ANL-4443
Chemistry
Transuranic Elements

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SPECTROPHOTOMETRY OF NEPTUNIUM IN PERCHLORIC ACID SOLUTIONS

by
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April 14, 1950

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SPECTROPHOTOMETRY OF NEPTUNIUM IN PERCHLORIC ACID SOLUTIONS

R. Sjoblom and J. C. Hindman

Several publications have emphasized the application of absorption spectrum measurements in studies involving the solution behavior of the actinide elements, particularly of uranium[1] and plutonium.[2,3] Preliminary data on the characteristics of the absorption spectra of the different oxidation states of neptunium have appeared.[4] The purpose of the present investigation was threefold: first, to obtain better data on the general features of the absorption spectra, including the ultraviolet region not previously investigated; second, to ascertain the usefulness of the principal neptunium absorption bands in quantitatively analyzing for the various oxidation states and third, to examine the spectra in perchlorate solutions for changes that might be correlated either with complex formation involving perchlorate or with hydrolysis of the neptunium ions. With respect to hydrolysis phenomena particular attention has been paid to examining evidence that would place limits on the range of acid concentration in which oxygenated ions such as NpO_2^+ and NpO_2^{++} are stable.

In the first part of this paper details of the absorption spectra of the different oxidation states are discussed. The second portion of the paper deals with the effect of perchloric acid concentration on the spectra and includes data on the previously unreported disproportionation reaction

$$2\ \mathrm{Np(V)} \rightleftharpoons \mathrm{Np(IV)} + \mathrm{Np(VI)}$$

which occurs in neptuniun(V) solutions in concentrated acid.

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[1] J. Sutton, CRC-325, "Ionic Species in Uranyl Solutions."

[2] G. E. Moore and K. A. Kraus, Paper No. 4.22, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.
R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, Paper No. 4.20, "The Transuranium Elements," Vol. 14B of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.

[3] J. C. Hindman, Papers 4.2, 4.4, 4.5 and 4.7, "The Transuranium Elements," Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.

[4] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, Jour. Am. Chem. Soc., 71, 687 (1949). Paper No. 15.2, "The Transuranium Elements" Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.

I. THE ABSORPTION SPECTRA OF Np(III), Np(IV), Np(V) AND Np(VI) IN 1.0 M $HClO_4$

Measurements of details of the absorption spectra of carefully prepared solutions of the oxidation states of neptunium in 1.0 M $HClO_4$ have been made. Aliquots of these solutions have been used for examination of the behavior of the principal absorption bands with respect to the Beer-Lambert Law.

$$\text{Log}_{10} \frac{I^0}{I} = kcl = \text{optical density} = d \qquad (1)$$

Deviations from this law are usually due to (a) a change in ionic species or (b) an instrumental defect (e.g., insufficient resolving power). It is possible to differentiate between these two possibilities since in the event that a purely instrumental effect is involved the density will be a constant at a constant product of $c \times \ell$. However, if a change in ionic species accompanied by a change in the absorption spectrum occurs with change in concentration the density will vary at a constant product of $c \times \ell$. The effect of slit width on the optical density readings of the principal absorption bands also was examined since in the case where there is insufficient resolving power the observed optical density will depend on the slit width.

Experimental

The absorption spectrum measurements from 215 millimicrons to 400 millimicrons were made with a Cary recording spectrophotometer model 12 (marketed by the Applied Physics Corporation, Pasadena, California) using silica 2 cm cylindrical cells. The slit width on the Cary spectrophotometer is automatically controlled. The measurements from 350 to 1050 millimicrons were made with a Beckman (Model DU) quartz spectrophotometer using matched 1.000 ± 0.001 cm and 1.003 ± 0.001 cm silica cells. Silica cells of 0.500 ± 0.002 cm were also used. Readings on the Beckman spectrophotometer were made at 2 millimicron intervals in the region 350-600 millimicrons and at 2.5 millimicron intervals from 600-1050 millimicrons except in the vicinity of the absorption bands where the region was carefully scanned to locate the exact peak position. The wavelength scales of the spectrophotometers were checked using mercury and hydrogen arcs. The density scales were checked by means of Bureau of Standards Corning HT yellow D13 and Jena Bg 14-38 filters.[5]

The stock solution of pure neptunium(V) in 1.0 M $HClO_4$ was prepared as follows: Neptuniun (IV) hydroxide was precipitated from a sulfuric

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[5] K. S. Gibson, G. K. Walker, M. E. Brown, Jour. Optical Society of America, 24, 58 (1934).

acid solution with sodium hydroxide, washed thoroughly, then dissolved in 1.0 M HCl. Nitric acid was added to make the solution 0.15 M in NO_3^- and the solution heated for several hours at 80°C to oxidize the neptunium(IV). The course of the oxidation was followed spectrophotometrically. After complete oxidation of the neptunium(IV), the solution was made approximately 0.1 M in $N_2H_4 \cdot HCl$ to reduce any neptunium(VI) that might have been formed to neptunium(V). The neptunium(V) hydroxide was then precipitated with sodium hydroxide, washed carefully, and dissolved in 1.0 M $HClO_4$ to give a solution 0.0430 M in neptunium(V). Aliquots of this solution were then diluted to give the desired concentrations.

Both neptunium(III) and neptunium(IV) solutions were prepared from the neptunium(V) stock in perchloric acid by hydrogen reduction. Since neptunium(III) is rapidly oxidized in the presence of air to neptunium(IV) precautions had to be taken to exclude air from the solutions. To serve as a means of introducing hydrogen into the solutions a one centimeter silica cell was fitted with a ground glass stopper through which was sealed a tube having an attached stopcock. A platinum coil was wound around that portion of the tube extending into the solution but so placed as not to obstruct the beam of light. The coil was platinized. A hole was drilled in the side of the cell and the side of the stopper was notched to allow the gas to escape. The cell was made air tight by rotating the stopper and turning the stopcock. A solution 0.015 M in neptunium(V) and 1.0 M in $HClO_4$ was completely reduced to neptunium(III) in one-half hour. After one week in the stoppered cell the solution showed no signs of oxidation. For the Beer-Lambert Law studies portions of this solution were diluted with 1.0 M $HClO_4$ to the desired neptunium concentration and these solutions again reduced to neptunium(III).

In the preparation of neptunium(IV), hydrogen reduction of a neptunium(V) solution in 1.0 M $HClO_4$ was also employed. Since partial reduction to neptunium(III) always occurred this was allowed to oxidize in air to neptunium(IV). On standing a very slow oxidation to neptunium(V) occurred. Spectral observations on the solution after standing one week showed the presence of 0.85% neptunium(V). All optical density values have been corrected for the presence of this oxidation state. For the Beer-Lambert Law studies solutions prepared in the above manner were diluted with 1.0 M $HClO_4$.

Neptunium(VI) was prepared by electrolytic oxidation of a neptunium(V) solution in 1.0 M $HClO_4$. The completeness of oxidation was checked spectrophotometrically. There was no evidence that either neptunium(IV) or neptunium(V) was present in the final solution.

All measurements were made at 25 ± 1.0°C. Merck 70% reagent grade perchloric acid was used for preparing the perchloric acid solutions. The neptunium concentrations of all dilutions were determined by radiometric assay of the Np^{237} isotope used in this work.

Results

Details of the absorption spectra of the various oxidation states are summarized in Figures 1, 2 and 3. Figure 1 shows the 350-1050 millimicron region for neptunium(III) and neptunium(IV). Figure 2 illustrates the 350-1050 millimicron region of the spectrum for neptunium(V) and neptunium(VI). Figure 3 shows the ultraviolet spectrum for all four oxidation states.

The spectrum of neptunium(III) in 1.0 M $HClO_4$ shown in Figure 1 agrees reasonably well with the spectrum previously reported for a 1.0 M HCl solution.[4] The spectrum is complex, showing a large number of bands. The four principal absorption bands in the visible and the two bands in the ultraviolet were found to obey Beer's Law. The peak locations and their molar extinction coefficients are listed in Table 1.

Table 1

Absorption Bands of Neptunium(III) in 1.0 M $HClO_4$

λ (mμ)	E	Slit width (mm)	λ (mμ)	E	Slit width (mm)
233.5	2295		532	15.76	0.0125
267.0	1593		553	44.52	0.035
384	26.62	0.050	602	25.78	0.030
402	29.72	0.040	661	30.45	0.0125
416	29.34	0.025	787.5	48.24	0.0125
462	16.97	0.0150	858	25.43	0.0125
470	12.67	0.0150	910	12.38	0.0125
492	3.32	0.0125	930-935	13.65	0.0125
512	5.58	0.0125	998	30.23	0.0125

The Beer's Law data for the principal absorption bands are summarized in Figure 4. Since the optical density varied linearly with concentration and was independent of slit width the effect of cell length was not investigated. The neptunium(III) is the only oxidation state whose spectrum shows any marked structure in the ultraviolet region.

