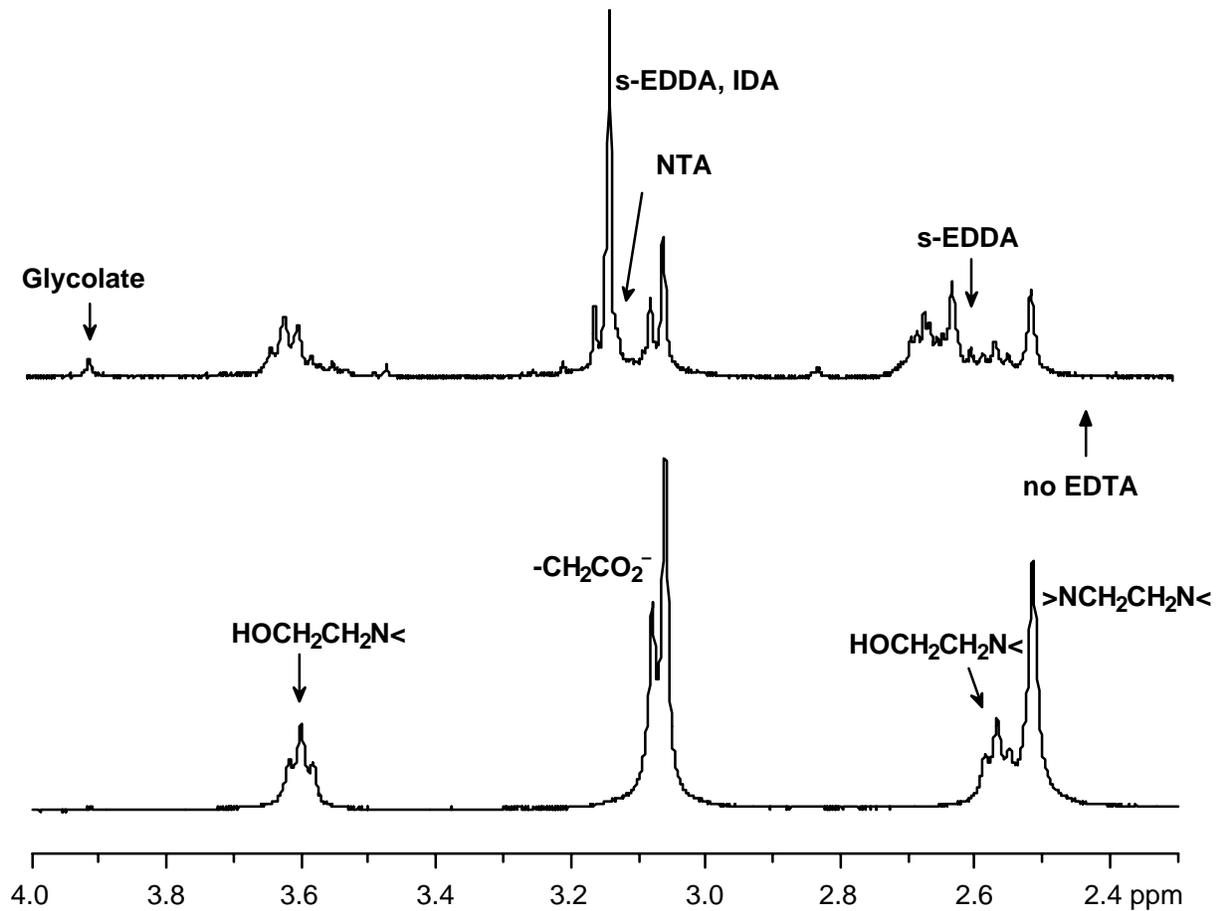
NTA/Formate Contacted with ~10 ppm NO₂

0.02 M NTA, 0.2 M H¹³CO₂⁻, 1 M OH⁻



^1H NMR Spectra of HEDTA in Waste Simulant before and after γ Radiolysis

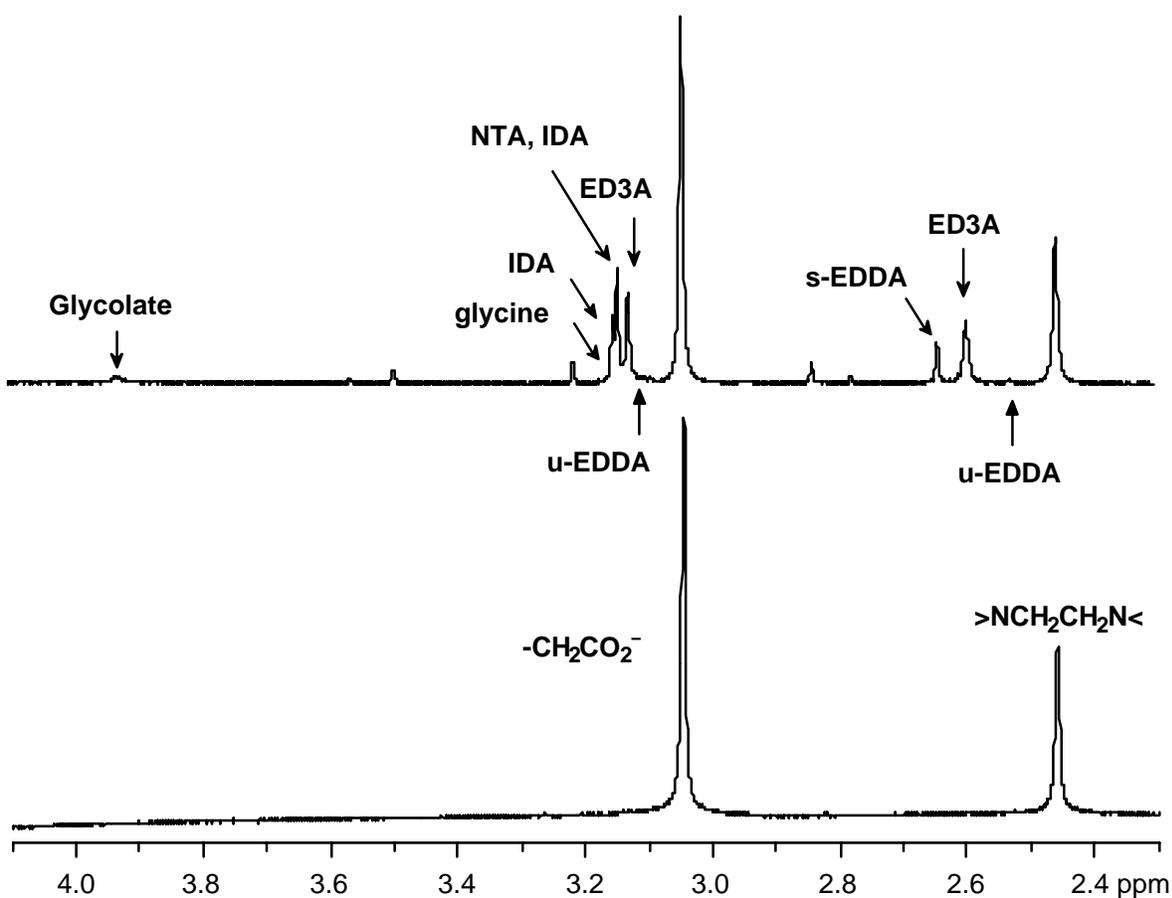
18 Mrad, at 25 °C



Initially 0.04 M HEDTA in 2 M NaNO₂, 2 M NaNO₃, 2 M NaOH

^1H NMR Spectra of EDTA in Waste Simulant before and after γ Radiolysis

18 Mrad, at 25 °C



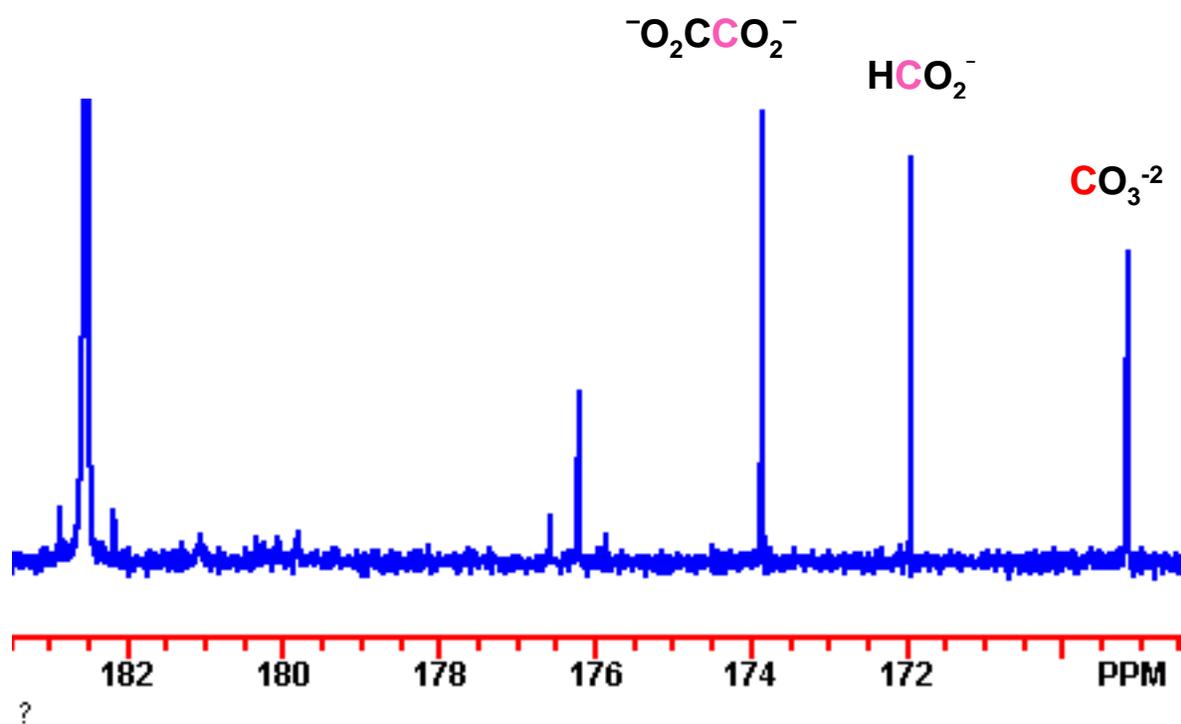
Initially 0.04 M EDTA in 2 M NaNO₂, 2 M NaNO₃, 2 M NaOH

^{13}C NMR Spectra of Products from 1- & 2- ^{13}C -Glycines

36 days, 10 ppm NO_2^- , RT

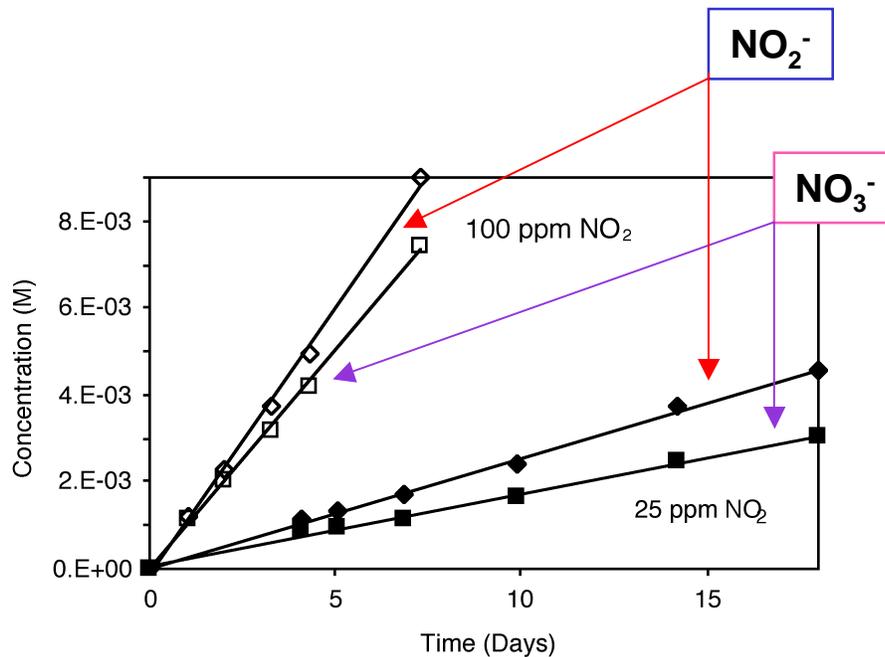
Initially:

- 0.1 M Glycines
- 1 M NaNO_2^-
- 1M NaOH

