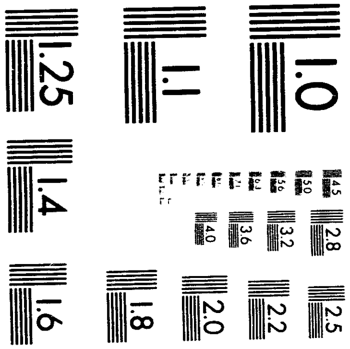
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1.6
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2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6

1 of 1

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Title: CHARACTERIZATION OF THE NITRATE COMPLEXES OF PU(IV) USING ABSORPTION SPECTROSCOPY, 15N NMR, AND EXAFS

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Characterization of the nitrate complexes of Pu(IV) using absorption spectroscopy, ^{15}N NMR, and EXAFS

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Keywords: Plutonium, nitrate, complex, absorption spectroscopy, NMR, EXAFS, nitric acid

The nitrate complexes of Pu(IV) are studied in solutions containing nitrate at concentrations up to 13 molar (M). Three major nitrato complexes are observed and identified using absorption spectroscopy, ^{15}N nuclear magnetic resonance (NMR), and extended x-ray absorption fine structure (EXAFS) as $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_4$, and $Pu(NO_3)_6^{2-}$. The possibility that $Pu(NO_3)_1^{3+}$, $Pu(NO_3)_3^{1+}$ and $Pu(NO_3)_5^{1-}$ are major species in solution is not consistent with these results and an upper limit of 0.10 can be set on the fraction for each of these three nitrate complexes in nitrate containing solutions. The fraction of the three major species in nitric acid over the 1-13 M range has been calculated from absorption spectroscopy data. The fraction of $Pu(NO_3)_6^{2-}$ as a function of nitric acid concentration is in good agreement with the literature, whereas the fraction of $Pu(NO_3)_2^{2+}$ and $Pu(NO_3)_4$ species differ from previous studies. We have modeled the chemical equilibria up to moderate ionic strength (< 6 molal) using the specific ion interaction theory (SIT). Comparison of our experimental observations to literature stability constants that assume the presence of mononitrato species is poor. The stability constant at zero ionic strength for the dinitrato complex is determined to be
$\log(\beta_2^0) = 3.77 \pm 0.14 \quad (2\sigma)$.

Introduction

The nitrate complexes of Pu(IV) in solution were first studied in detail by Hindman using absorption spectroscopy.[1] Hindman used intensity variations in the absorption spectra at 476 nm to identify the species that dominates at 3 M nitric acid as the mononitrato complex. The assignment was very sensitive to the absolute magnitude of the molar absorptivity at 476 nm for both the hydrated Pu(IV) ion and the complex. Hindman adjusted the molar absorptivity of the complex by successive approximation to ensure that the absorption data fit the model for the mononitrato complex. Hindman also identified a hexanitrato complex that dominates at 13 M nitric acid, and a third unassigned species that appears near 8 M nitric acid. Modern instrumentation has made it possible to repeat the earlier absorption spectroscopy work in more detail and allow the conclusions regarding the major nitrate complexes present in solution to be reexamined. Our work shows that the species associated with the peak in the absorption spectra at 476 nm is the dinitrato species. This conclusion affects the models previously used to calculate stability constants for the nitrato complexes of Pu(IV).

Numerous authors have derived stability constants for the mononitrato, dinitrato, and higher complexes of Pu(IV) at various ionic strengths and temperatures.[2,3,4,5] A complete set of stability constants referenced to zero ionic strength has been compiled from the literature and used to model the distribution of species in ground water.[6] The stability constants reported in the literature are based on the assumption that the dominant species at low nitrate concentration is the mononitrato species. We have calculated a stability constant for the dinitrato complex based on direct observation of this species by absorption spectroscopy. Because the mononitrato species was not observed spectroscopically, it must be less than 10% of the total plutonium at all nitrate concentrations. In order for this condition to be true the stability constant of the mononitrato species must be smaller then reported in the literature.

Experimental

Solution preparation. A stock solution of 70 g/l Pu(IV) in 7 M nitric acid was used in most cases. Carefully measured aliquots were added to previously prepared solutions containing appropriate amounts of the perchloric acid, nitric acid, and sodium nitrate required to obtain the desired ionic strength and nitrate concentration. In some cases a stock solution of 100 g/l Pu(III) in 3 M perchloric acid was used and the oxidation state of the plutonium in the resulting solution was adjusted electrochemically. In all cases, the oxidation state was monitored by absorption spectroscopy.

Absorption spectroscopy was done on a Perkin-Elmer Lambda 9 spectrometer using a 0.4 nm step size and a 0.4 nm slit width over the range of 400 - 900 nm in most cases. Variable temperature, multinuclear NMR was done on a Varian 300 MHz instrument. EXAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory.

Absorption spectra of solutions containing more than one nitrato complex are analyzed to obtain the fraction of each species. The observed spectra are assumed to be composed of absorbances from various complexes that add linearly. In addition, a constant background term is assumed; this term could arise, for instance, from non reproducible alignment of the cuvettes. At each wavelength, the absorbance is represented as the sum of the product of the normalized absorbance for each complex ($A_{1,\lambda n}$) and the mole fraction of the complex (x_m), and a background term (B_λ) as shown in Eq. 1.

$$A_{obs,\lambda_n} = x_1 \bullet A_{1,\lambda_n} + x_2 \bullet A_{2,\lambda_n} + x_3 \bullet A_{3,\lambda_n} \ldots + x_m \bullet B_{\lambda_n} \qquad (1)$$

An equation exists for each of the n wavelengths, resulting in n linear equations with m-1 unknowns representing each species. This set of linear equations can be written in matrix form as

$$\boldsymbol{A} \bullet \boldsymbol{x} = \boldsymbol{b} \qquad (2)$$

where A is an m column matrix consisting of the m-1 spectra of the "pure" complexes and a constant background term (we choose a value of 1) for all elements in the mth column. The matrix x is a single column of the m unknowns and the matrix b contains the observed spectrum. Eq. 2 is over determined in this case and the best fit is obtained directly using Eq. 3 in MathCad® where A^T denotes the transpose of

$$x = (A^T \bullet A)^{-1} \bullet (A^T \bullet b) \qquad (3)$$

the matrix A.[7] The "pure" spectrum of each complex is obtained either from spectra where only the aquo complex is present or by subtracting a fraction of one spectrum from another where the appropriate fraction is determined by visual inspection of the residuals. The "pure" spectra are normalized to a constant amount of plutonium.

Results and Discussion

The absorption spectra of Pu(IV) in 1 M perchloric acid, 1 M nitric acid, 8 M nitric acid, and 13 M nitric acid are shown in Fig. 1. The region between 450 - 500 nm shows the most systematic changes with identifiable peaks at 469 nm, 476 nm, 483 nm and 491 nm that are dominant in the respective solutions. Similar absorption spectra taken at small increments in nitrate concentration show that these absorption features rise and fall in intensity, one after the other, and do not shift in position as the nitrate concentration increases. This behavior suggests that four separate Pu(IV) species exist in these solutions.