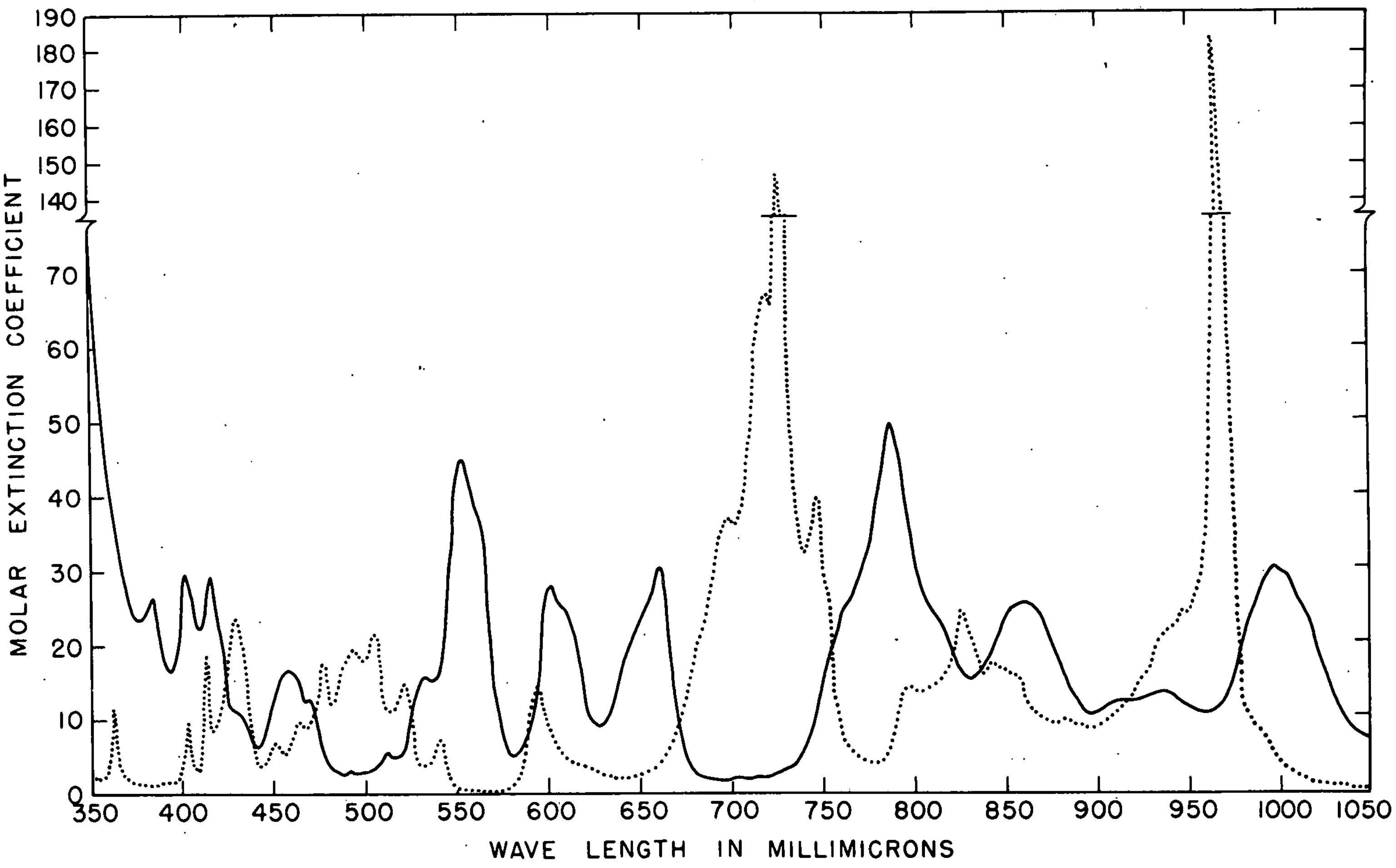

Figure 1

Absorption Spectra of the Neptunium(III) and (IV) Ions in 1.0 M $HClO_4$

——— Np(III)
------- Np(IV)

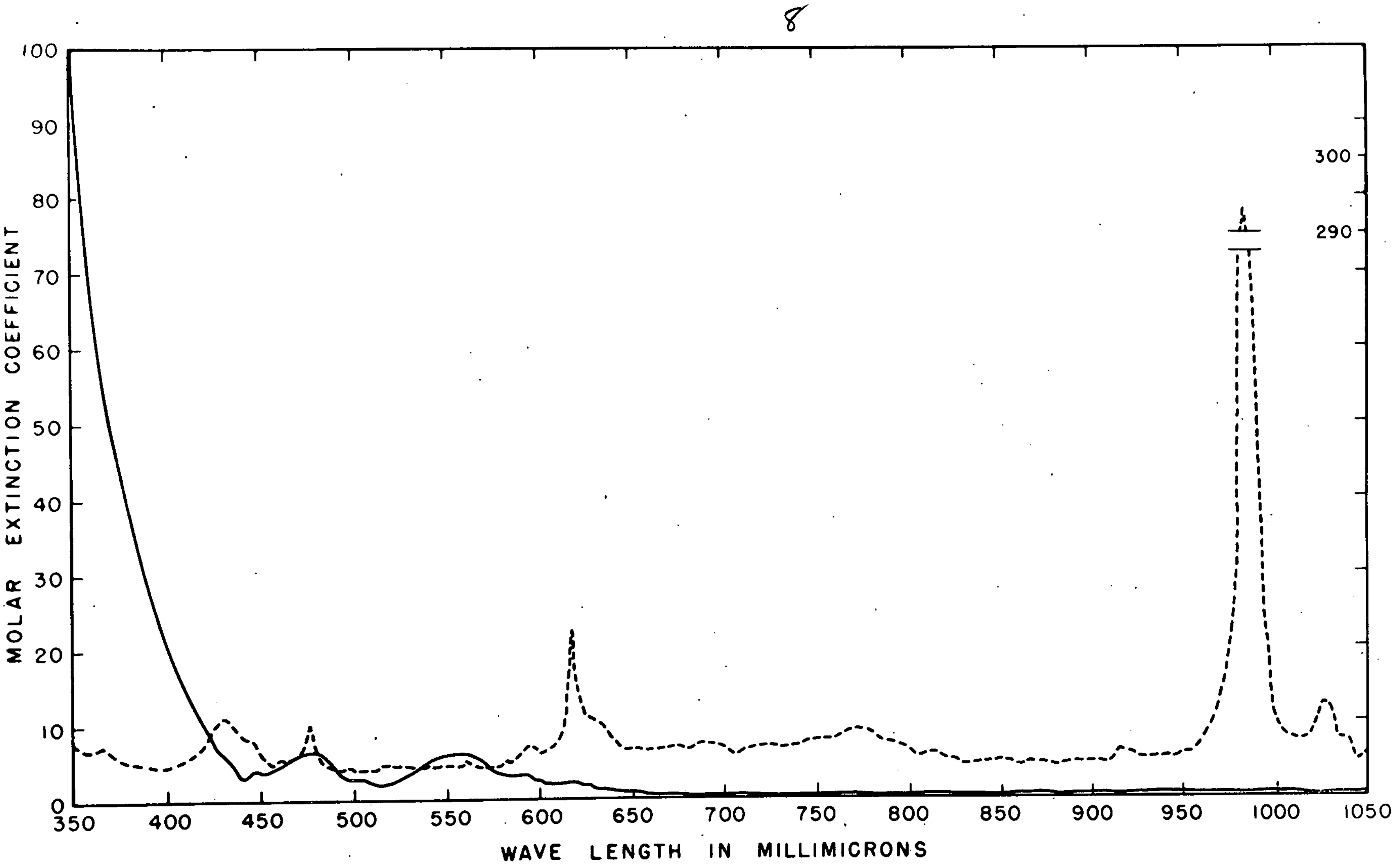

Figure 2

Absorption Spectra of the Neptunium(V) and (VI) Ions in 1.0 M $HClO_4$

———— Np(VI)

- - - - - Np(V)

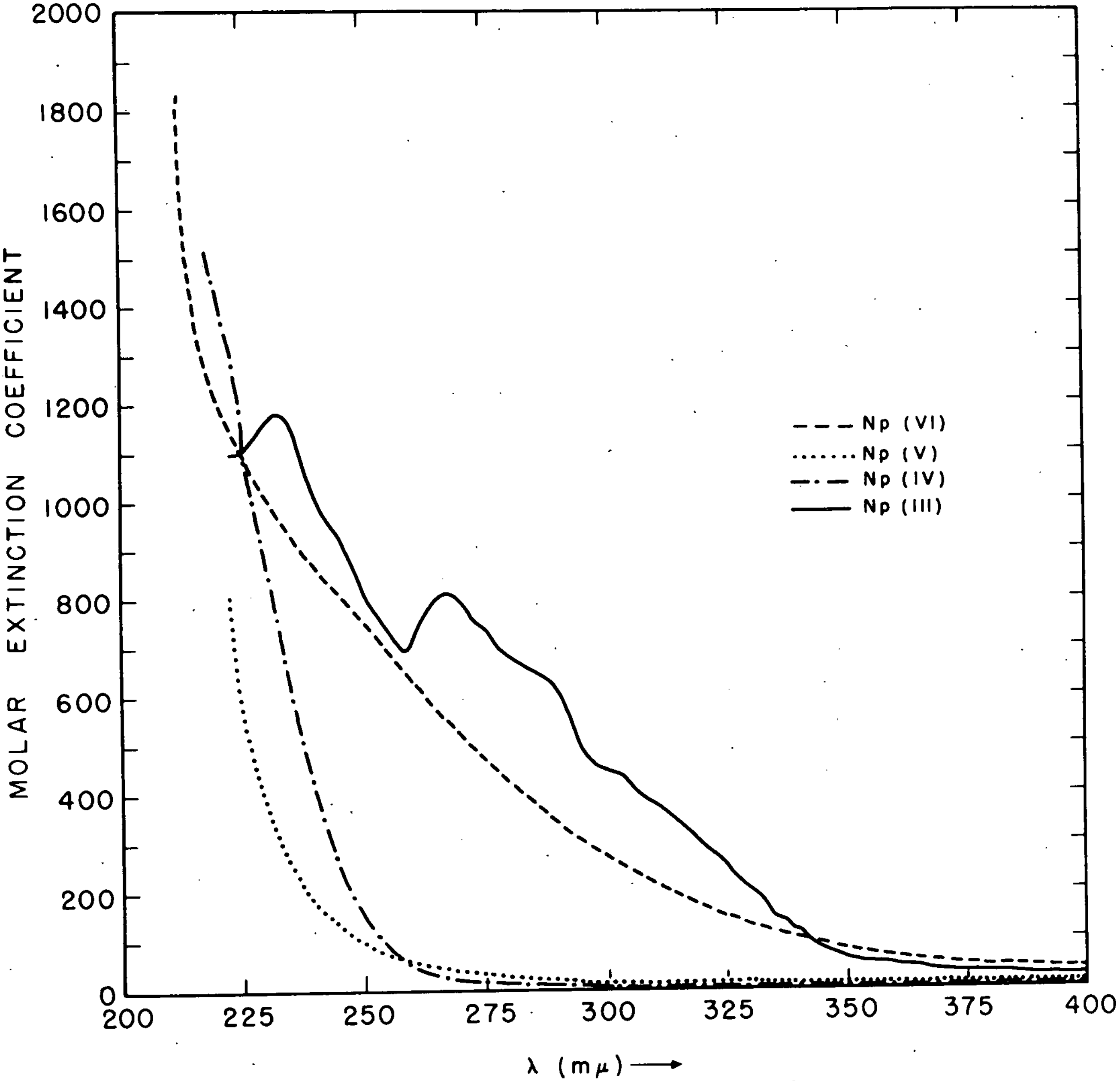

Figure 3

Ultra-Violet Absorption Spectra of Neptunium Ions in 1.0 M $HClO_4$

——— Np(III)	…… Np(V)
.——. Np(IV)	– – – Np(VI)