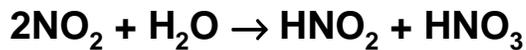
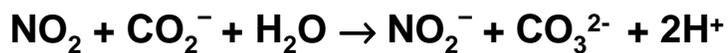


Nitrite Ion Traps Organic Radicals, Suppresses Formation of Adducts

Reduction of NO₂ by formate (contact experiments)

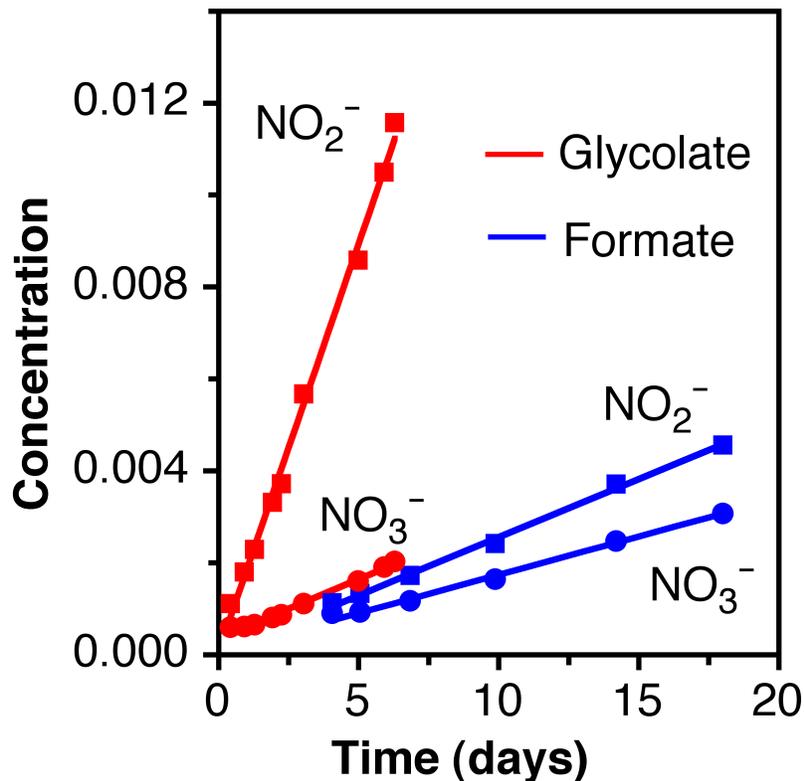


Concentrations of NO₃⁻ and NO₂⁻ in solution vs. time upon contact with NO₂/N₂ gas. NO₂⁻ grows faster than NO₃⁻ due to reduction by formate.



Comparison of Results for Formate and Glycolate Ions

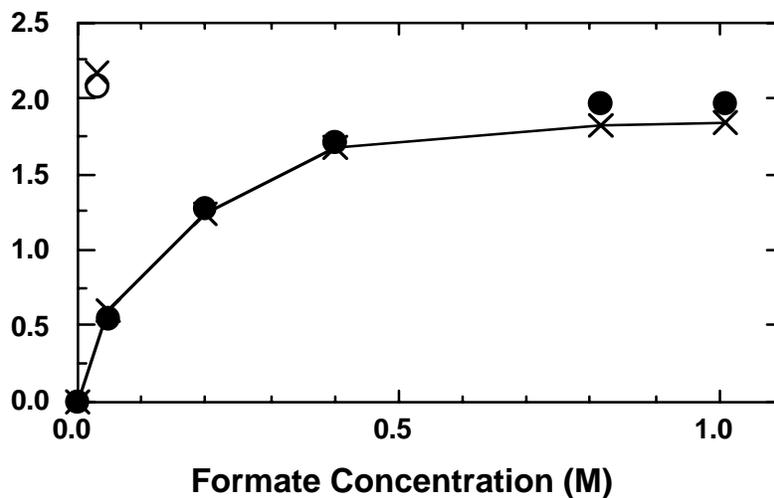
From Contact with 25 ppm NO₂ Gas



Glycolate is ~20 Times More Reactive Than Formate Ion
Relative Rate Measurements on Other Complexants Show
NTA (19) ~ Glycolate (19) > IDA (11) > Glycine (7) >
Formate (1)