Pu(IV) in solutions of perchloric acid ranging from 0.1 M to 7 M acid have identical spectra. The lack of change in the spectra of Pu(IV) across a wide range of perchloric acid concentrations is consistent with the noncomplexing nature of the perchloric anion. Thus, in 1 M perchloric acid the Pu(IV) is not complexed with perchlorate and the spectrum arises solely from hydrated Pu(IV). This observation is in agreement with previous studies.[8,9]

The absorption spectrum of TBA2Pu(NO3)6 (bistetrabutylammonium plutonium hexanitrate) solid is virtually identical with the spectrum of Pu(IV) in 13 M nitric acid.[12] The structure of the salts of plutonium hexanitrate derived from x-ray diffraction studies show that the Pu is twelve-coordinated to the oxygens of the six nitrates (each nitrate is bidentate) with the cations lying outside of the inner coordination sphere.[10] Thus, the spectrum in 13 M nitric acid is due to the hexanitrato complex with the all of the nitrates complexed bidentate.

The number of nitrates complexed to the species associated with the peak at 475 nm can be determined by studying the nitrate dependence of the 469 nm and 475 nm absorption features at constant ionic strength using Eq. 4b. The 469 nm feature has been shown to correspond to the hydrated Pu(IV) complex here and in previous work. The ratio of the nitrate complex to the hydrated Pu(IV) is calculated from the absorption spectra of solutions of varying nitrate concentration. This ratio is plotted

$$\beta = \frac{[\mathrm{Pu(NO_3)_x^{+4-x}}]}{[\mathrm{Pu^{+4}}][\mathrm{NO_3}]^x} \quad (4a) \qquad \frac{[\mathrm{Pu(NO_3)_x^{+4-x}}]}{[\mathrm{Pu^{+4}}]} = [\mathrm{NO_3}]^x \bullet \beta \quad (4b) \qquad \text{Eq. 4.}$$

versus nitrate concentration and nitrate concentration squared in Fig. 2 along with the corresponding linear least squares fit. It is clear that the ratio is linear with the square of the nitrate concentration; the data cannot be fit within experimental error to a function linear with nitrate concentration. Therefore, we conclude that the dinitrato complex of Pu(IV) is associated with the peak in the absorption spectrum at 475 nm.

The stability constant for the dinitrato complex at zero ionic strength, β_2^0, is calculated from experimental observations using the specific ion interaction theory (SIT theory). In this formulation the stability constant is a function of the ionic strength as shown in Eq. 5 where ΔZ^2=-14 for the dinitrato complex, I is the ionic strength, and $\Delta\varepsilon$ is the is the sum of ionic interaction coefficients.[11] A matrix of

$$\log(\beta_2^I) = \log(\beta_2^0) - \Delta Z^2 \frac{(0.509 \cdot I^{0.5})}{(1 + 1.5 \cdot I^{0.5})} - \Delta\varepsilon \cdot I \qquad \text{Eq. 5.}$$

solutions was used in which the nitrate concentration is varied for each of ten ionic strengths; 0.107, 0.207, 0.307, 0.407, 0.507, 1.01, 2.01, 3.01, 4.01, and 5.01 molal (m). At each ionic strength a series of five solutions with increasing nitrate concentration was studied (0.026, 0.046, 0.066, 0.086, and 0.106 m nitrate for ionic strengths between 0.107 and 0.507 m and 0.206, 0.406, 0.606, 0.806, and 1.006 m nitrate for ionic strengths between 1.01 and 5.01). The ratio of the dinitrato complex to the hydrated ion is determined using absorption spectra as described earlier. A typical set of absorption spectra at one ionic strength are shown in Fig. 3. The data set consists of 100 spectra; however, disproportionation of Pu(IV) to Pu(III) and Pu(VI) that occurs at low ionic strength with sodium as the cation made some spectra unusable. A total of 86 values for the ratio of the hydrated plutonium to the dinitrato complex was obtained. Fitting these ratios to Eq. 5 yielded a stability constant of $\log(\beta_2^0)=3.77\pm0.14$ (2σ) and $\Delta\varepsilon=0.32\pm0.18$ (2σ). The residuals of the fits to the data suggest that the maximum fraction of a mononitrato complex is less than 0.10 for these data. From this restraint, an upper limit on the stability constant for the mononitrato complex is calculated to be $\log(\beta_1^0)\lesssim1.0$.

Assignment of the nitrato complex associated with the 483 nm peak in the absorption spectrum is difficult using absorption spectroscopy alone. In order to study the nitrate complexes more directly a series of experiments using ^{15}N NMR was conducted. Thorium was used as a surrogate for plutonium in the initial studies because Th(IV) also forms hexanitrato anionic complexes, Th is more easily handled, and the crystal structures of thorium tetranitrato and hexanitrato salts are isomorphic with the crystal structures of the plutonium tetranitrato and hexanitrato salts.[10] A series of ^{15}N NMR spectra of nitrate complexed to thorium was obtained in a solvent of deuterated acetone and CFCl3 at -100 °C as ^{15}N-labeled nitric acid was added. As the nitrate to thorium ratio increases new NMR peaks appear and grow as previous ones diminish as shown in Fig. 4. The assignment of each peak to a specific nitrato complex can be made by the dependence of the intensities on the nitrate-to-thorium ratio. First, the order of the appearance of the peaks with increasing nitrate-to-thorium ratio gives the order of the complexes with increasing number of nitrates. Second, because the thorium concentration is constant, the intensities are directly related to the number of nitrates associated with each complex and the distribution of the complexes. Four nitrato complexes are observed and assigned to $Th(NO3)^{+3}$, $Th(NO3)2^{+2}$, Th(NO3)4, and $Th(NO3)6^{-2}$; no peaks due to the tri- and pentanitrato complexes were observed. The integrated intensities of the observed peaks are plotted as a function of the nitrate to thorium ratio in Fig. 5. The slow rise of the hexanitrato complex is due to competition with the water that is added along with the nitrate (the nitric acid reagent used to obtain the desired nitrate to thorium ratio always had water present). Anhydrous samples of thorium nitrate were made by adding stoichiometric amounts of TBAN (tetrabutyl ammonium nitrate) to Th(NO3)4 salts dissolved in CD3CN. At nitrate to thorium ratios of 4, 5, and 6, the ration of the tetra nitrato peak to the hexanitrato peak was observed to be 1.0:0.0, 0.5:0.5, and 0.0:1.0 respectively. The analogous experiment was carried out for plutonium with the results shown in Fig. 6. At a ratio of 4:1, no ^{15}N peak was observed; at 5:1 a peak was observed at -96.5 ppm; at 6:1 a peak twice as strong was observed at -96.5 ppm. The behavior of the hexanitrato peak is analogous to the behavior of the thorium hexanitrato species. The lack of any observable signal for the plutonium tetranitrato species may be due to changes in the electronic structure of the plutonium upon changes in the complexing ligands. Such behavior has been observed in Co.[12] The tetranitrato species may be more paramagnetic than the hexanitrato species, thereby strongly perturbing the signal from the tetranitrato species. This would result in a broadening of the signal to the extent that it would be lost in the noise. Taken together, these observations suggest that the tri- and pentanitrato complexes for plutonium may not exist to any appreciable extent. This also would suggest that the species associated with the 483 nm peak in the plutonium absorption spectrum arises from the tetranitrato species.