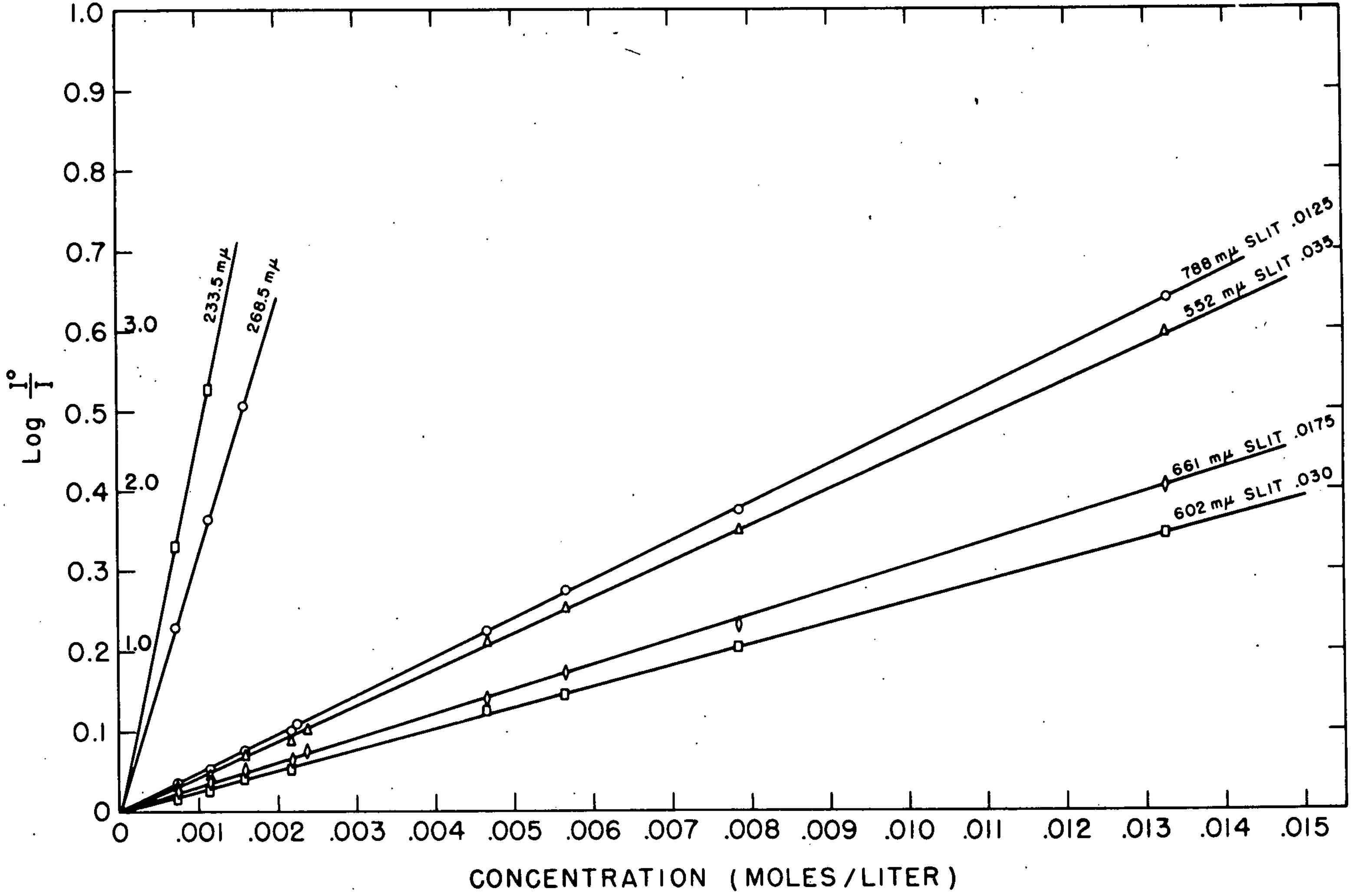

Figure 4

Beer's Law Behavior of Neptunium(III) Absorption Bands

The spectrum of neptunium(IV) in 1.0 M $HClO_4$ is shown in Figure 1. The various absorption bands of neptunium(IV) are listed in Table 2.

Table 2

Absorption Bands of Neptunium(IV) in 1.0 M $HClO_4$

λ (mμ)	E	Slit width (mm)	λ (mμ)	E	Slit width (mm)
†363	11.94	.080	†590.5	16.13	.0125
402	9.40	.0175	697.5	37.18	.020
412	18.52	.0150	715	67.00	.020
†428	23.85	.0125	†723	144.13	.0125
450	6.91	.0125	†743	43.02	.0125
463	9.55	.0125	792.5	14.25	.0125
476	17.34	.0125	†825	24.54	.0125
492	19.40	.0125	840	17.63	.0125
†504	22.89	.0125	877.5	9.97	.0125
521	14.70	.0125	*964	*193.40	.0125
540	7.20	.0125			

†Band checked and found to obey Beer's Law.
*Band does not obey Beer's Law.

The Beer's Law data for the principal bands at 723 and 964 millimicrons are summarized in Figure 5B and C. In the case of the 964 millimicron peak, the optical density varies linearly with neptunium concentrations up to 0.0035 M. At higher concentrations the deviations are such that the molar extinction coefficient decreases as the concentration increases. However, as can be seen from Table 3 the optical density is constant at a constant product of $c \times \ell$, thus indicating that the deviation is due to an instrumental optical effect rather than to a change in ionic species. The effect of slit width, summarized in Figure 5B and 5C, was essentially the same for both the 723 and 964 millimicron bands. In both cases the optical density (and extinction coefficient) decreased with increasing slit width.

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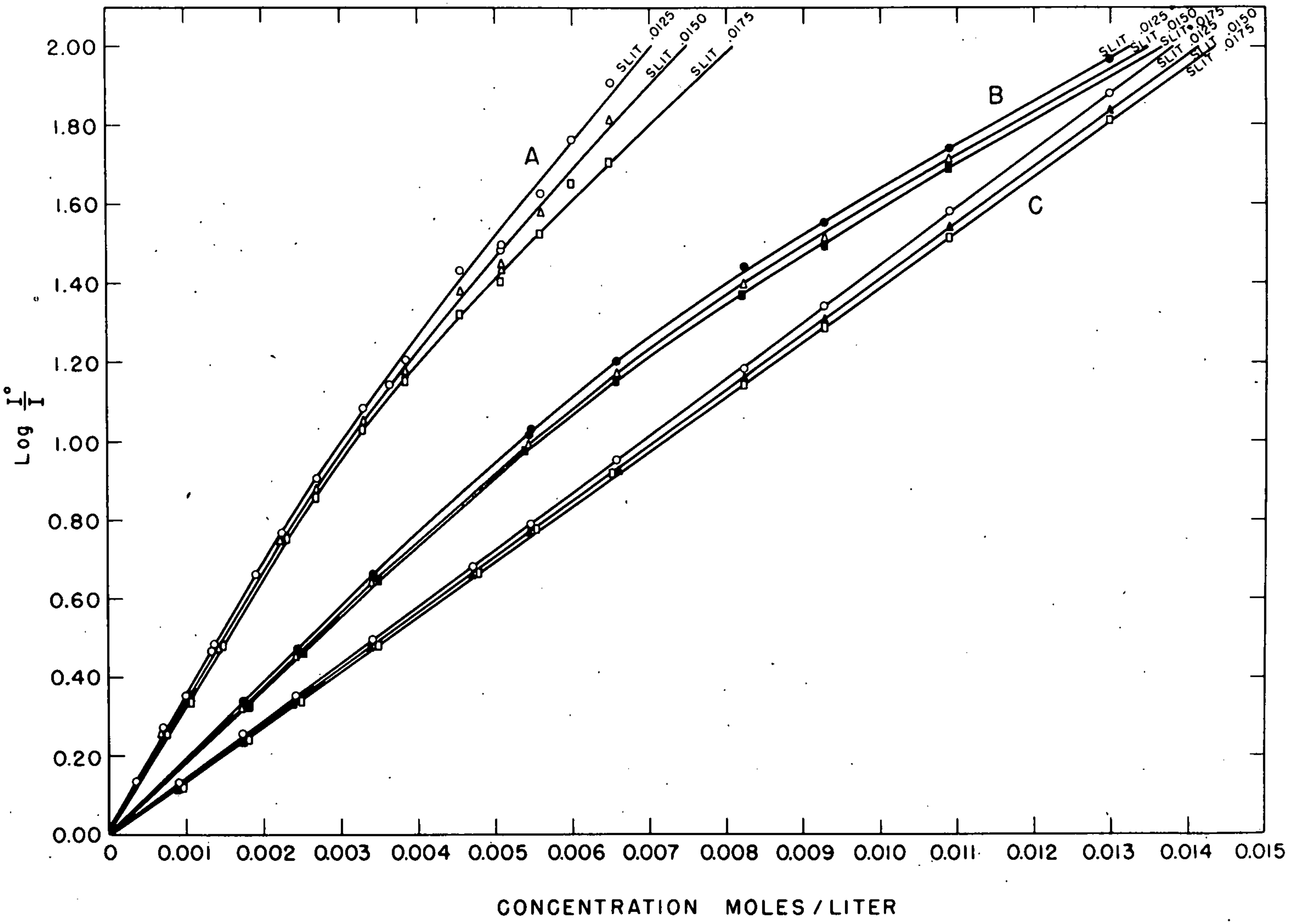

Figure 5

Variation of Optical Density with Molarity and Slit Width for Np(IV) and Np(V) Absorption Bands

(A) Np(V) peak at 983 mμ (B) Np(IV) peak at 964 mμ (C) Np(IV) peak at 723 mμ

Table 3

Neptunium(IV) in 1.0 M $HClO_4$
Observations at Constant Values of c x l

[Np] moles/liter	c x l x 10^4	d at 723 mμ	E at 723 mμ	d at 964 mμ	E at 964 mμ
0.01300	130.0	1.88	144.62	1.91	146.92
0.02576	129.1	1.86	144.07	1.88	145.62
0.01091	109.1	1.58	144.82	1.74	159.49
0.02144	107.4	1.54	143.39	1.73	161.08
0.006576	65.76	0.948	144.16	1.20	182.48
0.01295	64.88	0.939	144.73	1.19	183.41
0.004714	47.14	0.678	143.82	0.928	196.86
0.009339	46.98	0.677	144.70	0.928	198.34
0.003409	34.09	0.493	144.62	0.656	192.43
0.006507	32.65	0.474	145.17	0.634	194.18
0.002425	24.25	0.349	143.92	0.469	193.40
0.004843	24.36	0.351	144.09	0.479	196.63
0.001775	8.893	0.125	140.56	0.170	191.16
0.0009006	9.006	0.129	143.24	0.174	193.73

The spectrum from 350-1050 millimicrons for neptunium(V) in 1.0 M $HClO_4$ shows only two peaks of any consequence, one at 617 millimicrons and the other at 983 millimicrons (Figure 2). The various absorption bands of neptunium(V) are listed in Table 4. The behavior of the band at 617 millimicrons conforms to the Beer-Lambert Law. As in the case of the 964 millimicron band of neptunium(IV), the extinction coefficient of the 983 millimicron band of neptunium(V) decreases with increasing neptunium concentration. The data are given in Figure 5A. Again as for the 964 millimicron neptunium(IV) band it is found that optical density at the 983 millimicron peak is constant at constant product of $c \times \ell$ (Table 5). Presumably the failure of the 964 and 983 millimicron bands of neptunium(IV) and (V) to obey the Beer-Lambert Law is due to the fact that the spectral band width isolated by the slits is not sufficiently narrow with respect to the band width at the peaks of the absorption bands. Since no deviation from the Beer-Lambert Law can be detected for the 723 millimicron band despite this incomplete resolution it would appear that the actual spectral band isolated by the slits is not much less than the band width of the absorption band head. The decreased dispersion of the spectrophotometer with increasing wavelength

Table 4

Molar Extinction Coefficients of the Neptunium(V) Peaks in 1.0 M $HClO_4$

λ (mμ)	E	Slit width (mm)
366	7.46	.060
428	11.11	.025
441	8.29	.025
461	5.30	.025
476	10.28	.0175
594	7.13	.020
†617	23.67	.030
775	8.95	.0125
915	6.30	.0125
*984	263.83	.0125
1030	12.10	.0150

*peak does not obey Beer's Law.
†peak obeys Beer's Law.

increases the disparity between the spectral band width isolated by the slit and the band width of the absorption band.