Since $k \approx 1 \text{ M}^{-1}\text{s}^{-1}$ for Formate Ion, the Relative Reactivities
Equate to Absolute Rate Constants

Measured and Predicted Yield of CO_3^{2-}



Yields and Fractions of Carbonate Ion Produced from H, OH, O^- , and NO_2 During γ -Radiolysis of HLW Simulants Containing Formate

Concentration M		Dose Rate Rad/h	G(CO_3^{2-})		% Distribution of CO_3^{2-}			
OH^-	HCO_2^-		Model	Exp.	OH	O^-	NO_2	H
2	1.0	4.6×10^5	1.9	2.0	57	13	13	5
2	0.1	4.6×10^5	0.8	0.8	7	87	5	1
2	0.03	9.3×10^4	2.5	2.2 [‡]	3	96	0	2
0.1	0.1	4.6×10^5	0.2		42	32	22	5
2	0.1	4.6×10^2	1.5		3	44	52	1

Simulant: 1.25 M NaNO_2 , 3.75 M NaNO_3 , 2 M NaOH . [‡] 0.03 M NaNO_2 , 0.1 M NaNO_3

Abstract Cont.

Heterog. Effects

On the heterogeneity issue, the following discoveries can be noted:

1. All electrons that are produced by the radiation in solid (silica) particles, at least up to 22 nm in diameter, escape the solid and appear in the water. Thus small particles (or high porosity and large surface area materials) will not prevent some of the effects of radiation on water. However, these observations depend on the material
2. All the holes that are generated in the same solid are trapped in the particles. Oxidative processes may or may not (depending on the trap in the solid) be prevented by the solid particle.
3. Either one of these observations can be manipulated by modifying the surface of the particles. However, merely changing the surface charge will not alter the initial conclusions.
4. The charge separation that occurs across the solid/water interface, as described above, may lead to back-reactions at later stages of the radiolytic effects. Thus, H₂ yields may be modified because of re-oxidation of molecular hydrogen by trapped holes.

Specific technological problems that utilized the scientific knowledge developed here can now be outlined:

- A. Quantitative computation of the rate of the degradation of organic compounds in HLW simulants was instrumental in the resolution of the organic tanks issue.
- B. The outlined mechanisms, and later quantitative calculation of the rate of hazardous gas generation in simulants, eventually lead to predictive calculations of gas generation in waste tanks.
- C. Escape of electrons from silica (and/or holes from zirconia) simulates the contribution from near-surface water to gas generation (e.g. in transportation of fissile materials). It should be included in modeling of these systems.

Sources of H₂ from Irradiated H₂O

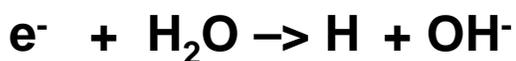
Electrons:



H atoms:

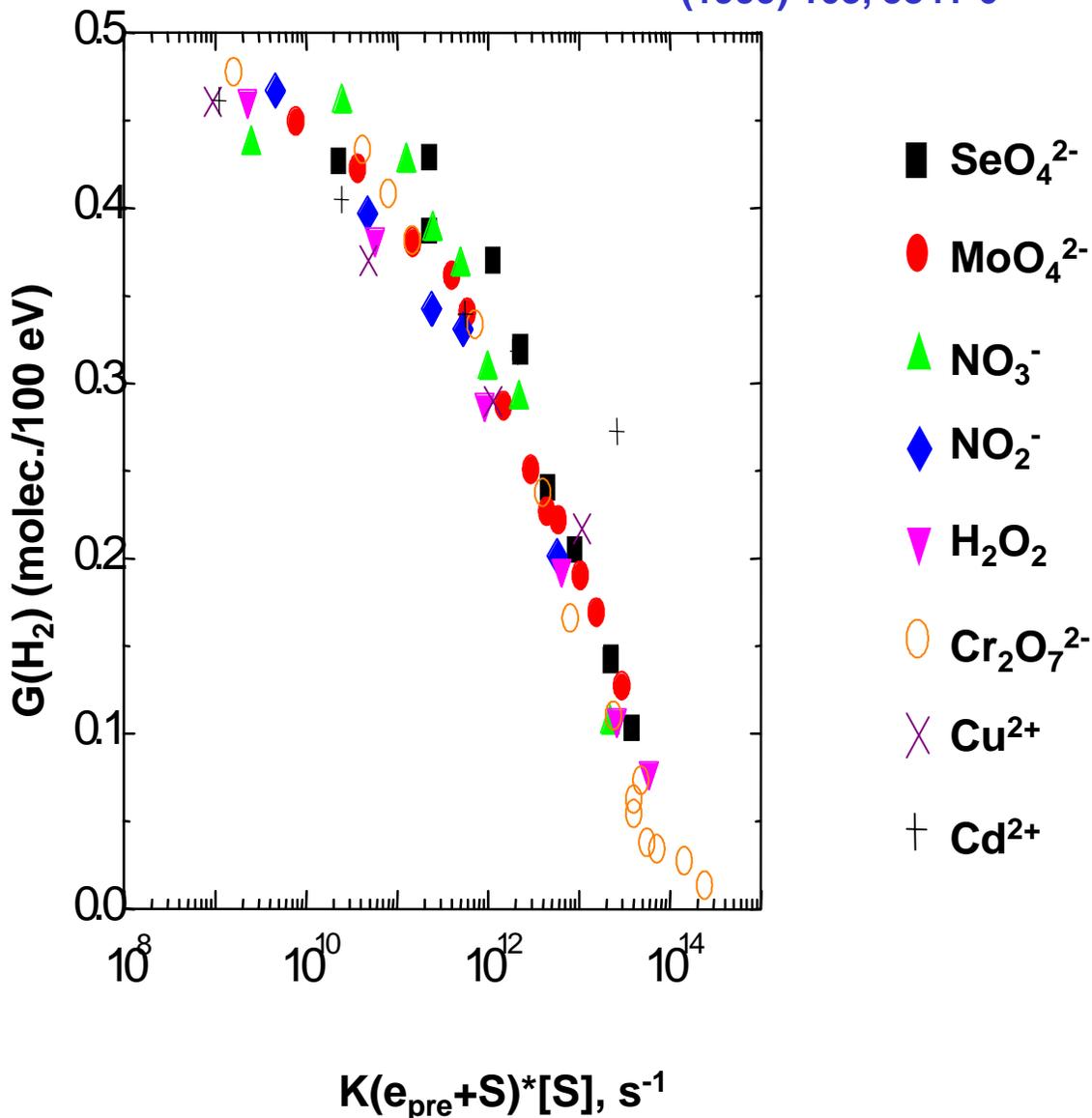


Precursor:



A single curve: H₂ formation from a single precursor

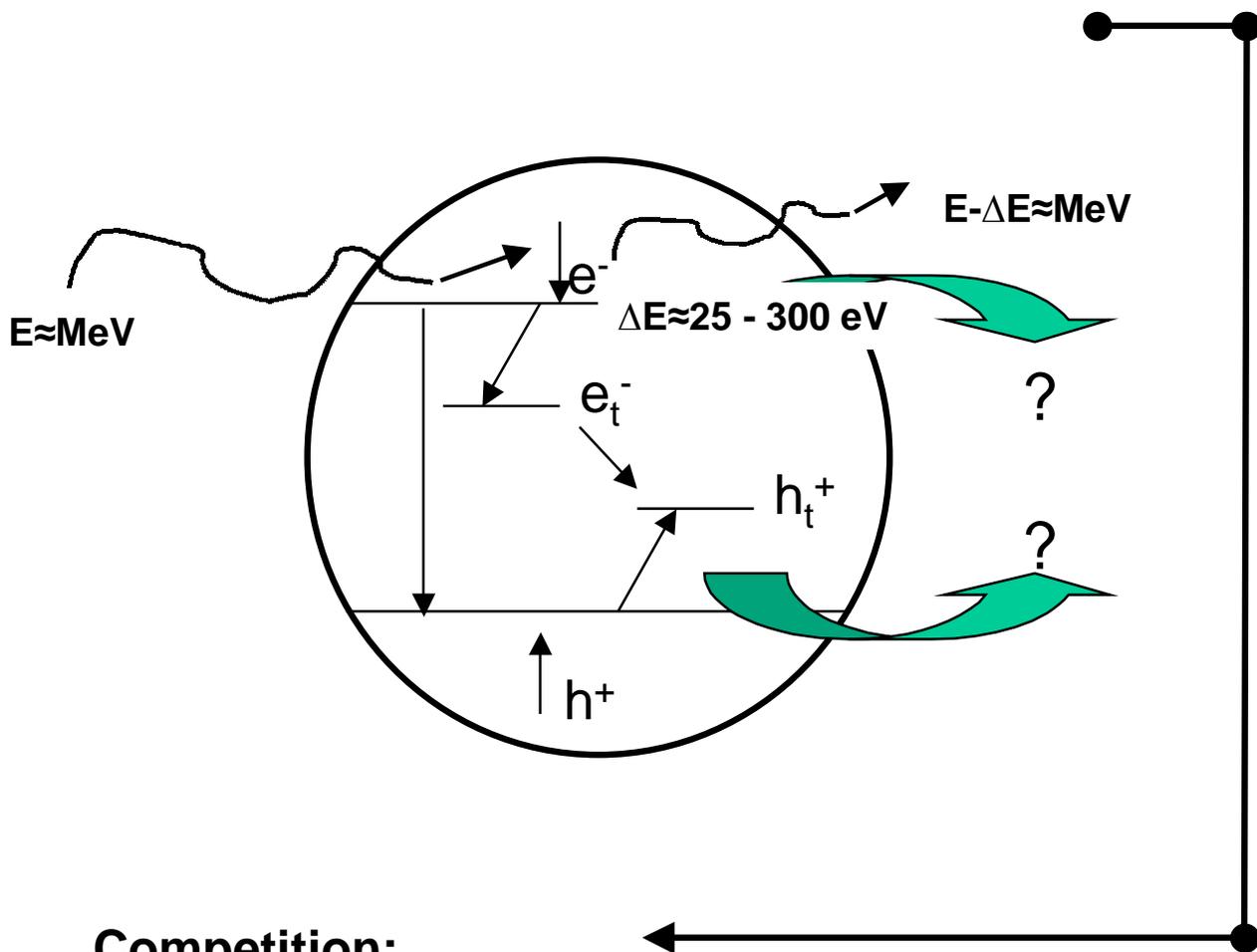
Patina, LaVerne, Pimblott, JPC-A (1999) 103, 5841-6



Energy Deposition in $\text{SiO}_2 / \text{H}_2\text{O}$ Suspensions

High energy particle (e^- , α) travels in the suspension.
 Every so often it encounters:

1. H_2O molecules \rightarrow Water ionization $\rightarrow \text{H}_2$
2. SiO_2 Particle \rightarrow SiO_2 ionization \rightarrow ??

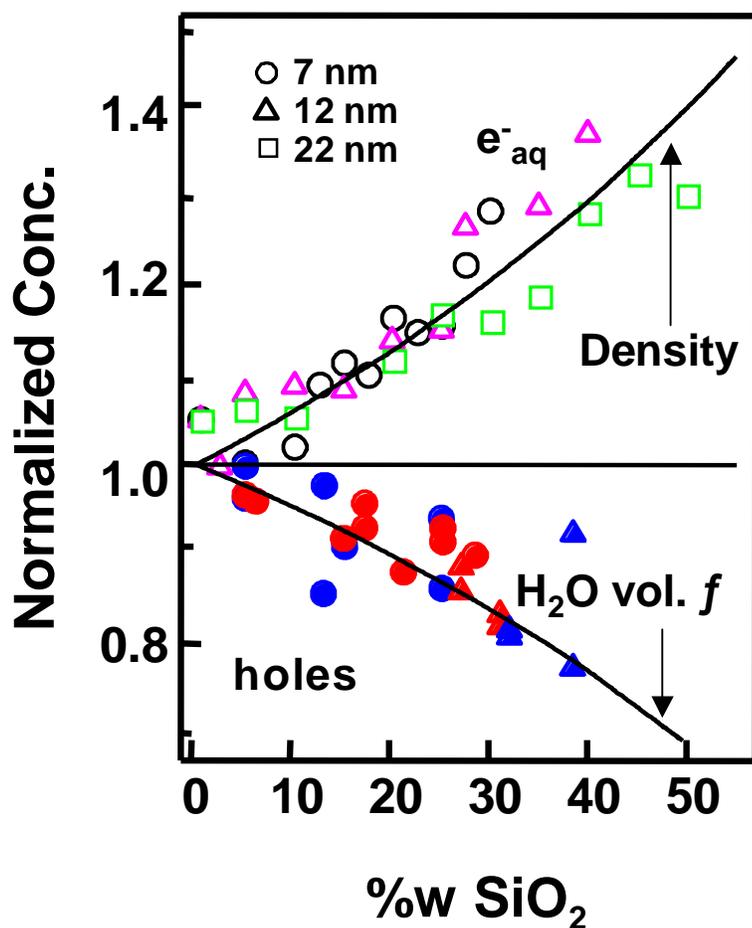


Competition:

1. Thermalization
2. Recombination
3. Trapping
4. Interf. Transfer to Water $\rightarrow \text{H}_2$
 How much?

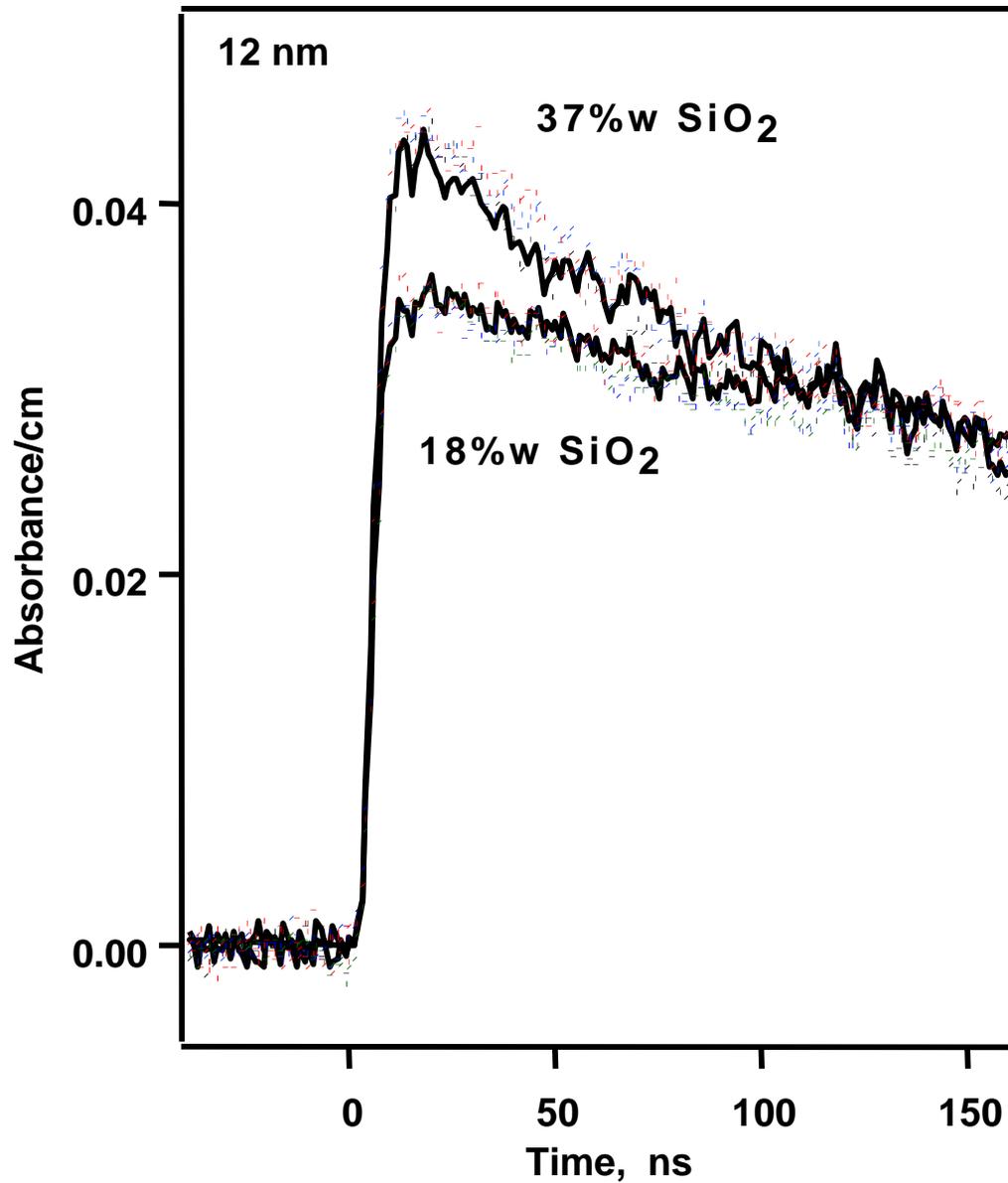
Energy Deposition in SiO₂ / H₂O Suspensions