Absorption spectra of Pu(IV) in solutions of nitric acid varying from 1 - 13 M in steps of 1 M were obtained and analyzed using "pure spectra" of the three complexes that are observed in this region. The fraction of each species as a function of nitric acid is shown in Fig. 7. We have labeled these species as $Pu(NO3)2^{2+}$, Pu(NO3)4, and $Pu(NO3)6^{2-}$ based on the arguments given above and supported by evidence we will discuss next.[13]. At 8 M nitric acid the three species exist in nearly equal proportions.

EXAFS spectra of Pu(IV) were obtained in nitric acid solutions of 3 M, 8 M, and 13 M. Pu concentration was 0.025 M. Initial results (not corrected for the phase shifts associated with nitrogen and oxygen) are shown in Fig. 8. The phase shifts will shift the distance scale but are not expected to substantially change the distances between the observed peaks, nor substantially affect the intensities. Three peaks representing the inner coordination sphere dominate the spectra. Oscillations prior to the largest peak are artifacts. Beyond the third peak there is no structure, *i.e.* no order exists beyond the first coordination sphere, as expected for an ion in solution. Preliminary analysis indicates that the first peak arises from the oxygens closest to the Pu cation. The second peak occurs at a distance of 0.5 Å from the first peak and the third peak occurs at a distance of 1.2 Å from the first peak. These distances are consistent with a bidentate coordinated nitrate anion. The nitrogen in nitrate occurs at 0.45 Å beyond the bridging oxygens and the lone oxygen in nitrate occurs at 1.20 Å from the central nitrogen.[14] The intensities of peaks occurring at the same distance and assigned to the same element can be compared to obtain the ratios of the number of atoms. Intensities of peaks that occur at different distances, even if assigned to the same element, cannot be directly compared without a detailed analysis (to be completed later). The intensities of the third peak arise from the apical oxygen of a nitrate species and can be used to count the number of nitrates. These intensities are in a ratio of 6:4.4:2.6. Using the distribution of Pu nitrato species in Fig. 7 for 3 M, 8 M, and 13 M nitric acid, the expected ratio would be 6:4.3:2.5 which is in good agreement with the observed intensities. The intensity of the second peak is due mainly to the nitrogens in the complexed nitrates. The ratio of these intensities follow the ratio of the intensities of the third peak, consistent with each representing one oxygen and one nitrogen of the complexed nitrate. The intensities of the first peak represent the number of closest oxygens. In the 13 M solution the inner coordination sphere consists of 6 bidentate nitrates with 12 closest oxygens. Taking the peak height of the 13 M spectrum as representing 12 oxygens, the average number of oxygens closest to the plutonium in both the 8 M and 3 M solutions is 11. This implies that the hydration number is 7 for the dinitrato species and 3 for the tetranitrato species. Since the crystalline structures for the thorium and plutonium tetranitrate pentahydrate compounds are isomorphous and the thorium compound has three waters in the inner coordination sphere, then the plutonium tetranitrate pentahydrate has three waters in the inner coordination sphere.[10] Thus, for the tetranitrato species, the solid and the solvated ion appears to have the same number of waters in the inner coordination sphere.

Summary

Three spectroscopically distinct Pu(IV) nitrato species are observed in absorption spectra of nitrate containing solutions of Pu(IV). Identification of these three species as the dinitrato, tetranitrato, and hexanitrato complexes of Pu(IV) provides a consistent interpretation of experimental data from three distinct methods. The equilibrium between the hydrated Pu(IV) ion and the dinitrato species was studied at a variety of ionic strengths by varying the nitrate concentration. The observed ratio between these species was used to calculate a stability constant at zero ionic strength. The specific ion interaction theory was necessary to obtain a good fit to the data.

Acknowledgement

We thank Dr. Wayne Smith for his assistance in the electrochemical adjustment of the oxidation state of plutonium in perchloric acid solutions. This work was supported by the U.S. Department of Energy under contract W-7405-ENG-36.

Figure captions

Fig. 1. Absorption spectra of Pu(IV) at a concentration of 4.8 g/l in 1 M, 8 M and 13 M nitric acid and in 6 M perchloric acid. The inset highlights the wavelength region where the largest changes occur. In the inset the vertical dotted lines at 469 nm, 476 nm, 483 nm, and 491 nm show where the maximum absorbance occurs for the hydrated Pu(IV) ion, the dinitrato complex, the tetranitrato complex, and the hexanitrato complex respectively.

Fig. 2. The ratio of intensity of the spectrum associated with the peak at 476 nm to the intensity of the hydrated Pu(IV) ion calculated from absorption spectra is plotted versus (a) the nitrate concentration and (b) the nitrate concentration squared. The solid line is from a linear least-squares fit of the ratio to the (a) nitrate concentration and (b) nitrate concentration squared.

Fig. 3. Absorption spectra of Pu(IV) at a constant ionic strength of 0.106 m are shown as the nitrate concentration increases from 0.02 m to 0.10 m. Perchloric acid is used to maintain the constant ionic strength. The spectra are offset for clarity.

Fig. 4. ^{15}N NMR spectra of ^{15}N-labeled NO_3^- shows the presence of four thorium nitrato complexes at -7.2 ppm, -7.6 ppm, -3.4 ppm, and -4.8 ppm. The solvent is a mixture of deuterated acetone and $CFCl_3$ and the spectra were obtained at -100 °C. Free nitrate first appears at a nitrate-to-thorium ratio of 5.0 at -14.8 ppm and shifts to -9.6 ppm as the ionic strength of the solution increases.

Fig. 5. The integrated intensity of the four ^{15}N NMR peaks shown in Fig. 4 versus the nitrate-to-thorium ratio. The changes in the intensities lead to an unambiguous assignment as shown. No peak is observed for the tri- or pentanitrato thorium complexes.

Fig. 6. The ^{15}N NMR spectra of $^{15}NO_3$- complexed to Pu(IV) at a nitrate-to-plutonium ratio of 5:1 and 6:1. The essentially anhydrous samples were made by adding tetrabutyl ammonium nitrate

Fig. 6. The ^{15}N NMR spectra of $^{15}NO_3$- complexed to Pu(IV) at a nitrate-to-plutonium ratio of 5:1 and 6:1. The essentially anhydrous samples were made by adding tetrabutyl ammonium nitrate stoichiometrically to $Pu(NO_3)_4 \cdot 5H_20$ dissolved in CD_3CN. The peak at -96.5 ppm is assigned to the $Pu(NO_3)_6^{2-}$ species. In the 5:1 solution the intensity of this peak is one half that of the 6:1 solution. A peak for the 4:1 species was not observed, apparently due to an increased paramagnetism of the tetranitrato complex.