It may be concluded from these experiments that the principal neptunium(IV) and neptunium(V) bands can be used for accurate work if a suitable calibration curve is constructed and care is taken to duplicate the settings of the slit width. Comparison of values obtained for the neptunium(IV) peaks on two different Beckman spectrophotometers showed that there is an appreciable variation between the different instruments and calibration curves are not interchangeable from one instrument to another.

The absorption spectrum of neptunium(VI) in the visible region shows no absorption bands as suitable for analytical use as those of the other oxidation states. The distinguishable bands of neptunium(VI) are listed in Table 6.

Table 5

Np(V) in 1 M $HClO_4$ 983 mμ Peak
Observations at Constant Product c x l

[Np] moles/liter conc.	c x l x 10^4	d	E
.005084	51.00	1.49	292.15
.01012	50.90	1.48	290.77
.003622	36.33	1.14	313.79
.007030	35.36	1.12	316.74
.002709	27.17	.901	331.62
.005141	25.86	.866	334.88
.001903	19.09	.657	344.16
.003728	18.75	.647	345.07
.0007161	7.182	.266	370.37
.001341	6.745	.250	370.64

Table 6

Molar Extinction Coefficients of the
Neptunium(VI) Peaks in 1.0 M $HClO_4$

λ (mμ)	E	Slit width (mm)
448	3.92	.020
476	6.36	.0150
504	2.72	.0125
557	6.79	.0125
590	3.16	.0125
620	2.12	.040

The Vibrational Fine Structure in the Spectra of Neptunium(V) and (VI) -

Probably the most distinctive feature of the neptunium(VI) absorption spectrum is the existence of a number of weak regularly spaced bands occurring in the blue-violet and near ultraviolet region of the spectrum. Similar bands are observed in the absorption spectra of both the uranyl ion, UO_2^{++}, and the plutonyl ion, PuO_2^{++}. They are attributable to the symmetrical vibrations in the metal-oxygen bonds.[6,7] In the spectrum of neptunium(VI) in 1.0 M $HClO_4$ there are eight of these vibrational bands in the 370-475 millimicron region having an average frequency difference of 715 cm^{-1}. The positions and character of these bands are illustrated in Figure 6. In solutions of the uranyl ion, UO_2^{++}, there are eleven regularly spaced bands for which Kasha[7] gives a value of 724 cm^{-1} for the frequency interval in 0.1 M $HClO_4$. Similar measurements by us for 1.0 M $HClO_4$ solutions gave a frequency interval of 712 cm^{-1}. For comparison, the spectrum of uranium(VI) in 1.0 M $HClO_4$ is shown in Figure 6. For plutonium(VI) Kasha also reported for the series of four regularly spaced bands in the region 390-430 millimicrons, which he ascribed to the symmetrical vibrations in the Pu-O bonds, a frequency difference of 708 cm^{-1}. Betts and Harvey[8] reported an average value of 657 cm^{-1} for the frequency interval of the plutonyl vibrational bands in 0.9 M HNO_3.

A similar vibrational fine structure in the absorption spectrum would also be expected for the ion NpO_2^+. Examination of a neptunium(V) spectrum in 1.0 M $HClO_4$ shows eight bonds in the 430-600 millimicron region having an average frequency interval of 753 cm^{-1}. Figure 7 illustrates the location of these bonds. It can be noted that the increase in frequency of vibration in the NpO_2^+ ion as compared with the NpO_2^{++} ion is consistent with the looser bonding which would be expected for the Np(V) ion.

It should be pointed out that the existence of the vibrational structure in the solution absorption spectra of these oxygenated ions is probably the best available evidence that these ions are of the type XO_2^+ or XO_2^{++} and are not $X(OH)_4^+$ or $X(OH)_4^{++}$.

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[6] G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," The National Nuclear Energy Series. McGraw-Hill, New York, 1949.

[7] M. Kasha, J. Chem. Phys. 17, 349 (1949).

[8] R. H. Betts and B. G. Harvey, J. Chem. Phys. 16, 1089 (1948).

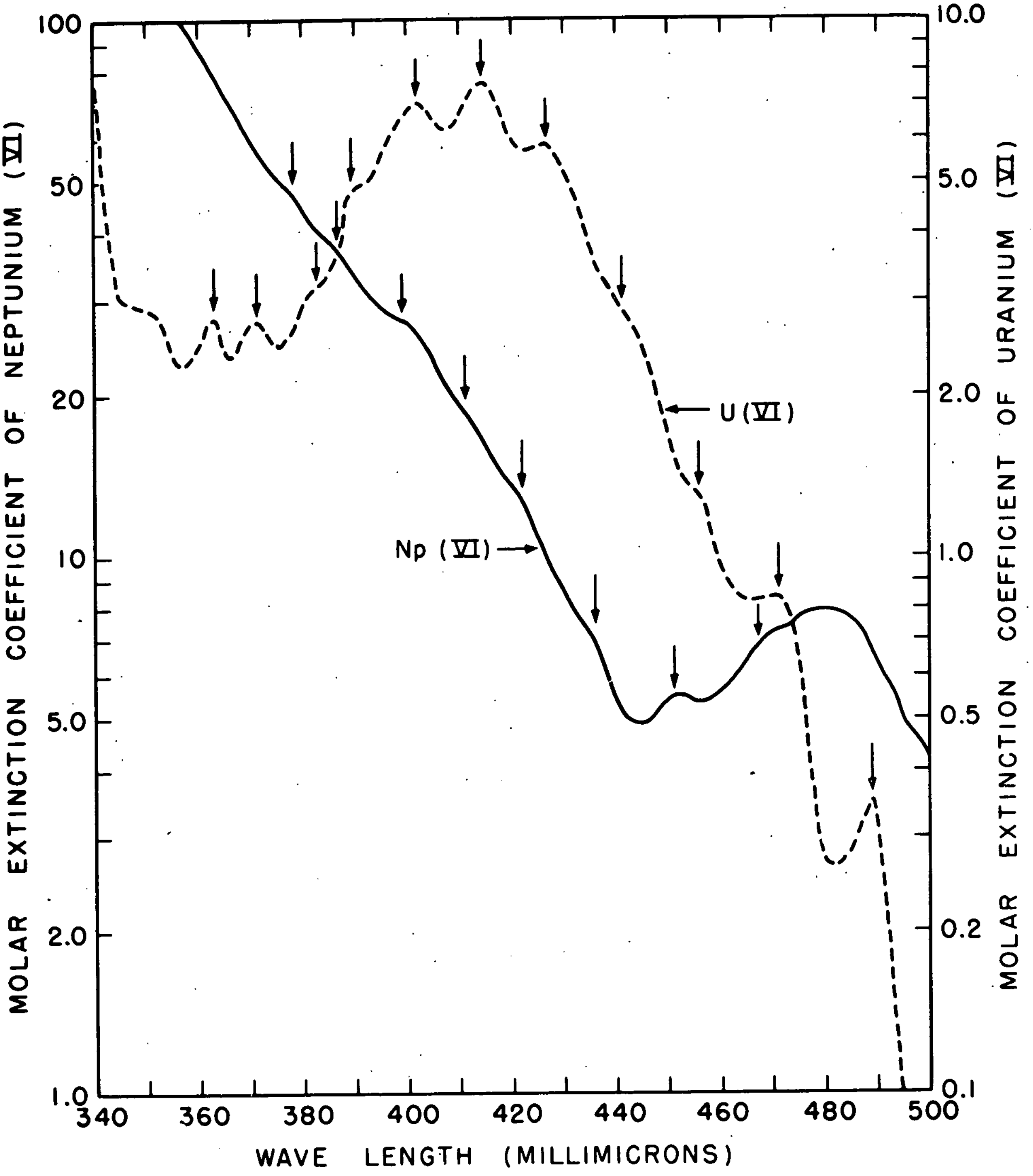

Figure 6

Absorption Spectra of Uranium(VI) and Neptunium(VI) in 1.0 $\underline{M}$ $HClO_4$ Showing Vibrational Fine Structure

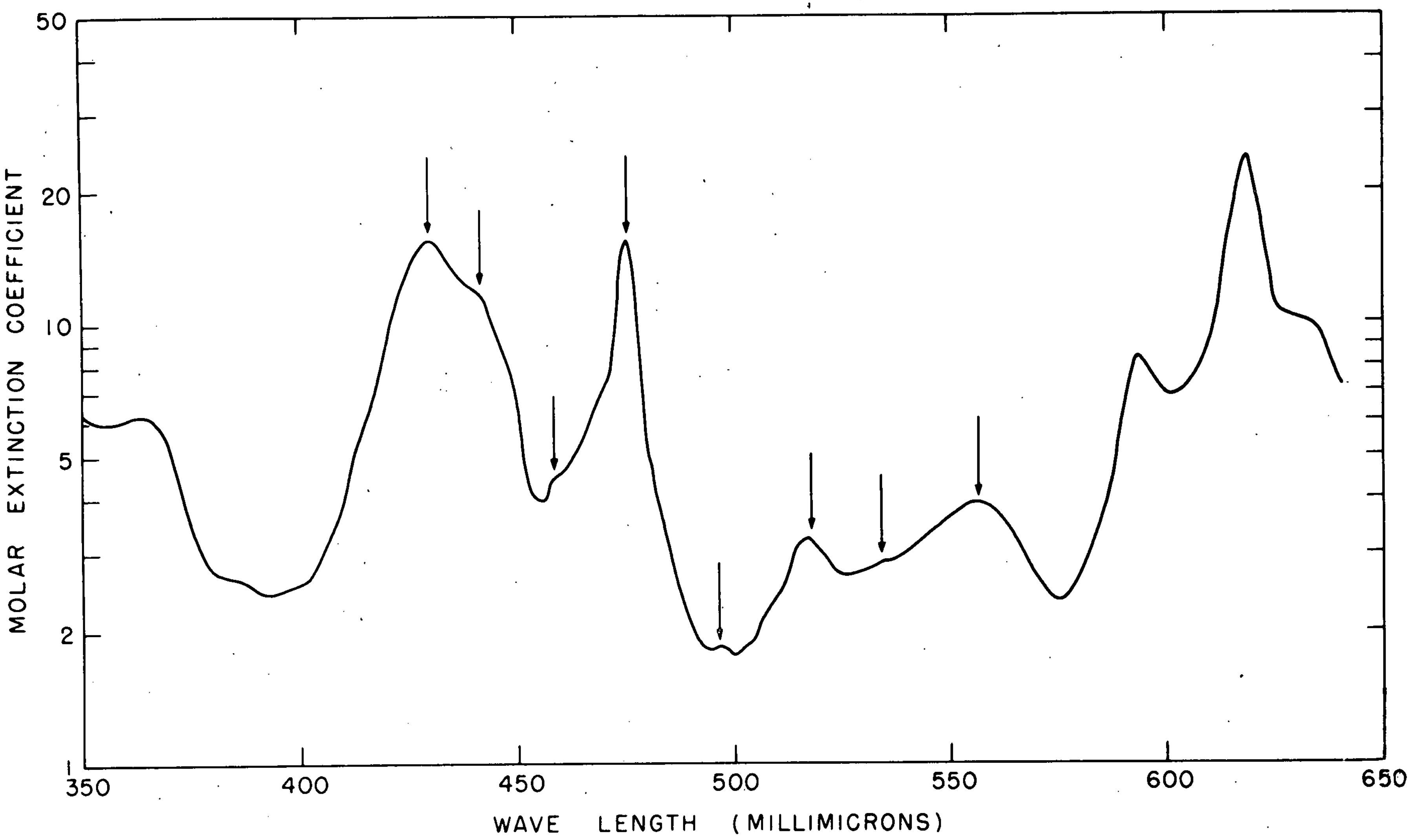

Figure 7

The Absorption Spectrum of Neptunium(V) in 1.0 M $HClO_4$ Showing Vibrational Fine Structure