All e⁻ escape. All h⁺ remain



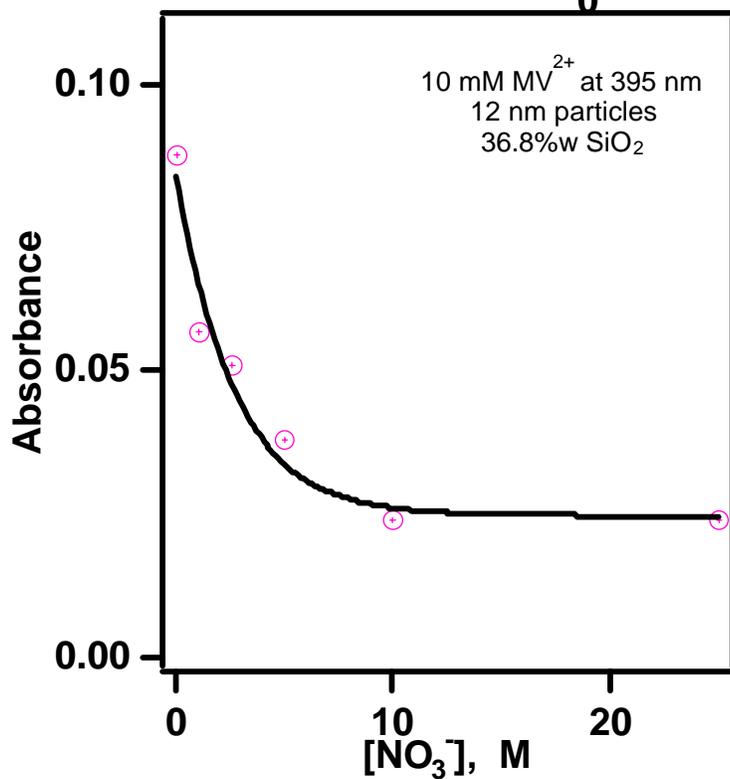
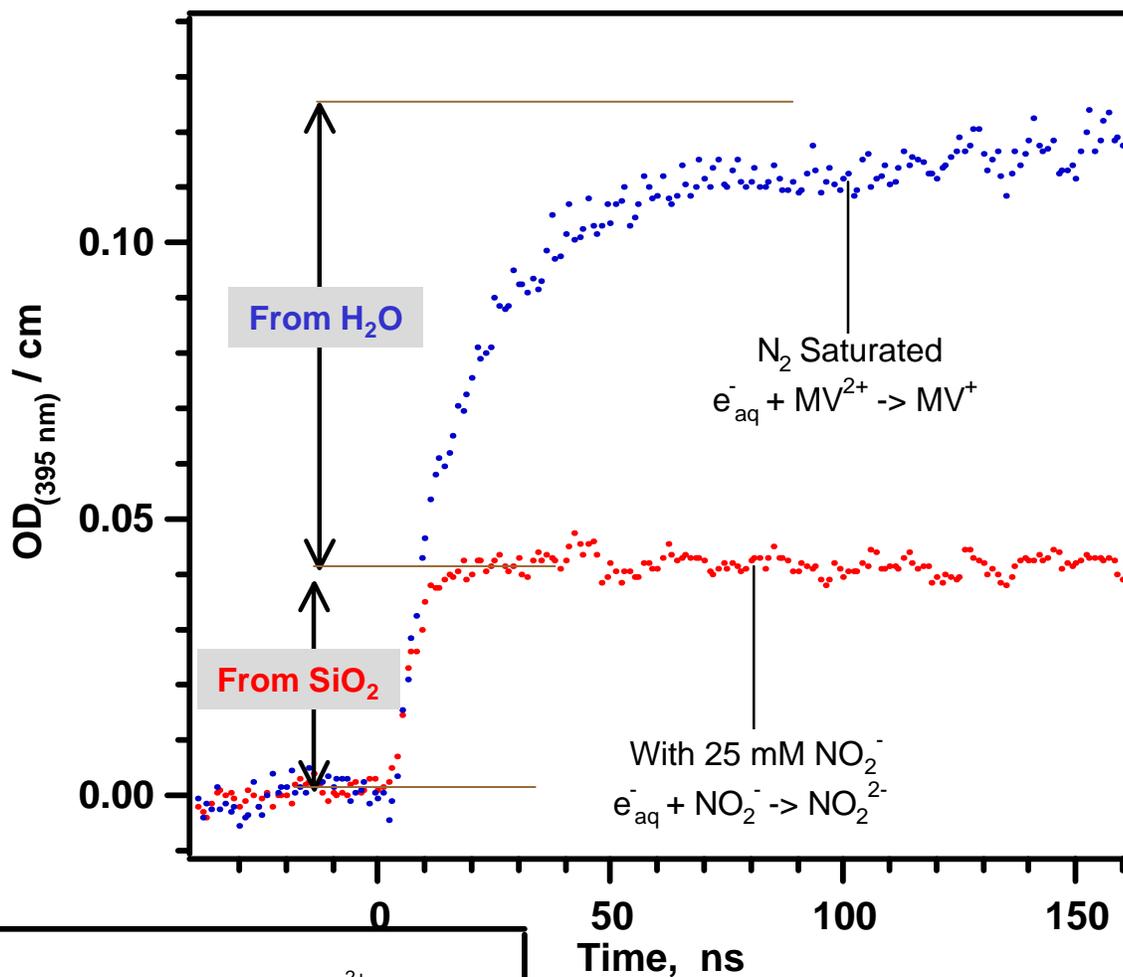
Replacing water with silica (up to 50%w at least) leads to higher yields of e⁻_{aq} (particles ≥ 22 nm)

Surface Potential Effect on e^-_{aq} Yields



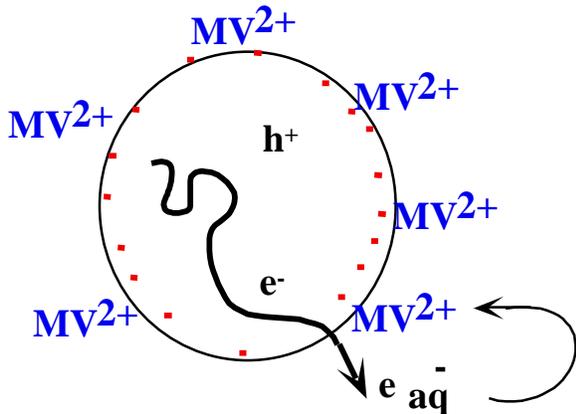
**Mg²⁺ ions, inert to e^-_{aq} but adsorb on the surface.
No effect up to 25 mM Mg²⁺.**