Fig. 7. The fraction of the dinitrato, tetranitrato, and hexanitrato complexes of Pu(IV) calculated from absorption spectra are shown as a function of nitric acid concentration.

Fig. 8. Radial distribution function from EXAFS data for Pu(IV) in 3 M, 8 M, and 13 M nitric acid. The magnitude of the Fourier transform of the raw data is shown.

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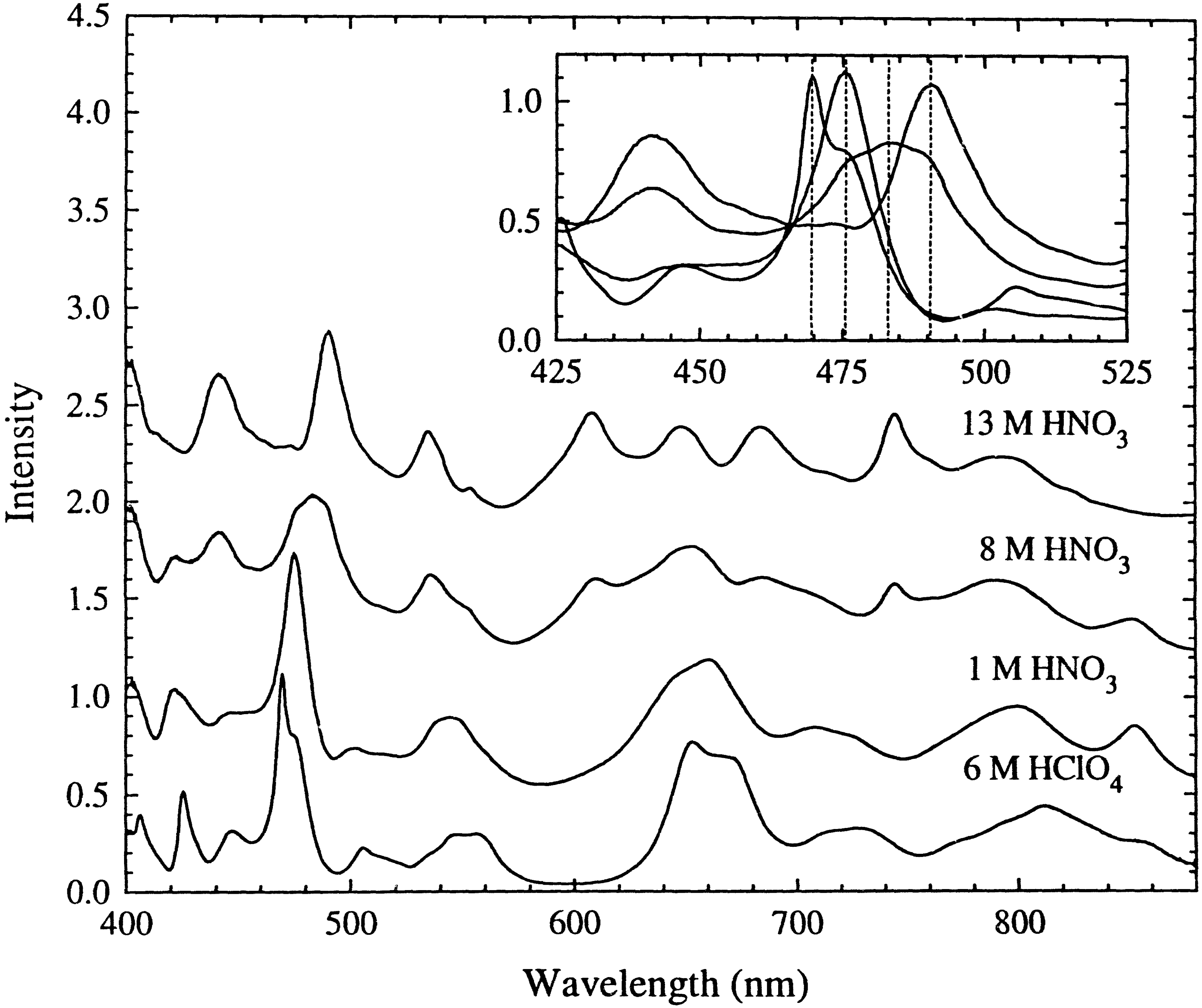
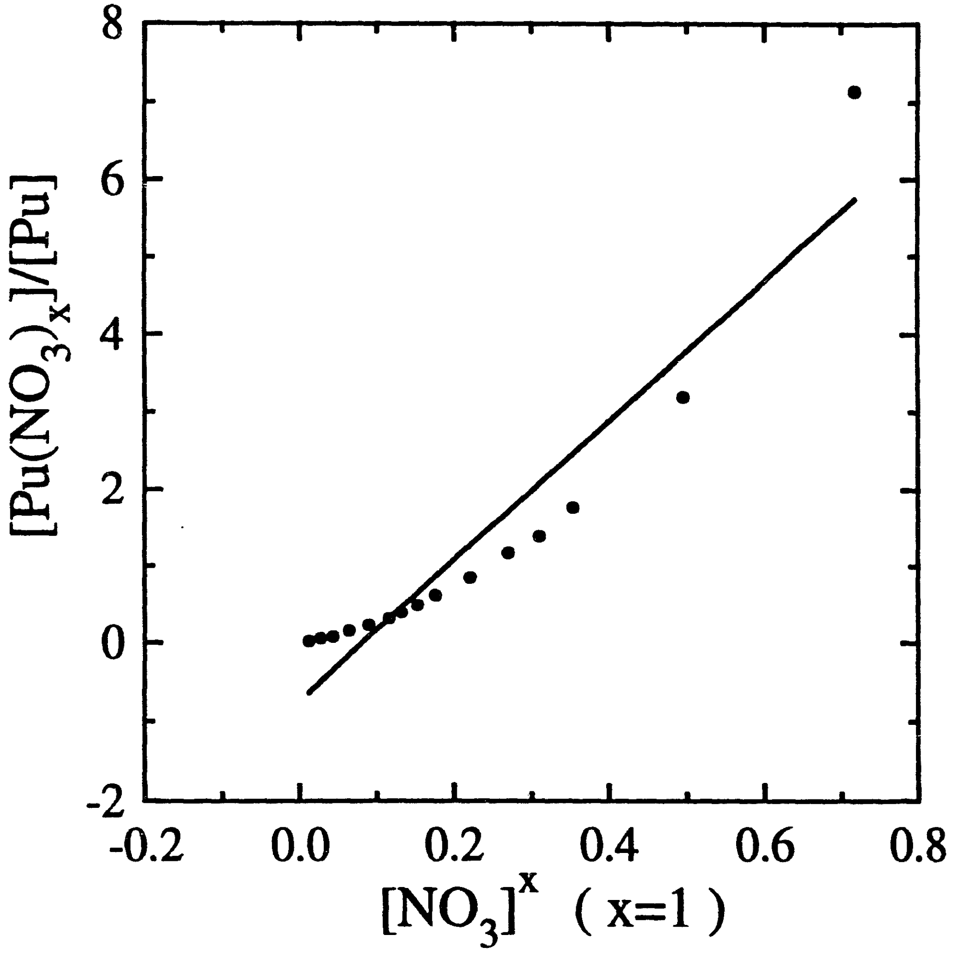
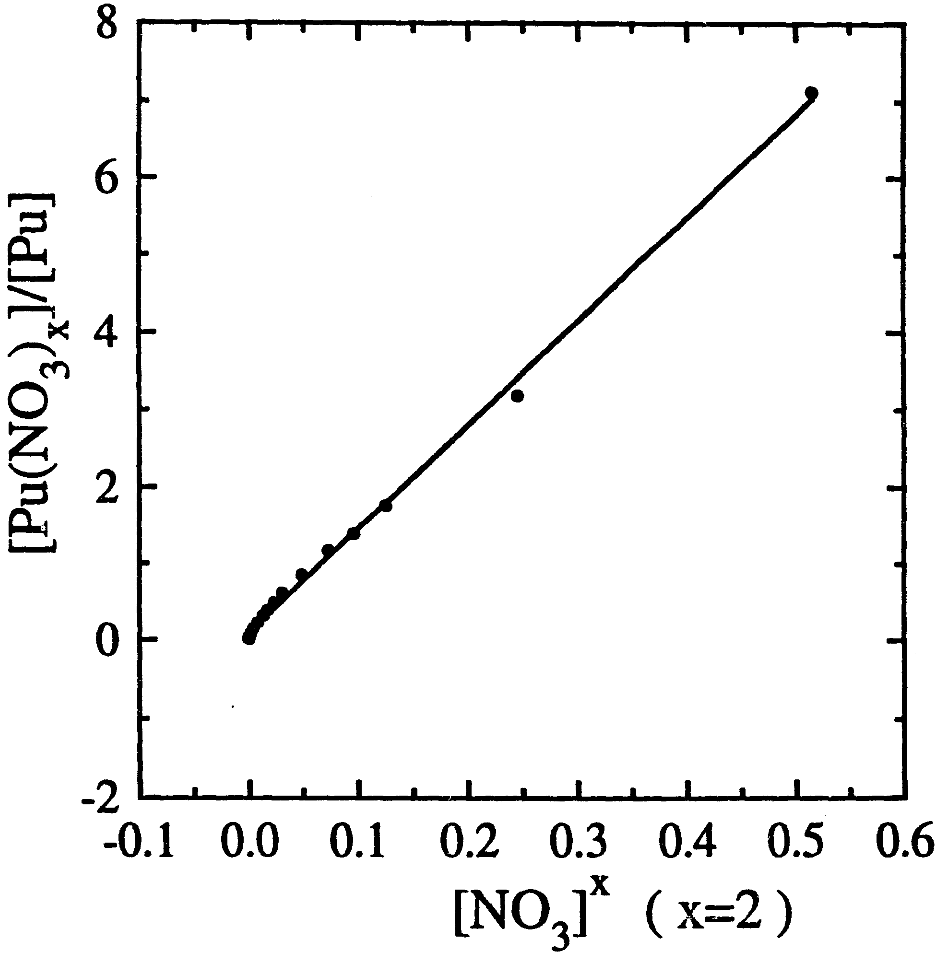
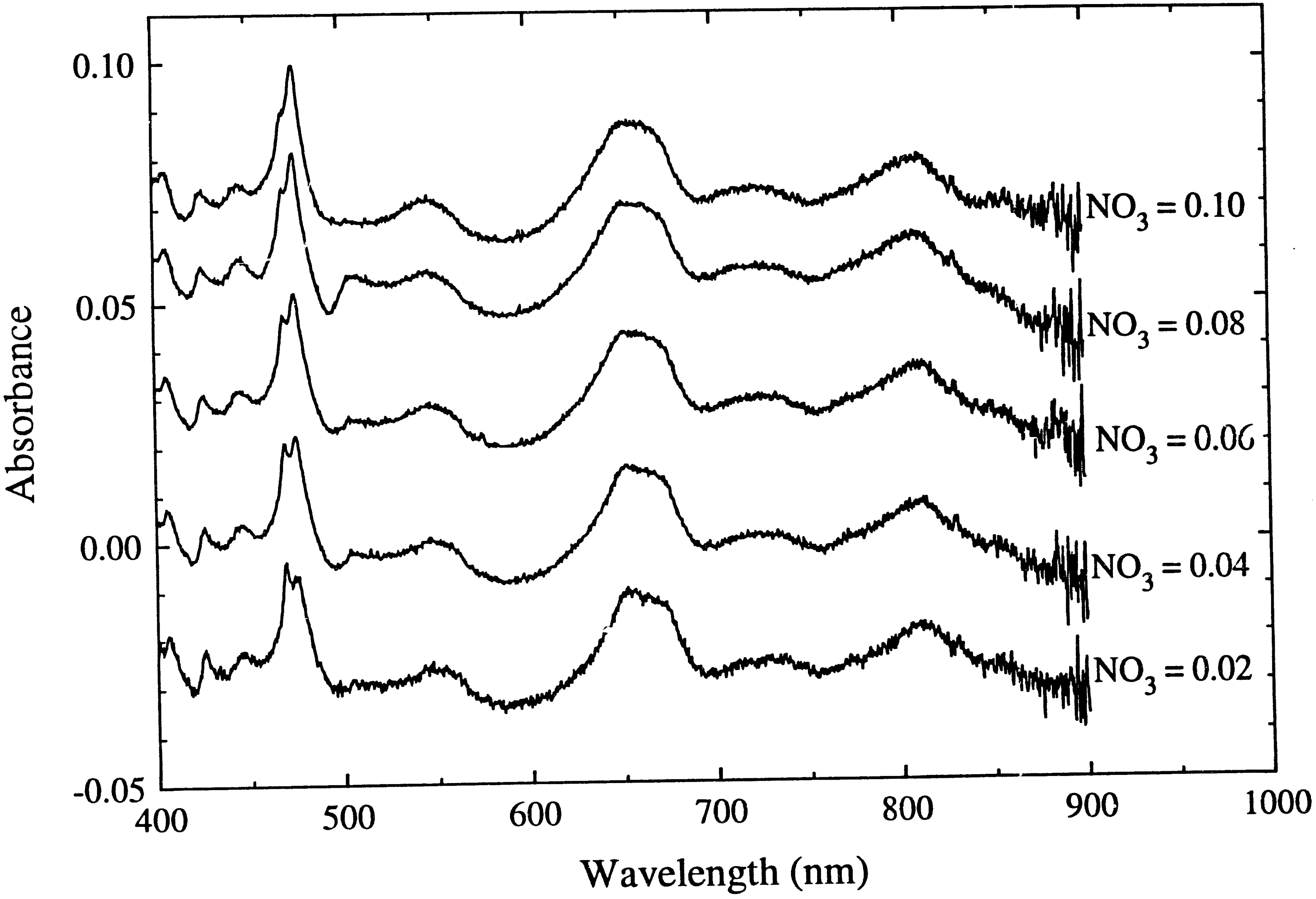
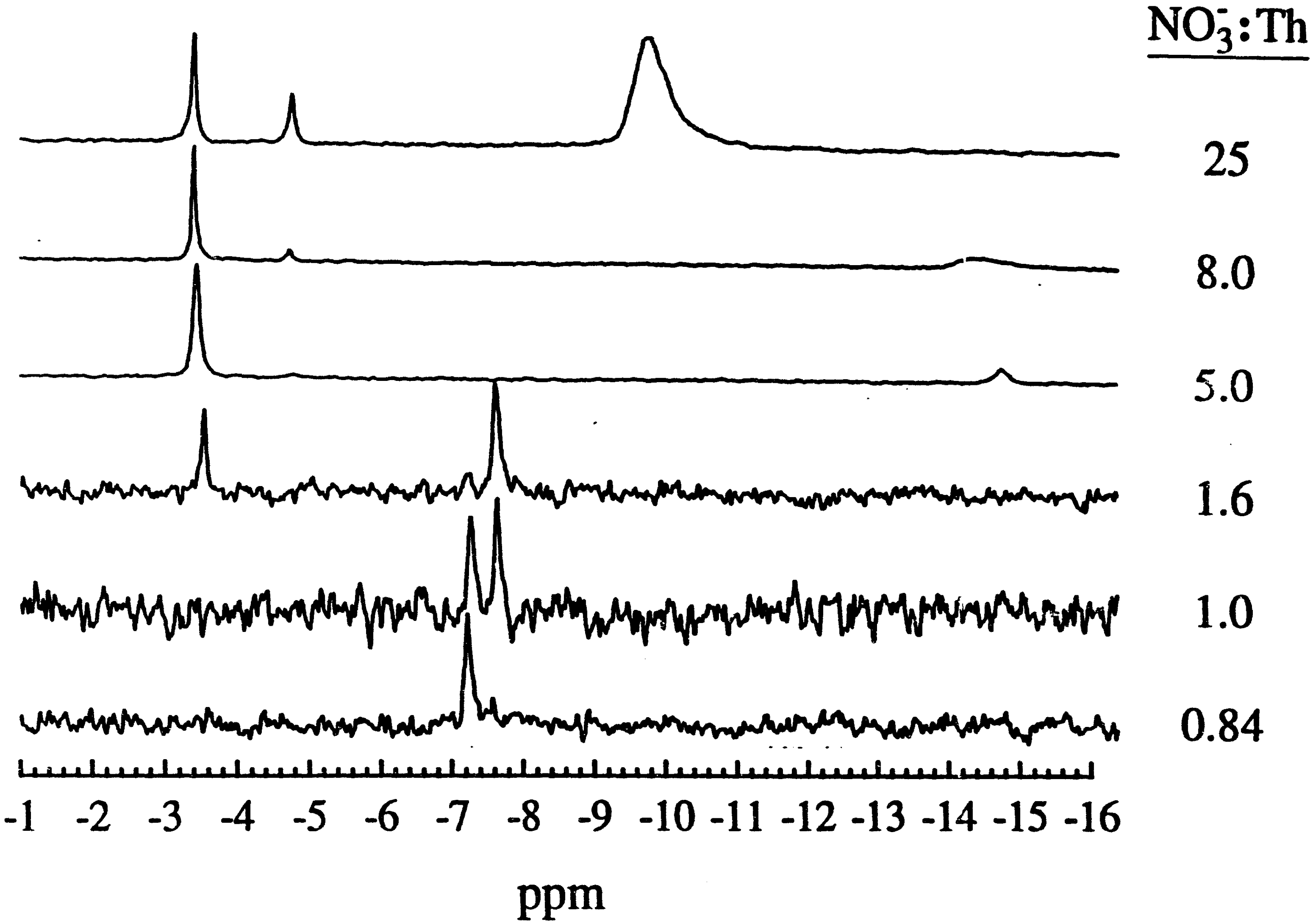