II. INFLUENCE OF PERCHLORIC ACID CONCENTRATION ON THE ABSORPTION SPECTRA OF NEPTUNIUM IONS. THE DISPROPORTIONATION OF NEPTUNIUM(V)

In studying the effect of perchloric acid concentration on the neptunium absorption spectra, the measurements have, except in the case of neptunium(III) solution, been made over a range of acid concentration ranging from those sufficiently low to show the effect of hydrolysis on the spectra to concentrated acid solutions. This was not possible in the case of neptunium(III) since the insolubility of the neptunium(IV) hydroxide would make the neptunium(III) ion unstable with respect to oxidation by water at acidities sufficiently low for hydrolysis to occur.

Experimental

For the studies on neptunium(V) solution in concentrated acid four solutions of varying perchloric acid concentration were prepared by diluting Merck reagent grade 70% perchloric acid with redistilled water. Np(V) in 1.0 M $HClO_4$, from the stock solution previously described, was added to each of the acids in turn and a portion of the solution titrated with standardized sodium hydroxide solution to the methyl orange endpoint. The acid molarities of the resultant neptunium solutions were thus determined to be 5.34 M, 7.11 M, 8.45 M, and 8.67 M respectively. Np(V), in each of these solutions, was found to disproportionate in the following manner. $2Np(V) \rightleftharpoons Np(IV) + Np(VI)$. The optical densities of the main Np(IV) and Np(V) peaks were followed from the time of mixing until equilibrium was reached, using a Beckman (Model DU) quartz spectrophotometer with quartz cells of 1.003 ± 0.001 cm length. The slit width used was 0.0125 mm.

The data on the disproportionation reaction are summarized in Table 7. Figure 8 illustrates the spectra of equilibrium solutions of Np(IV), (V) and (VI) in 5.34 and 8.67 M $HClO_4$.

In order to find the concentrations of Np(IV) and Np(V) present at equilibrium, the values of the main peaks of the equilibrium mixtures were corrected for the contributions from the other oxidation states. Data on the peak heights of the pure Np(IV) and Np(VI) states were obtained by reducing each equilibrium mixture to pure Np(IV), recording the spectrum, and then oxidizing the resultant Np(IV) solutions to Np(VI). The background readings at the peak positions of the pure Np(V) spectra were derived by extrapolation of density-time plots. The concentrations of the Np(IV) and Np(V) states present at equilibrium found by the above method are listed in Table 7. Since Np(VI) has no peaks suitable for analytical use, the concentration of Np(VI) was determined as the difference between the neptunium(IV) and (V) concentrations as determined spectrophotometrically

Table 7

The Disproportionation Reactions of
Neptunium(V) as a Function of Perchloric Acid Concentration

Acid conc. moles/liter	Equilibrium conc. Np(IV) from E_{723} moles/liter	Equilibrium conc. Np(IV) from E_{964} moles/liter	Equilibrium conc. Np(V) from E_{983} moles/liter	Total Conc. from peak heights moles/liter	Total Conc. from assay moles/liter	% error in conc.	$t_{\frac{1}{2}}$ hrs.	$K = \frac{(IV)\ (VI)}{(V)^2}$
1.0*								$4 \times 10^{-7*}$
5.34	.001239	.001178	.003299	.005655	.005608	.83	52.0	.1267
7.11	.002229	.002226	.0009258	.005378	.005567	3.4	12.5	5.781
8.45	.003480	.003502	.0002598	.007262	.007246	.2	0.78	168.5
8.67	.002968	.002924	.000207	.006055	.005495	10.1	1.42	199.5

*Estimated from potential measurements

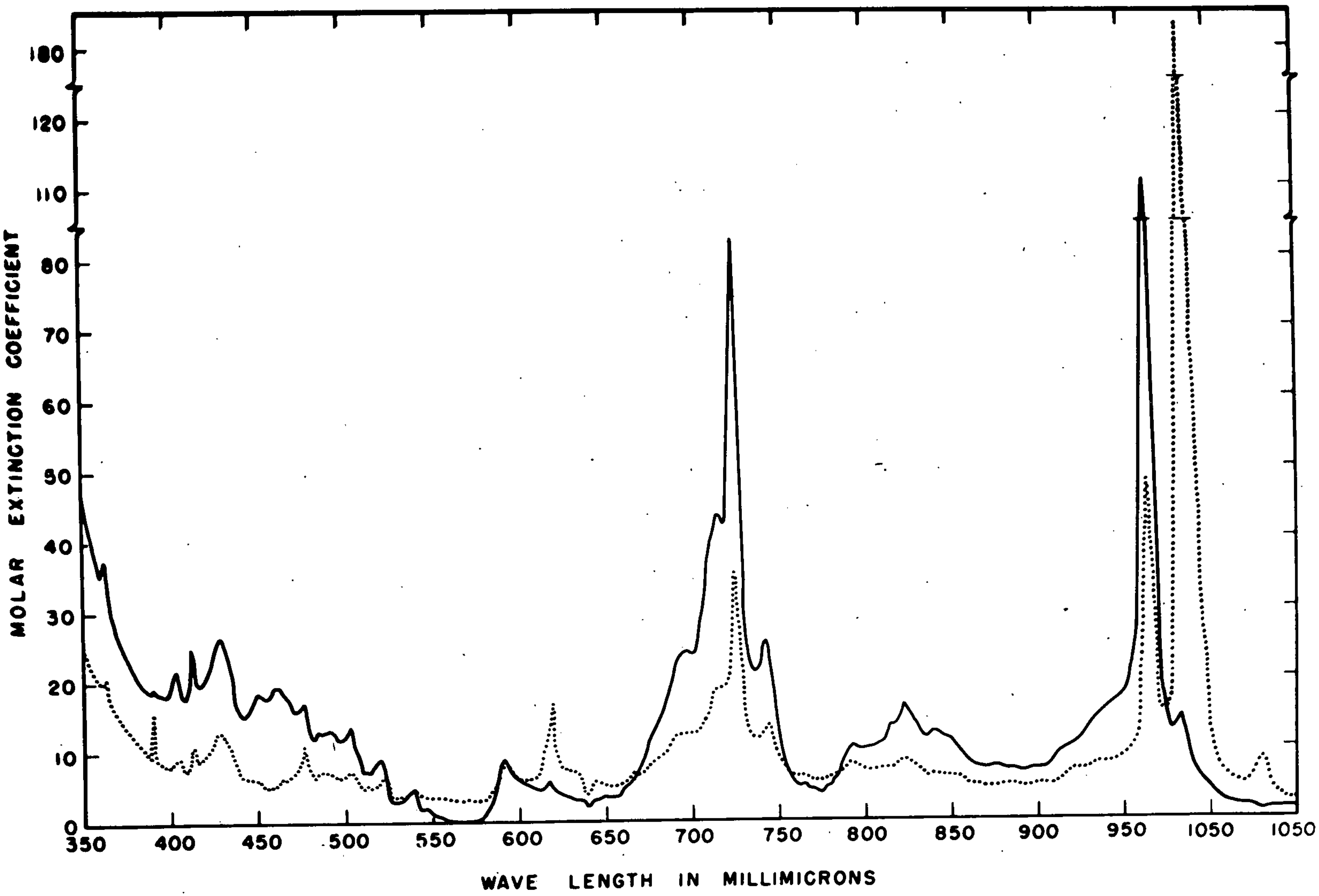

Figure 8

Absorption Spectra of Solutions of Neptunium(IV), (V) and (VI) in Disproportionation Equilibrium

——— 2 Np(V) $\rightleftharpoons$ Np(IV) + Np(VI)
in 8.67 M $HClO_4$

……… 2 Np(V) $\rightleftharpoons$ Np(IV) + Np(VI)
in 5.34 M $HClO_4$

and the total neptunium concentration obtained from radiometric assay or taken to be equal to the neptunium(IV) concentration. The last column of the table lists the constant K for the reaction

$$2\mathrm{Np(V)} \rightleftharpoons \mathrm{Np(IV)} + \mathrm{Np(VI)}. \qquad (2)$$

Also given in the table are the observed times for 50% reaction. The kinetics of the disproportionation reaction will be discussed in detail in a subsequent publication.

The spectrum of a neptunium(V) solution at pH 5.7 was obtained from a solution prepared by addition of sodium hydroxide to a 1 $\underline{M}$ $HClO_4$ stock solution. The pH was measured with a Beckman Model G Laboratory pH meter.

The absorption spectra of the neptunium(IV) solutions in concentrated acid were obtained by reducing the equilibrium mixtures with hydrogen to Np(IV). The reduced solution was checked spectrophotometrically and found to contain no Np(V) or Np(III). To obtain the spectrum of neptunium(IV) at a pH of 2.0, neptunium(V) from the stock solution was added to 1.0 $\underline{M}$ perchloric acid and the pH adjusted by adding sodium hydroxide solution. The solution was then reduced by hydrogen.

Solutions of neptunium(III) in 5 $\underline{M}$ and 10 $\underline{M}$ perchloric acid were similarly prepared by hydrogen reduction of neptunium(V) solutions in these concentrations of perchloric acid.