Competition on e^-_{aq} not e^-

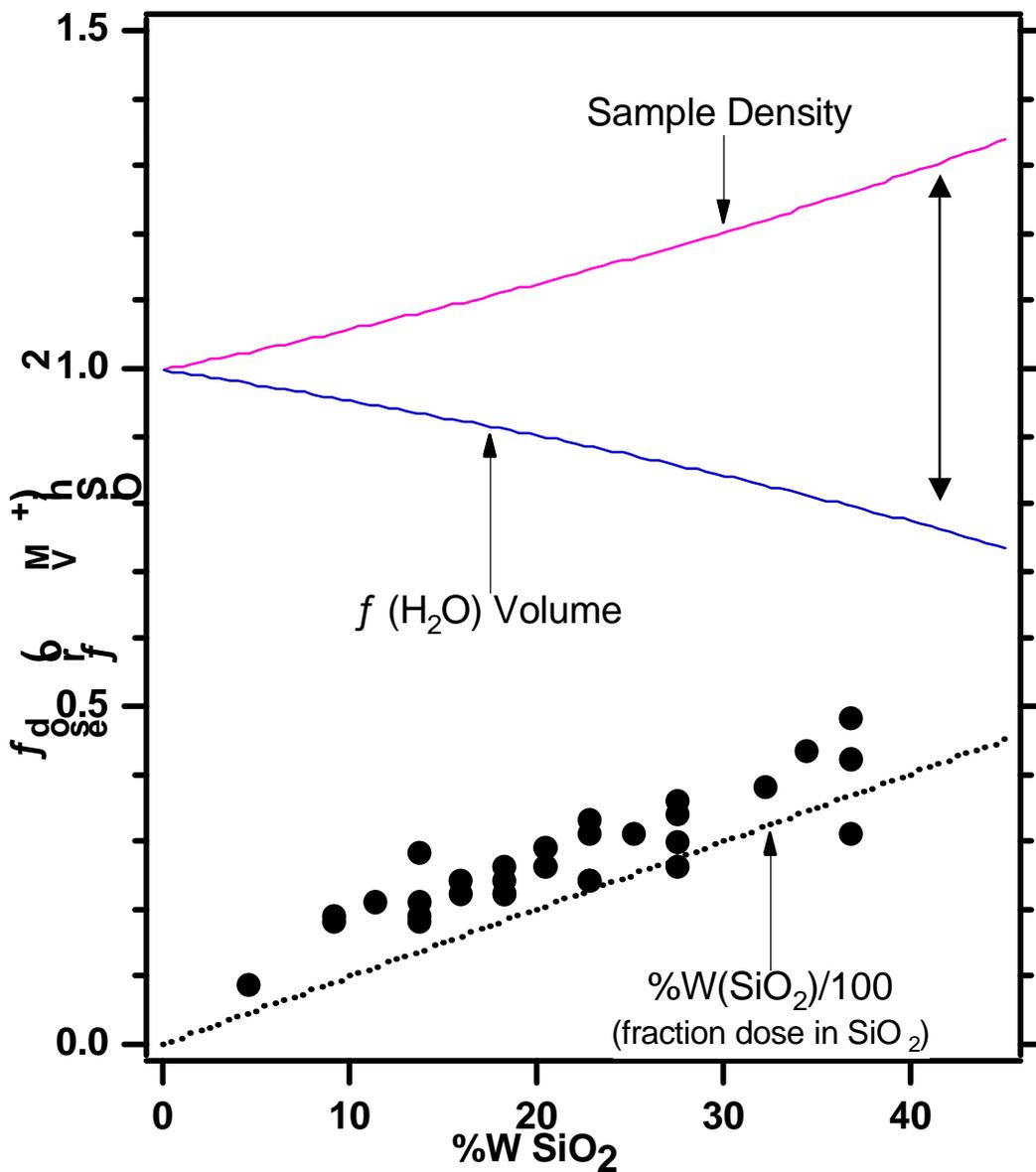


Catching electrons on the fly?

MV^{2+} on SiO_2



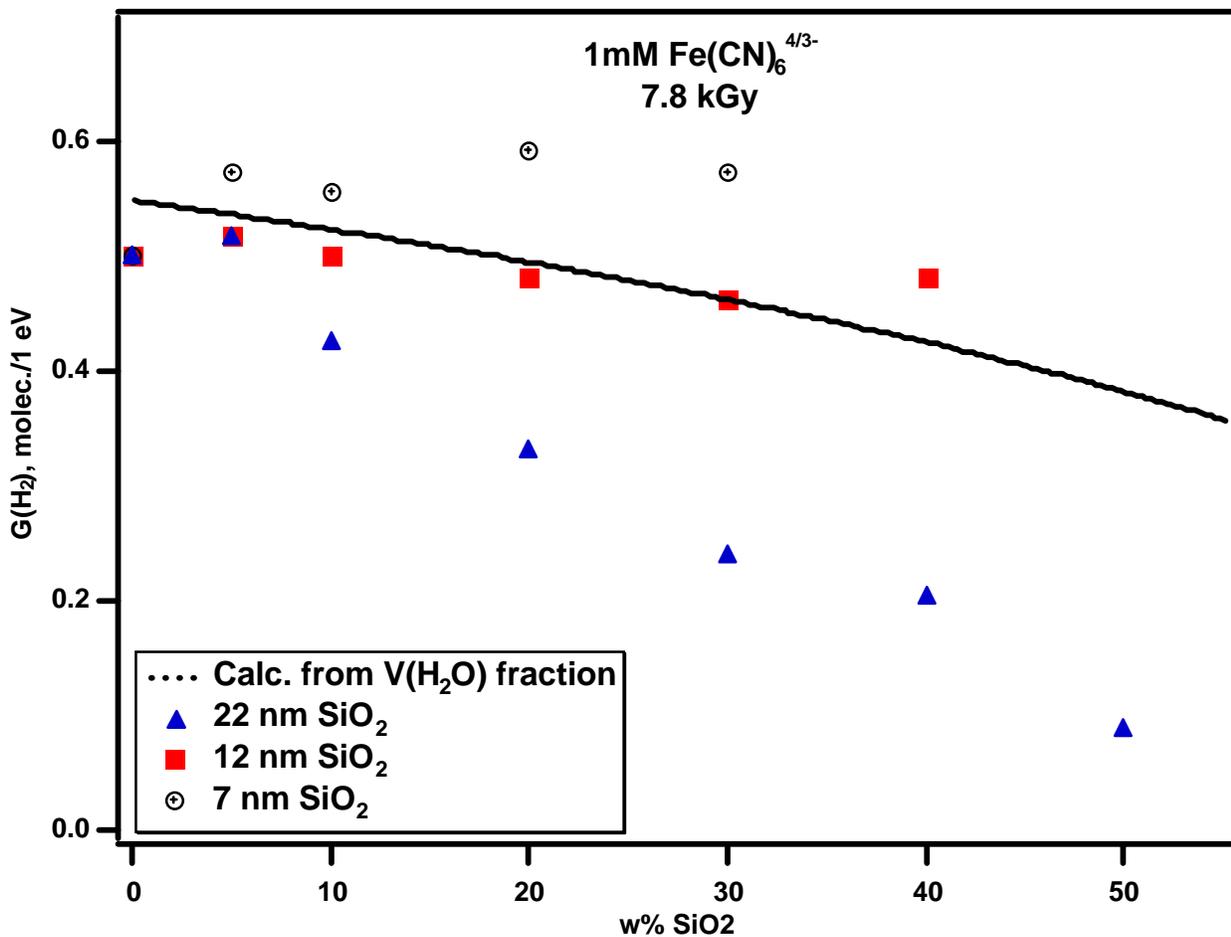
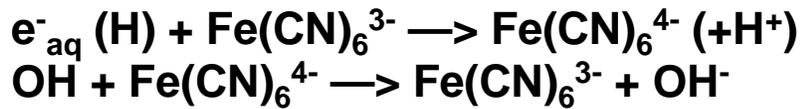
At least all e^- from SiO_2 solvate
(but may be more)



G(H₂) in SiO₂ suspensions

inc. Fe(CN)₆^{3/4-} 1 mM. Away from SiO₂

e⁻_{aq}, & H atoms scavenged by Fe(CN)₆³⁻, OH by Fe(CN)₆⁴⁻:

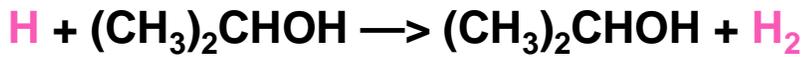


Why is the size dependence?