Intensity
Wavelength (nm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
400
500
600
700
800
13 M HNO_3
8 M HNO_3
1 M HNO_3
6 M $HClO_4$
1.0
0.5
0.0
425
450
475
500
525

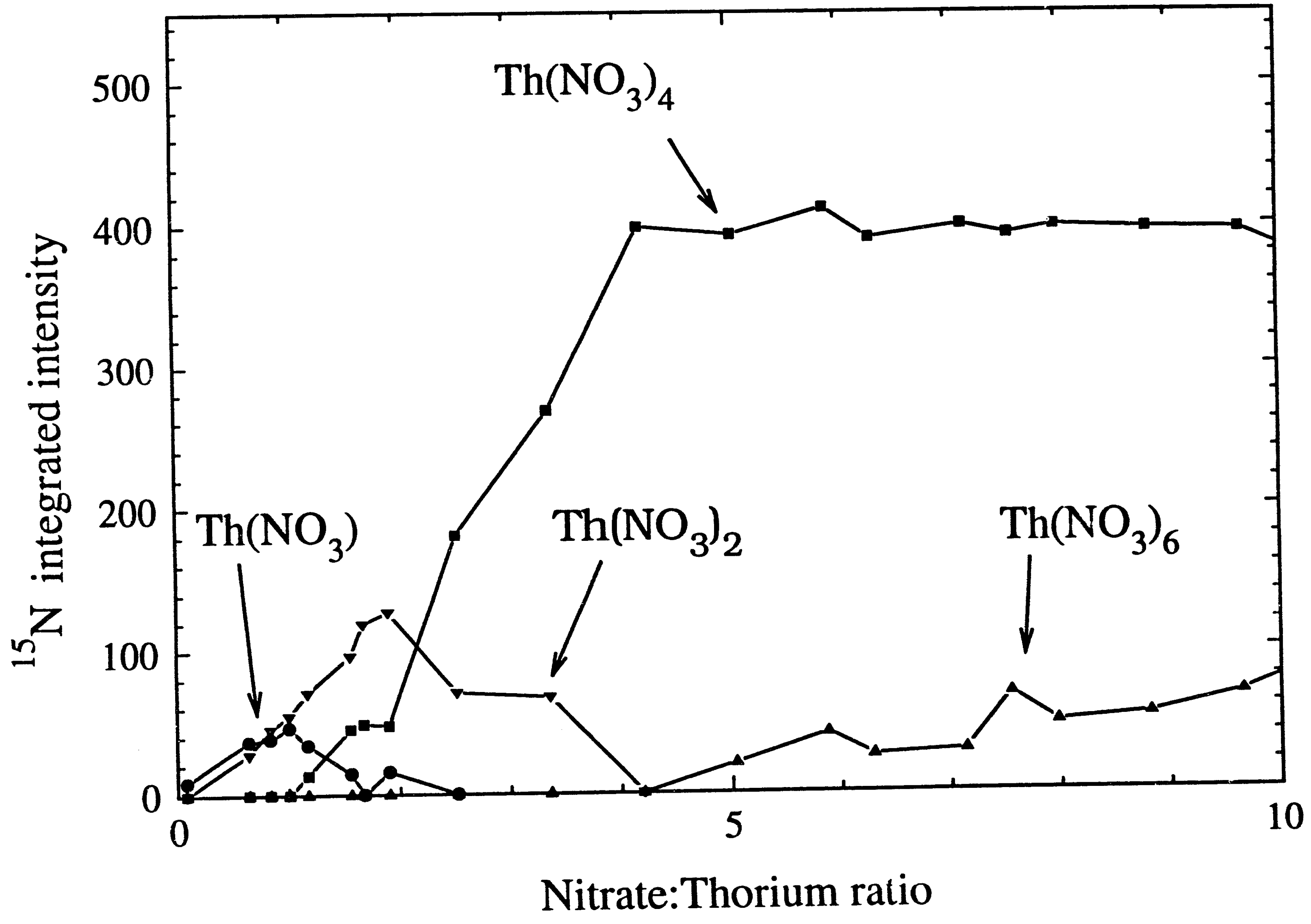

$[Pu(NO_3)_x]/[Pu]$
8
6
4
2
0
-2
-0.2
0.0
0.2
0.4
0.6
0.8
$[NO_3]^x$ (x=1)


$[Pu(NO_3)_x]/[Pu]$
8
6
4
2
0
-2
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
$[NO_3]^x$ (x=2)

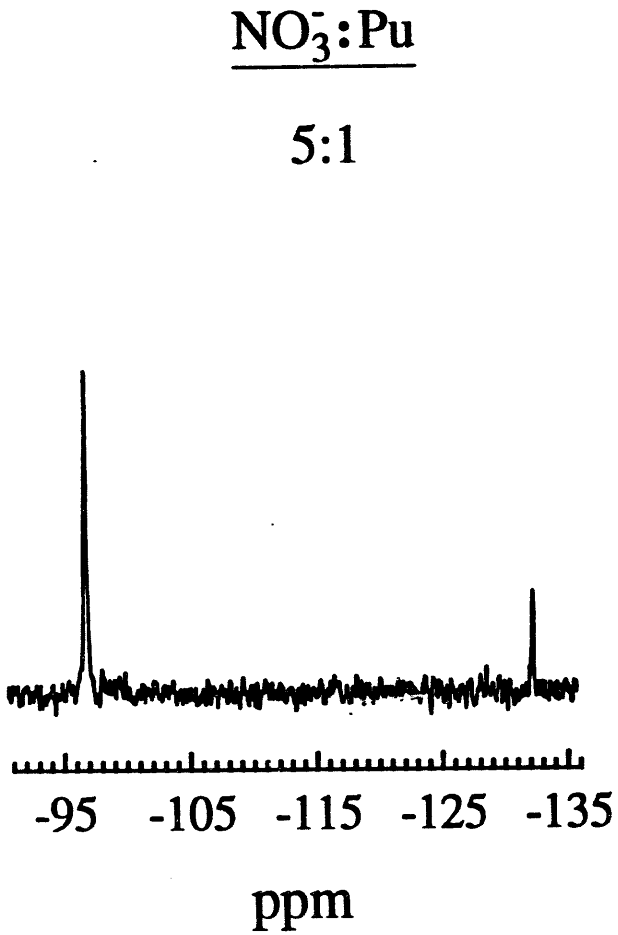

0.10
0.05
0.00
-0.05
Absorbance
400
500
600
700
800
900
1000
Wavelength (nm)
NO$_3$ = 0.10
NO$_3$ = 0.08
NO$_3$ = 0.06
NO$_3$ = 0.04
NO$_3$ = 0.02

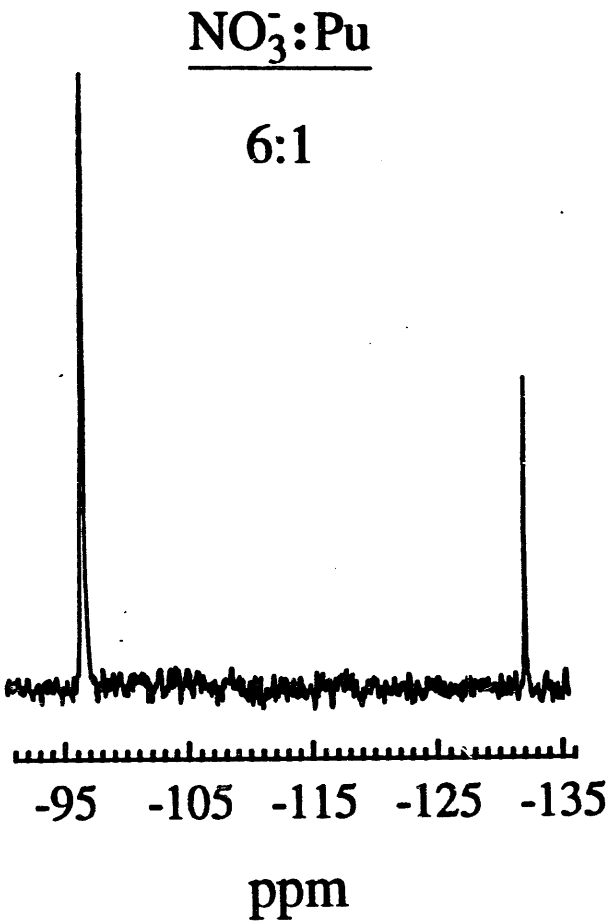


$NO_3^-:Th$
25
8.0
5.0
1.6
1.0
0.84
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
ppm



Th(NO3)4
Th(NO3)
Th(NO3)2
Th(NO3)6
15N integrated intensity
0
100
200
300
400
500
0
5
10
Nitrate:Thorium ratio