Solutions of Np(VI) for spectrophotometric examination were prepared by electrolytic oxidation of a concentrated neptunium(V) solution in 1 $\underline{M}$ perchloric acid. Portions of this latter solution were then added to the proper perchloric acid solution. The spectra at pH 2.7, pH 4.0 and pH 4.9 were of solutions prepared by adding sodium hydroxide solution to an electrolytically prepared Np(VI) solution in 1 $\underline{M}$ $HClO_4$. The solutions of U(VI) in perchloric acid used as a comparison for the Np(VI) solutions were prepared by dissolving a weighed quantity of pure UO_3 in perchloric acid to give a stock solution 0.9506 $\underline{M}$ in U(VI) and 1.0 $\underline{M}$ in $HClO_4$. Aliquots of this stock solution were added to the proper perchloric acid concentration for the absorption spectra studies. The uranium content was checked by gravimetric analysis.

The neptunium concentrations were determined radiometrically for each sample.

Results

Neptunium(III) resembles plutonium(III)[9] in that change of perchloric acid concentration from 1 to 10 M does not significantly affect the absorption spectrum.

Decreasing the hydrogen ion concentration sufficiently causes the occurrence of very definite changes in the spectrum of neptunium(IV). This is illustrated in Figure 9, which shows the spectrum observed at a pH = 2.00. The type of changes associated with the hydrolysis reaction are very similar to those observed in the hydrolysis of the Pu^{+4} ion to give $PuOH^{+3}$.[10] There is an increase in general absorption below 450 millimicrons. At longer wavelengths the spectrum becomes more diffuse, the principal absorption bands disappearing and the small sharp peaks being replaced by broader bands. That the solution initially formed at this pH is not stable is shown by the observation that changes occur on standing. These changes are manifest by a decrease in the extinction of the principal absorption bands. This optical phenomenon appears similar to that observed during formation of the polymers of plutonium(IV).[11] The further investigation of the spectrophotometric phenomena associated with the hydrolysis of neptunium(IV) will be discussed in a subsequent paper. It is sufficient at this time to note that the spectral changes caused by hydrolysis are very marked.

Increasing the perchloric acid concentration from 1 to 7.11 molar does not appreciably affect the absorption spectrum. In 8.67 M $HClO_4$, however, both the 723 and 964 millimicron peaks show a diminution in height of approximately five per cent. At a still higher perchloric acid concentration, the peak heights are further reduced, the reduction amounting to about eight per cent in 10 M $HClO_4$. Since considerable evidence has been accumulated to show that the tripositive and tetrapositive ions of uranium,[12] neptunium,[13] and plutonium[10,14] are X^{+3}(hydrated) and X^{+4} (hydrated) in acid solution, these

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[9] J. C. Hindman and D. P. Ames, Paper No. 4.2 "The Transuranium Elements" Vol. 14B of Plutonium Project Record of National Nuclear Energy Series. McGraw-Hill, New York, 1949.

[10] J. C. Hindman, Paper No. 4.4 "The Transuranium Elements" Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.

[11] K. A. Kraus, Metallurgical Laboratory Report No. 2289, Nov. 11, 1944.

[12] E. S. Kritchevsky and J. C. Hindman, J. Am. Chem. Soc., 75, 2096 (1945), also unpublished results on hydrolysis measurements of UCl_4 in perchlorate solution.

[13] J. C. Hindman and E. S. Kritchevsky, J. Am. Chem. Soc., In press.

[14] K. A. Kraus and J. R. Dam, Paper No. 4.14 "The Transuranium Elements" Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, (1949).

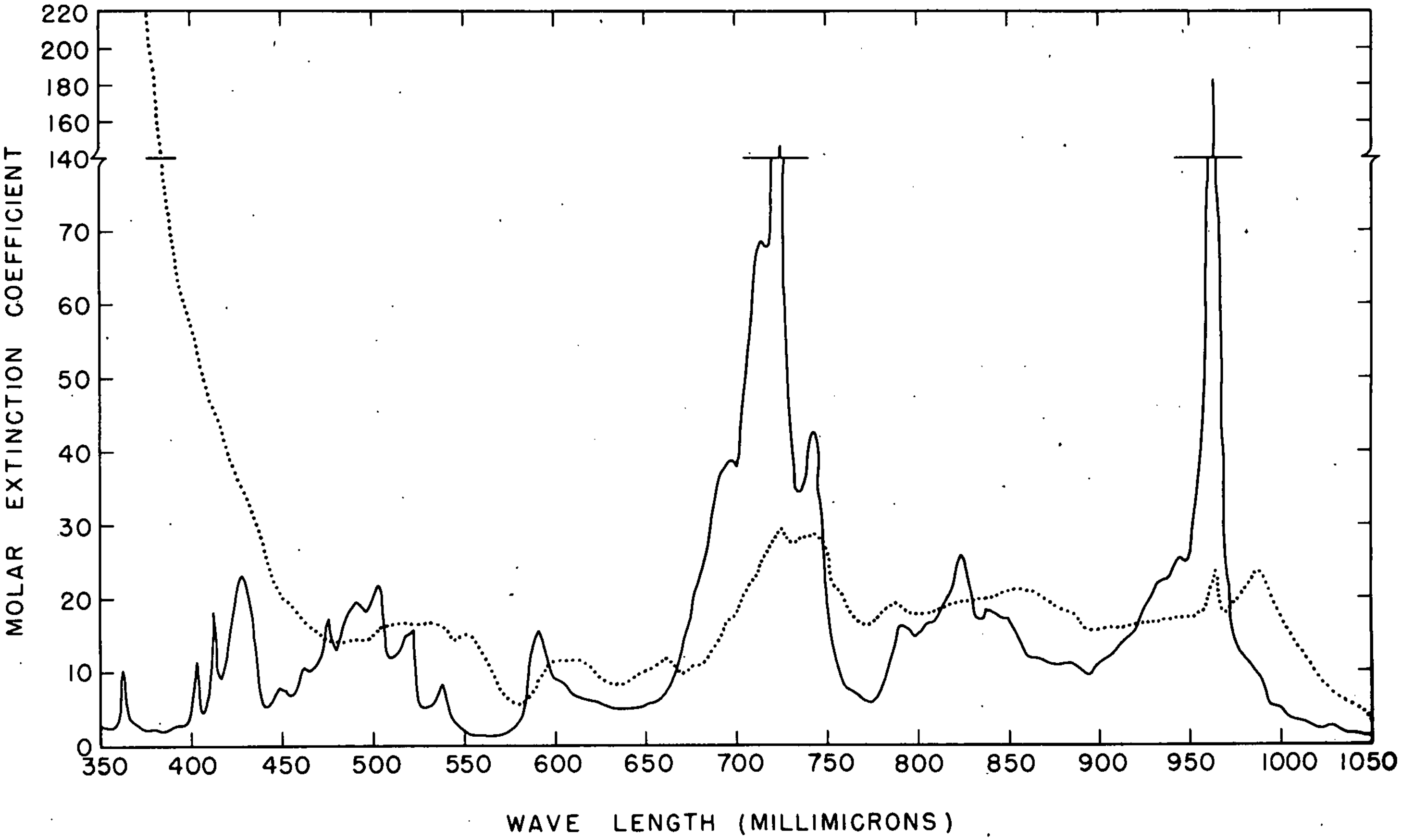

Figure 9

Effect of Decrease in Hydrogen Ion Concentration on the Absorption Spectrum of Neptunium(IV)

—— 1.00 M $HClO_4$
...... pH = 2.00

changes must be ascribed either to complex formation with the perchlorate or to a secondary effect ascribable to the change in the medium caused by the high acid concentration.

In arriving at an interpretation of the results, it is perhaps worthwhile to consider the nature of the absorption spectra of these ions. At the present time, the preponderance of evidence favors the hypothesis that these elements are part of a series in which the 5f shell is being filled. The data leading to this conclusion have been summarized by Seaborg.[15] Presumably, therefore, the characteristic sharp bands in the absorption spectra arise as in the case of the rare earths[16] from forbidden transitions in the f shell. According to this hypothesis the ground and upper states belong to the same configuration, $4f^x$ or for the new series, $5f^x$, the upper state differing only in the value of the collective azimuthal quantum member L or in the spin S, the individual l's remaining the same. With respect to the appearance of forbidden lines various explanations have been advanced[16] which include (1) quadrupole radiation, (2) magnetic dipole radiation, (3) electric dipole radiation due to an asymmetric field and (4) electric dipole radiation in which the field is symmetrical but the symmetry is removed by vibration from the equilibrium position. As a result of extensive researches on the absorption spectra of solutions of the rare earth ions, Broer, Gorter and Hoogschagen[17] have concluded that, with certain exceptions, the intensities of the sharp absorption lines can be accounted for if they arise from electric dipole radiation resulting from a perturbing electric field having no center of symmetry (hemihedric field). The splitting of the lines into several component levels in crystals or the broadening of the bands in solution is presumably due to an internal Stark effect induced by the symmetrical (holohedric) field of the surrounding anions.

Although the absorption spectra of the transuranium elements in solution resemble those of the analogous rare earths in general complexity of structure and sharpness of bands, there are certain points of difference. In the first place, the relative intensity of absorption is much greater for the principal bands of the transuranium elements than for the equivalent bands of the rare earths. In the case of the tripositive ions the intensity of absorption for the sharp characteristic bands is as much as ten times as great for the transuranium elements as for the rare earths. The transuranium element ions of higher charge show even more intense absorption, as much as a hundred times as great as for the tripositive rare earths.

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[15] G. T. Seaborg, Paper No. 21.1 "The Transuranium Elements" Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, (1949).

[16] J. H. Van Vleck, Jour. Phys. Chem. <u>41</u>, 67 (1947).

[17] L. J. F. Broer, C. J. Gorter and J. Hoogschagen, Physica <u>11</u>, 231 (1945).

These observations suggest a much greater interaction between the external field and the electrons in the 5f shell of the transuranium elements, an interaction that is intensified by the higher formal charge on the ions of higher oxidation number. One might expect this to have two results: (1) the effect of change in the environment should be more readily detected in solutions of ions of the transuranium elements and (2) sufficient distortion of the transuranium element ion by an anion might actually result in the transitions of the type $5f^x6d$. In the case of the rare earths such transitions are presumably responsible for the diffuse ultraviolet absorption spectrum of cerium(III). It would appear quite possible that the relatively intense diffuse ultraviolet absorption bands of neptunium(III) also result from such transitions. That similar transitions for the ions of neptunium(IV), (V) and (VI) may exist are suggested by the marked increase in absorption in the ultraviolet indicating the presence of intense absorption bands in the far ultraviolet beyond the range of the spectrophotometers used in this investigation.

If it is assumed on the basis of the above discussion that the absorption spectra of these ions would be reasonably sensitive to a change in the external field, it would appear that the absence of any effect caused by increasing perchloric acid concentration on the absorption spectrum of neptunium(III) can reasonably be interpreted as indicating the absence of any complex formation. With respect to neptunium(IV) if the slight effect observed is attributed to complex formation with perchlorate then either only a small amount of complex formation has taken place (as indicated by the relatively slight alteration in spectrum in comparison with changes observed in other cases for the transuranium elements where complex formation is known to occur[4,18]) or the effect of replacement of water molecules in the hydration sphere by perchlorate ions does not markedly affect the field. Another possible interpretation is that the spectral changes represent only a secondary effect. Since the observed spectral change is a decrease in absorption intensity it is perhaps due to a decrease in the asymmetric field caused by the disruption of the solution structure by the high perchloric acid concentration and the surrounding of the hydrated ion by a cloud of perchlorate ions.