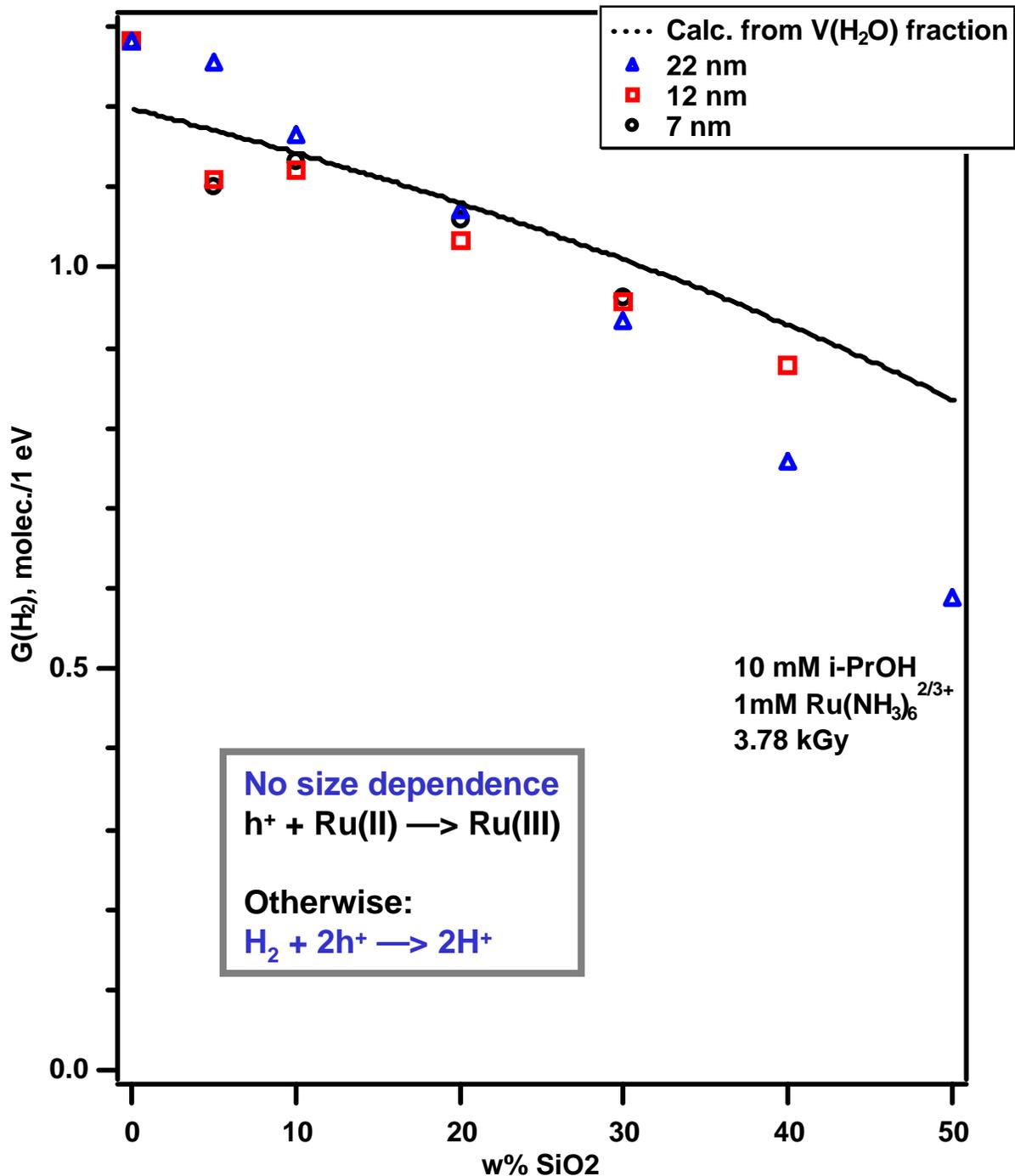
G(H₂) in SiO₂ suspensions

inc. Ru(NH₃)₆^{2/3+} 1 mM, on SiO₂ particles & 10 mM i-PrOH

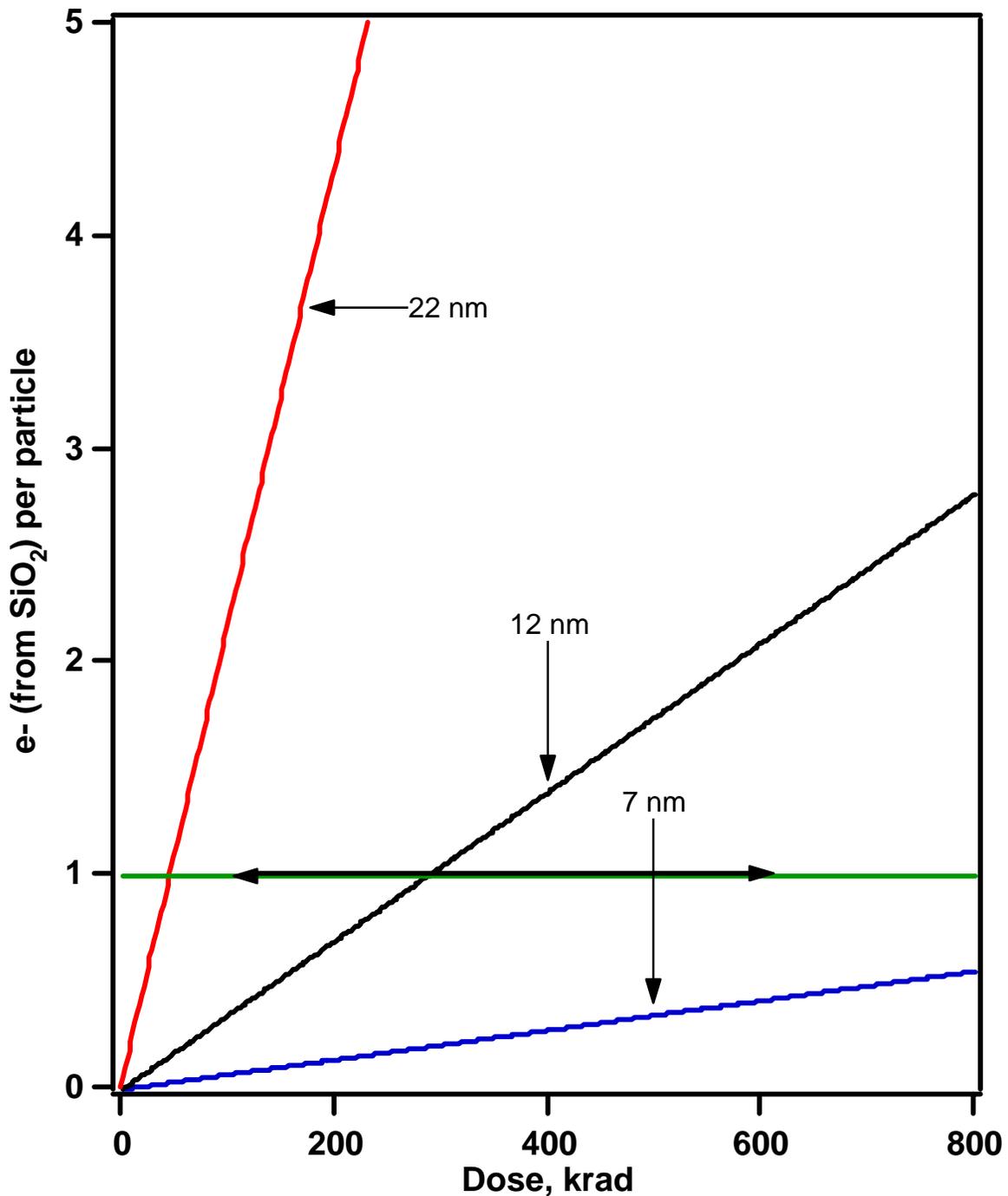
OH & H atoms react w/i-PrOH:



e⁻, e⁻_{aq}, h⁺, & OH react w/ Ru(NH₃)₆^{2/3+} at the surface

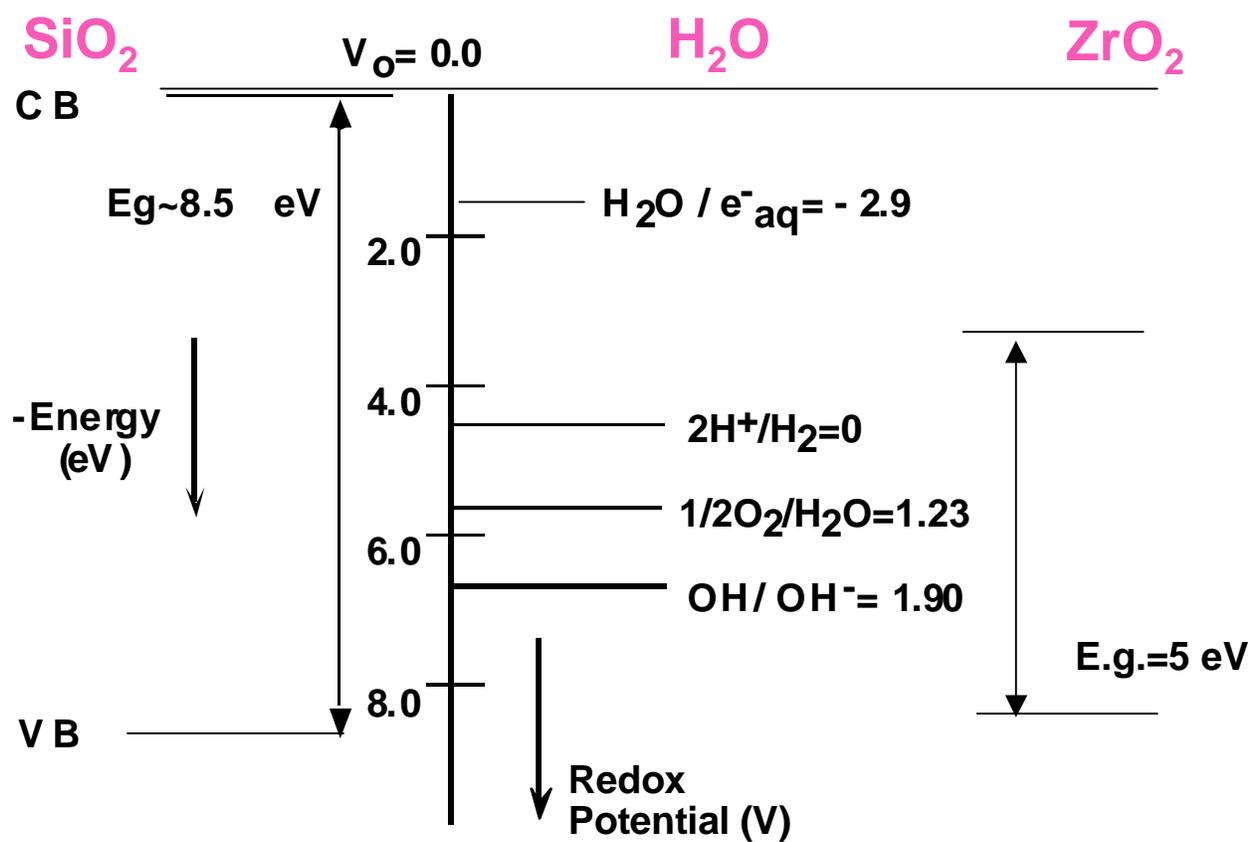


Holes / Particle Reduce $G(H_2)$

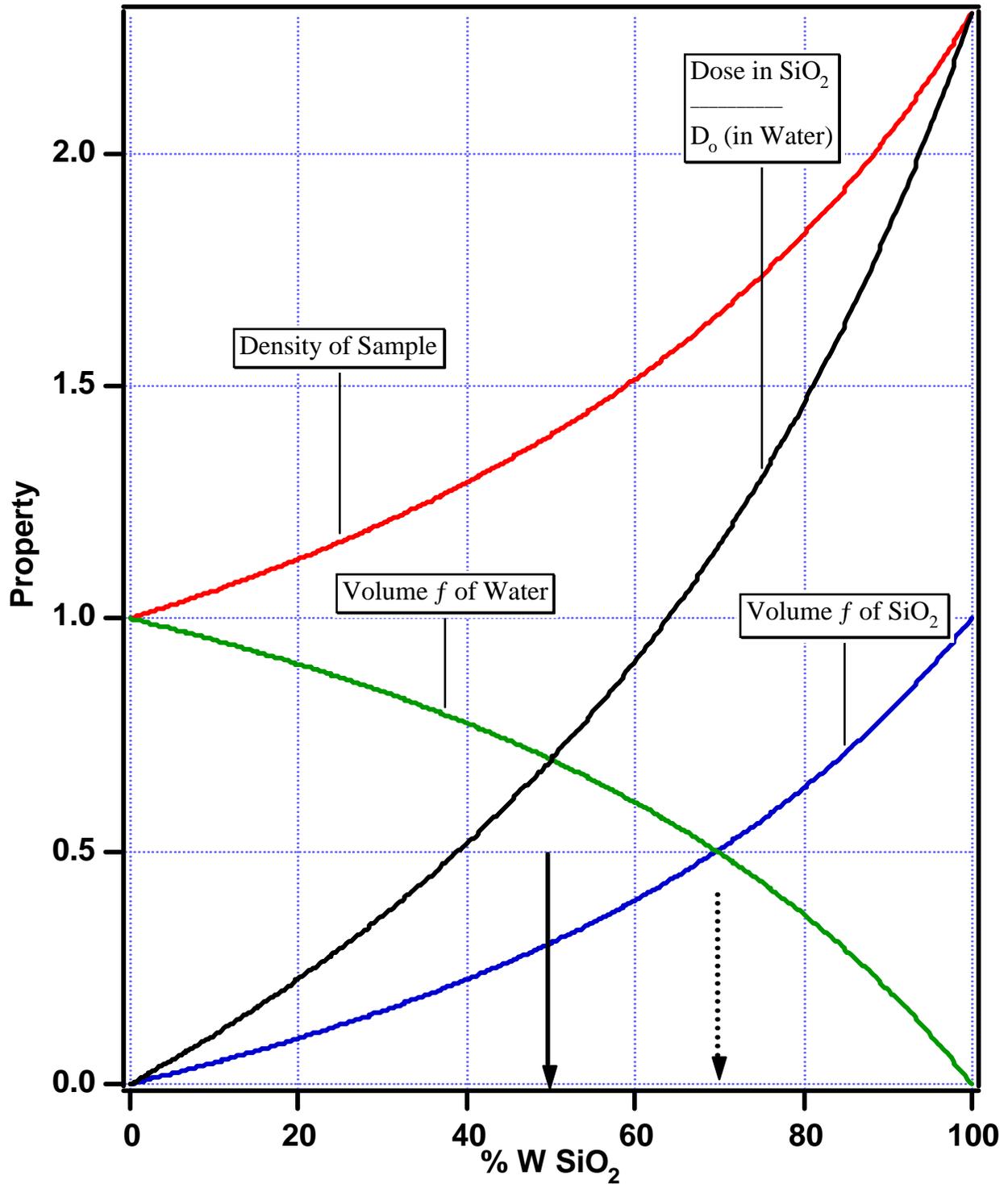
$$h^+ + H_2 \rightarrow 2H^+$$


Size dependence is due to the strong particle conc. dependence. At small sizes (high conc. particles) most particles contain no hole

Energy Levels SiO_2 , ZrO_2 & H_2O



Absorption of Energy in $\text{SiO}_2\text{-H}_2\text{O}$ Suspensions



Conclusions

All of e^- from SiO_2 appear in water

Yield from silica is same as from water

These e^- can contribute to H_2 (like those from water)

Acceptors at the surface can capture e^-

No holes from SiO_2 appear in water

Charges are separated across the interface

h^+ accumulate in particles

Holes may reduce yield of H_2 by back-reactions

ZrO_2 suspensions:

Electron yields much higher

Holes also escape but less efficiently

Caution: adsorption effects of ZrO_2

Acknowledgements

Thanks to:

EMSP

For support of this research

Basic Energy Sciences- DOE

For use of the facilities

Building the expertise

RL and Contractors

For many interactions & coordination meetings that

Provide access to needs

Transfer of knowledge

Implementation of conclusions

Collaborators: For doing the work

At NDRL (& formerly ANL): A. R. Cook (now BNL), N. Dimitrijevic (now ANL), R.W. Fessenden, A. Henglein, H. Miyoshi (now at Tokoshima U., Japan), T. Schatz (now at NSF)

At PNNL: N. Petrik, K. Knutsen, T. Autrey, A. K. Sharma, J. C. Linehan, S. Lea

N. Zevos (SUNY-Potsdam), E. Paparazzo (CNR, Roma)