NO_3^-:Pu
5:1
-95
-105
-115
-125
-135
ppm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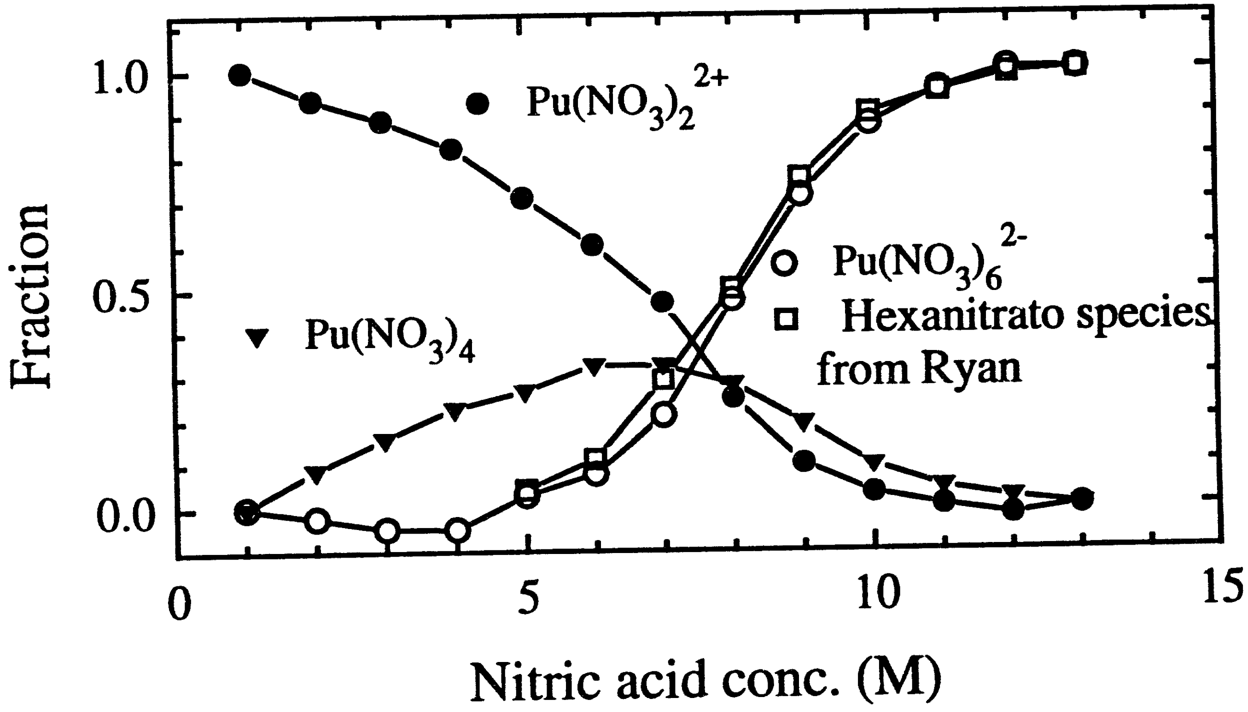
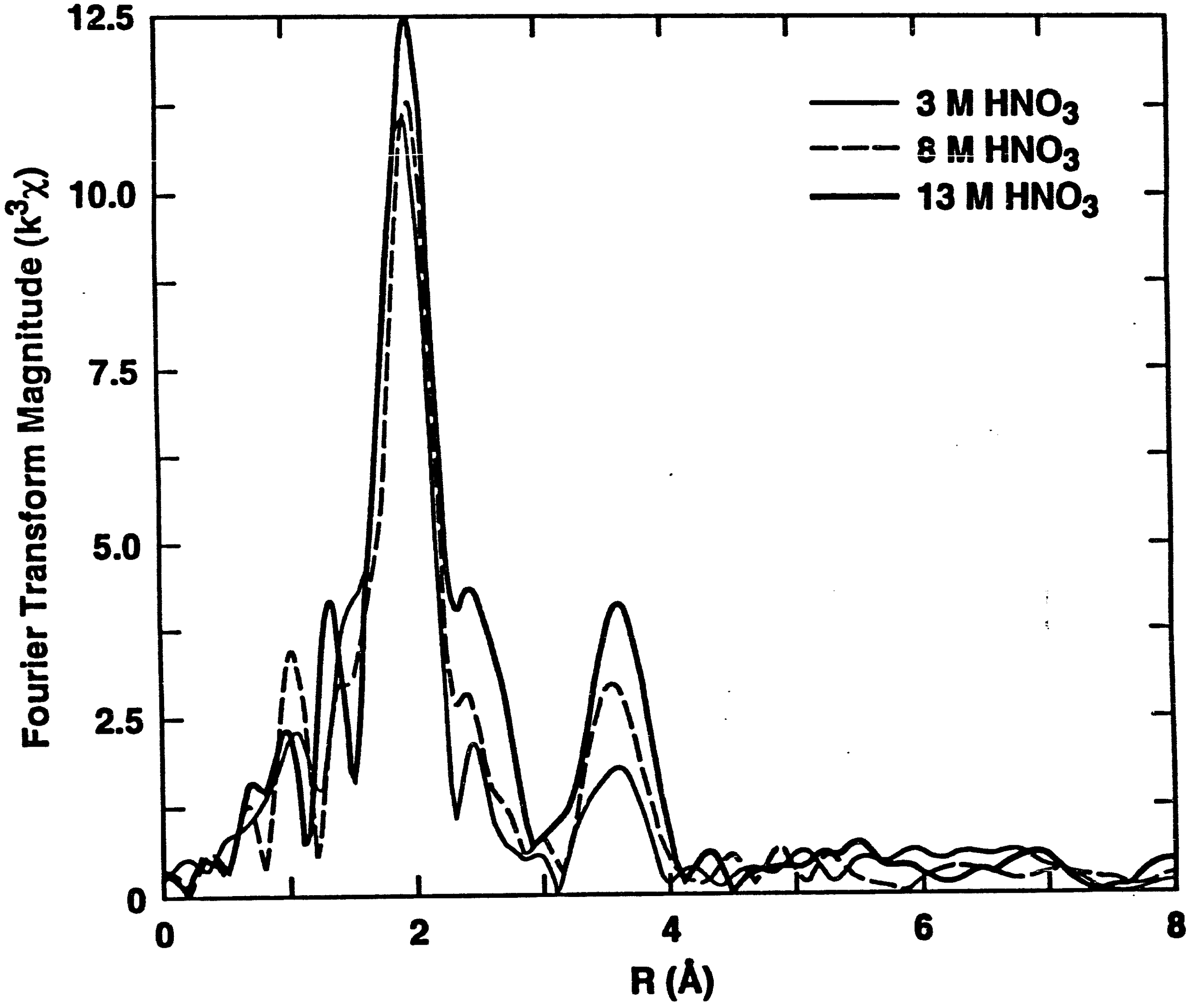


1.0
0.5
0.0
Fraction
0
5
10
15
Nitric acid conc. (M)
● $Pu(NO_3)_2^{2+}$
▼ $Pu(NO_3)_4$
○ $Pu(NO_3)_6^{2-}$
□ Hexanitrato species from Ryan


3 M HNO$_3$
8 M HNO$_3$
13 M HNO$_3$
Fourier Transform Magnitude ($k^3\chi$)
12.5
10.0
7.5
5.0
2.5
0
0
2
4
6
8
R (Å)

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END