In the case of neptunium(V) decreasing the acid concentration to pH 5.7 does not affect the spectrum. Further decrease in acid is only accompanied by precipitation of the neptunium(V) hydroxide. This behavior is consistent with the hypothesis that Np(V) in acid solution exists as NpO_2^+[19] and that no intermediate ions exist between NpO_2^+ and NpO_2OH. It is more

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[18] J. C. Hindman, Chap. IV. Vol. 14A of the Plutonium Project Record of the National Nuclear Energy Series. In preparation.

[19] L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "The Transuranium Elements," Paper No. 15.4 of Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series.

difficult to assess the effect of increasing acid concentration on the spectrum of neptunium(V) because of the disproportionation reaction occurring at high acid concentration. The only evidence for a change in the spectrum is the non-additivity of the spectra at high acid concentration. This non-additivity could be attributed by a decrease of approximately 10 per cent in the peak height of the 983 millimicron band. The fact that the disproportionation of neptunium(V) is observed in strongly acid solutions, is support for the view that the neptunium(V) ion remains oxygenated even in concentrated perchloric acid. This point will be discussed in more detail after the effect of perchloric acid concentration on the spectrum of neptunium(V) is considered.

Figures 10 and 11 illustrate the effect of changing perchloric acid concentration on the spectrum of neptunium(VI). As in the case of uranium[1] and plutonium[20] decreasing the acid concentration sufficiently to cause hydrolysis causes marked changes in the absorption spectrum. These changes are a general loss of structure in the 400-640 millimicron region, a marked increase in the absorption intensity in the visible and ultraviolet regions and the disappearance of the vibrational bands. Since the hydrolysis to form ions such as NpO_2OH^+ involves the formation of additional metal oxygen bonds with a consequent disruption of the symmetry of the neptunyl ion the disappearance of the vibrational structure is not unreasonable.

The effect of increasing acid concentration on the neptunium(VI) spectrum is much less marked. There is an increase in the absorption in the 390-540 millimicron region accompanied by a shift to the violet of the 478 and 556 millimicron bands. Certain of the bands are not affected. These include the 448, 505 and 592 millimicron bands and the vibrational bands. The frequency interval found for the vibrational bands was 715 cm^{-1} in 1.0 M $HClO_4$, 709 cm^{-1} in 10 M $HClO_4$ and 704 cm^{-1} at pH 2.7 (in 1 M $NaClO_4$). In solutions of the uranyl ion, the effect of increasing the perchloric acid concentration is less marked than for neptunium(VI). There is a general decrease in absorption together with a general shift of all the absorption bands to the red without, however, affecting the frequency interval between the vibrational bands.

It is apparent from these observations that even at high perchloric acid concentrations ions of the type NpO^{+4} and UO^{+4} are not formed since the vibrational structure characteristic of the symmetrical vibrations in the $O = X^{++} = O$ ions persists. It is less easy to rule out the possibility that ions of the type $X(OH)_2{}^{+4}$ are formed. In this case, the situation might be considered as somewhat analogous to that existing in crystals of such salts as the double nitrate of uranium(VI). Depending on the strength of

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[20] G. E. Moore and K. A. Kraus, Paper No. 4.22, "The Transuranium Elements" Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series. McGraw-Hill, New York, 1949.

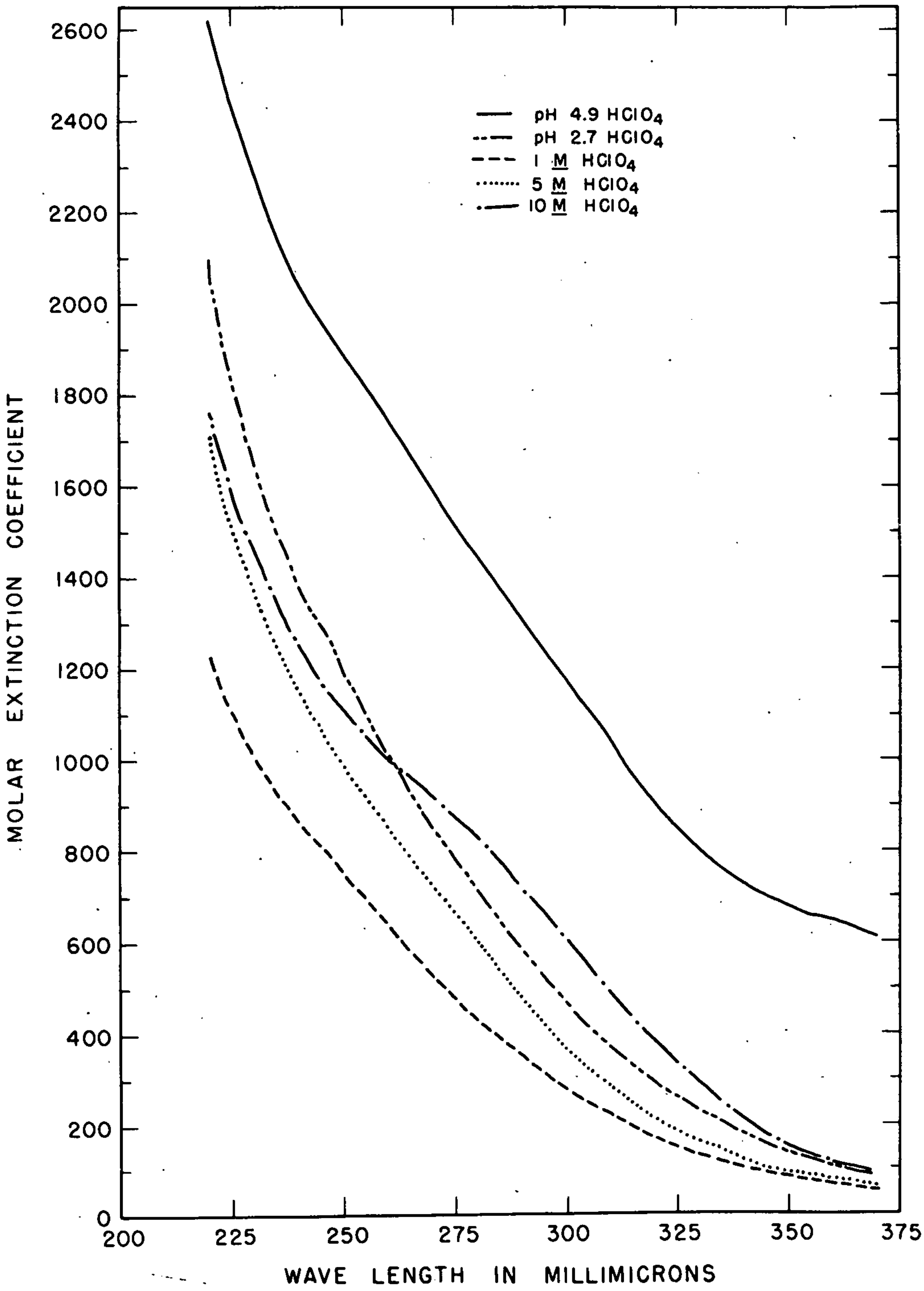

Figure 10

Influence of Hydrogen Ion Concentration on the Ultraviolet Absorption Spectra of Neptunium(VI)

——— Np(VI) in $HClO_4$ pH 4.9
———.. Np(VI) in $HClO_4$ pH 2.7
- - - - Np(VI) in 1.0 M $HClO_4$
...... Np(VI) in 5.0 M $HClO_4$
.———. Np(VI) in 10.0 M $HClO_4$

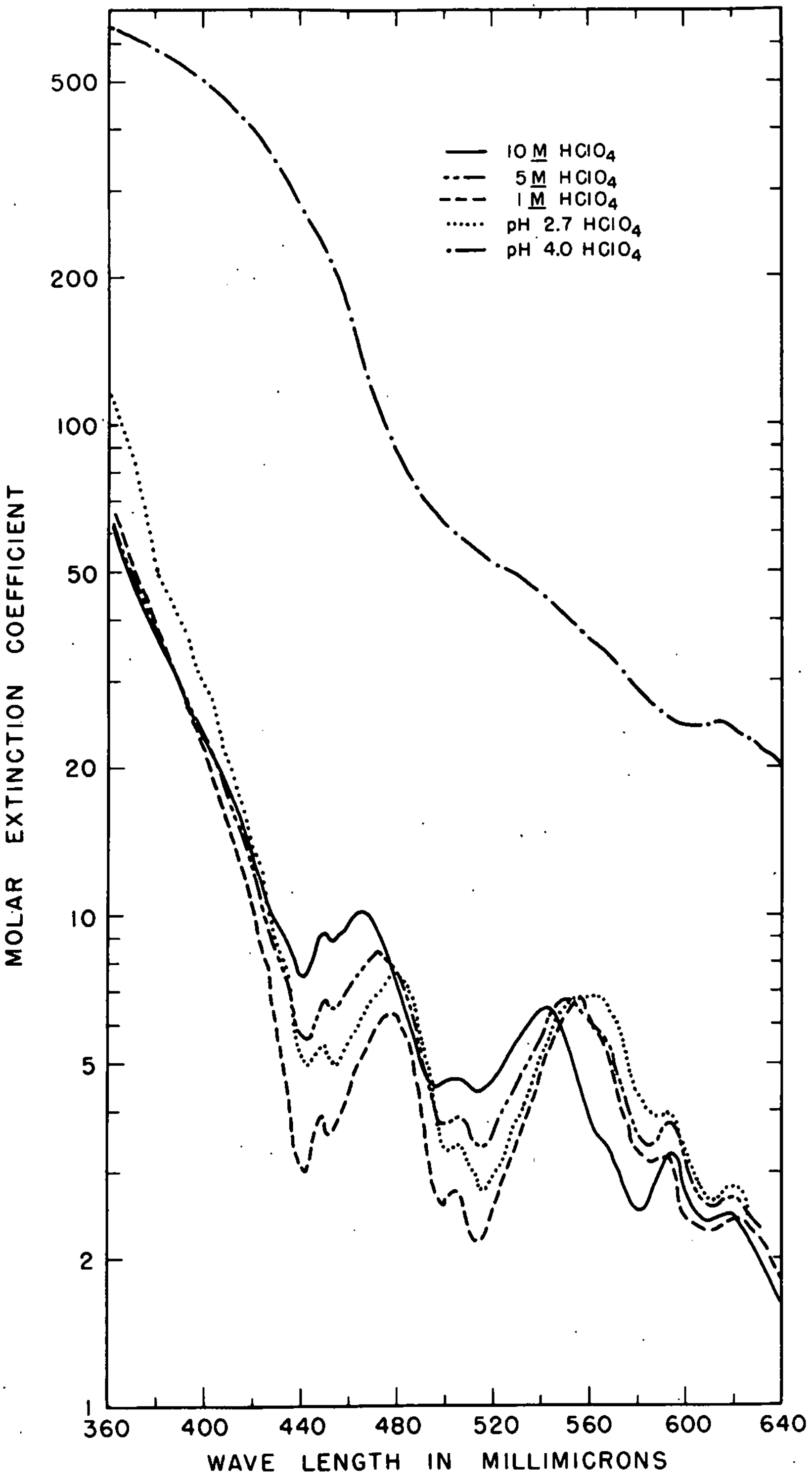

Figure 11

Influence of Hydrogen Ion Concentration on the Absorption Spectra of Neptunium(VI)

———	Np(VI) in 10.0 $\underline{M}$ $HClO_4$	-------	Np(VI) in 1 $\underline{M}$ $HClO_4$
— -- —	Np(VI) in 5.0 $\underline{M}$ $HClO_4$	....	Np(VI) in $HClO_4$ pH 2.7
.——.——.	Np(VI) in $HClO_4$ pH 4.0		

the hydrogen bonds we might then expect a shift in vibrational frequency similar to that found in going from one double nitrate to another. Since this would probably not exceed 10-25 cm^{-1}, it might easily be undetected in the solution measurements. To elaborate this point other methods of investigation than the measurement of solution absorption spectra will have to be used.

Before concluding the discussion the deductions that can be made from the fact that the neptunium(V) ion disproportionates at high acid concentrations should be considered. In the following table various possible ions of neptunium(V) and (VI) are listed, together with the hydrogen ion functions that would be observed in each case for the reaction

$$2Np(V) + XH^+ \rightleftharpoons Np(IV) + Np(VI) + yH_2O \qquad (3)$$

It can be seen by examination of Table 8, that the maximum number of hydrogen ions involved in the disproportionation reaction could exceed four only if it was postulated that the neptunium(VI) ion was more susceptible

Table 8

Possible Neptunium Ion Species Taking Part in Disproportionation Reaction

Possible Ions of Neptunium			H^+ Power	H_2O Power
Np^{+4}	NpO_2^+	NpO_2^{++}	4	-2
Np^{+4}	$NpOOH^{+2}$	NpO_2^{++}	2	-2
Np^{+4}	NpO^{+3}, $Np(OH)_2^{+3}$	NpO_2^{++}	0	0, -2
Np^{+4}	$NpOH^{+4}$	NpO_2^{++}	-2	0
Np^{+4}	NpO_2^+	$NpOOH^{+3}$	5	-2
Np^{+4}	$NpOOH^{+2}$	$NpOOH^{+3}$	3	-2
Np^{+4}	$Np(OH)_2^{+3}$, NpO^{+3}	$NpOOH^{+3}$	1	0
Np^{+4}	$NpOH^{+4}$	$NpOOH^{+3}$	-1	0
Np^{+4}	$Np(OH)_2^{+3}$	$Np(OH)_2^{+4}$	2	-2
Np^{+4}	$Np(OH)^{+4}$	$Np(OH)_2^{+4}$	0	0

to reaction with hydrogen ion than the neptunium(V) ion. This would appear unlikely in view of the greater formal charge on the neptunium(VI) atom. As has been pointed out, the data on the vibrational frequencies for the two ions would indicate a stronger binding for the oxygens in the Np(VI) ion hence one would expect the Np(V) ion to react more readily with hydrogen ions. Furthermore, in view of the persistence of the vibrational structure even in very concentrated acid solutions, it appears that the possibility of ions having fewer than two OH groups can also be excluded insofar as the neptunium(VI) is concerned. A similar argument can be made against the formation of neptunium(V) ions of the type NpO^{+3} or $NpOH^{+4}$ since marked spectral changes would be expected in these cases. The fact that the disproportionation reaction occurs also eliminates those ion species giving a zero or inverse hydrogen ion function for the reaction. With these restrictions in mind reference can be made to the data on the disproportionation reaction summarized in Table 7. The constant for the reaction can be written in the form

$$K_1' = \frac{[Np(IV)]\,[Np(VI)]}{[Np(V)]^2\,[H^+]^x} = K_1 \frac{\gamma^x H^+ \gamma^2 Np(V)}{\gamma Np(VI) \quad \gamma Np(IV)\ [^aH_2O]^y} \qquad (4)$$

In the absence of any quantitative data on the activity coefficients of any of the neptunium ions, an approximate calculation of the hydrogen ion power on the assumption that the activity coefficient ratio, $\frac{\gamma^2 Np(V)}{\gamma Np(VI) \quad \gamma Np(IV)}$, is unity, neglecting the water activity term, and using the mean activity coefficients of perchloric acid from the data of Robinson and Baker[21] for the hydrogen ion activity gives an approximately third power dependence between the 1.0 M and 5.34 M acid solutions. Although this might be interpreted as indicating the formulae $NpOOH^{+2}$ and $NpOOH^{+3}$ for the neptunium(V) and (VI) ions respectively, in view of the rather drastic assumptions involved this cannot be taken as conclusive. Further investigation of the disproportionation reaction at constant ionic strength are contemplated to settle the question.

Summary

1 Details of the absorption spectra of the neptunium(III), (IV), (V) and (VI) ions in 1 M perchloric acid are given. The principal bands have been tested for adherence to the Beer-Lambert Law. 2

Vibrational fine structure has been found in the absorption spectra of Np(V) and Np(VI). As for U(VI) and Pu(VI), this fine structure is interpreted as being due to symmetrical metal-oxygen vibrations in ions of the type NpO_2^+ and NpO_2^{++}. The vibrational frequency of the Np(V) ion is

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[21] R. A. Robinson and O. J. Baker, Trans. Royal Soc. New Zealand 76, 250-54 (1946).

753 cm^{-1} and that of the Np(VI) ion is 715 cm^{-1} in 1 $\underline{M}$ $HClO_4$.

The interpretation of effect of change in perchloric acid concentration on the absorption spectra of the ions of the various oxidation states is discussed.

Preliminary data on the disproportionation reaction

$$2\ \mathrm{Np(V)} \rightleftharpoons \mathrm{Np(IV)} + \mathrm{Np(VI)}$$

which has been found to occur in concentrated perchloric acid solutions is given. (auth)

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Appendix

Summary of Beer-Lambert Law Data for Neptunium Absorption Bands

Table A

Neptunium(III) in 1.0 M $HClO_4$

Beer's Law Data

[Np] moles/liter	Slit .035 mm λ = 552 mμ		Slit .030 mm λ = 602 mμ		Slit .0125 mm λ = 661 mμ		Slit .0125 mm λ = 788 mμ		λ = 233.5 mμ		λ = 267.0 mμ	
	d	E	d	E	d	E	d	E	d	E	d	E
.01326	.598	45.10	.347	26.16	.406	30.45	.638	48.11	-	-	-	-
.005644	.251	44.47	.144	25.51	.174	30.83	.275	48.72	-	-	-	-
.007855	.348	44.30	.205	26.10	.233	29.66	.375	47.74	-	-	-	-
.004654	.213	45.77	.126	27.07	.141	30.29	.225	48.35	-	-	-	-
.002379	.107	44.98	.091	25.64	.074	31.10	.115	48.34	-	-	-	-
.002241	.099	44.18	.057	25.43	.065	29.00	.110	49.09	-	-	-	-
.001590	.073	45.91	.042	26.42	.049	31.08	.077	48.43	-	-	2.53	1591
.001143	.048	42.03	.027	23.62	.033	28.87	.054	47.24	2.632	2303	1.835	1605
.0007275	.032	43.98	.019	26.11	.023	31.62	.035	48.11	1.663	2286	1.153	1585

Table B

Beer's Law Data for Neptunium(IV) Bands at 723 and 964 Millimicrons

Slit width / Np moles/liter conc.	964 mμ								723 mμ	
	d	d	d	d	E	E	E	E	d	E*
	.0125	.0150	.0175	.020	.0125	.0150	.0175	.020	.0125	.0125
.01300	1.91	1.87	1.82	1.80	146.92	143.85	140.00	138.46	1.88	144.62
.01091	1.74	1.71	1.69	1.64	159.49	156.74	154.90	150.32	1.58	144.82
.009281	1.55	1.51	1.49	1.47	167.00	162.69	160.53	158.38	1.34	144.38
.008236	1.44	1.40	1.36	1.35	174.83	169.97	165.12	163.90	1.18	143.28
.006576	1.20	1.17	1.15	1.11	182.48	177.92	174.88	168.80	.948	144.16
.004714	0.928	0.907	0.876	0.854	196.86	192.40	185.83	181.16	.678	143.82
.003409	0.656	0.644	0.634	0.622	192.43	188.91	185.98	182.46	.493	144.62
.002425	0.469	0.465	0.463	0.456	193.40	191.75	190.93	188.04	.349	143.92
.001740	0.336	0.332	0.329	0.324	193.10	190.80	189.08	186.21	.251	144.25
.0009006	0.174	0.170	0.168	0.165	193.20	188.76	186.54	183.21	.129	143.25

*Average E values for varying slit widths

.0150 mm $E_{aver.}$ = 141.72
.0175 mm $E_{aver.}$ = 140.09
.020 mm $E_{aver.}$ = 137.89

Table C

Np(V) in 1 M $HClO_4$

983 Peak

Slit width Np moles/liter conc.	d	d	d	d	E	E	E	E
	.0125	.0150	.0175	.020	.0125	.0150	.0175	.020
.006512	1.90	1.81	1.70	1.63	292.08	277.84	260.95	250.21
.006000	1.76	1.76	1.65	1.60	293.33	293.33	275.00	266.67
.005603	1.63	1.58	1.60	1.53	290.02	281.98	285.55	273.06
.005100	1.49	1.45	1.43	1.40	292.16	284.30	280.38	274.50
.005090	1.48	1.44	1.40	1.36	290.77	282.90	275.04	267.19
.004552	1.43	1.39	1.32	1.30	318.32	305.36	289.98	285.58
.003847	1.20	1.18	1.15	1.14	311.93	306.73	298.93	296.33
.003633	1.14				313.79			
.003294	1.08	1.05	1.03	1.01	327.87	318.76	312.69	306.62
.002709	.901	.874	.857	.843	332.62	322.62	316.34	311.18
.002241	.763	.754	.744	.736	340.47	336.46	331.99	328.42
.001909	.657				344.16			
.001378	.480	.470	.460	.440	348.33	341.07	333.81	319.30
.001350	.462	.458	.454	.451	342.22	339.26	336.30	334.07
.001012	.340	.337	.331	.330	335.97	333.30	327.07	326.09
.0007182	.266	.259	.255	.252	370.37	360.61	355.04	350.86
.0003603	.130	.1295	.129	.1285	360.81	359.41	358.03	356.64