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LASER SPECTROSCOPY OF NEPTUNIUM; FIRST IONIZATION POTENTIAL, LIFETIMES AND NEW HIGH LYING ENERGY LEVELS OF Np I

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Laser spectroscopy of neptunium; first ionization potential, lifetimes and new high lying energy levels of Np I

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The first ionization potential of neptunium has been determined from the photoionization threshold and from Rydberg series observed by laser spectroscopy techniques. The Rydberg series convergence limits yield the most accurate value of 50 536(4) cm^{-1} [6.2657(5) eV]. The radiative lifetimes of five levels in the 26 200 to 29 050 cm^{-1} range have been measured. New energy levels, 27 odd and 37 even, in the 33 000 to 37 000 cm^{-1} range have been determined with approximately ±0.5 cm^{-1} precision.

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48."

INTRODUCTION

We have used the laser spectroscopy techniques[1,2] developed to study uranium and the lanthanides to investigate neptunium. The first ionization potential (IP) of Np was determined by both the threshold of photoionization and the convergence of Rydberg series. Thresholds and Rydberg series were obtained from several different laser populated excited levels. The Rydberg convergence values are the most accurate and yielded a value of 50 536(4) cm^{-1} [6.2657(5)eV] for the IP of Np. (Throughout this paper, numbers in paranthesis give the uncertainly in the last digit). This value is somewhat larger and much more accurate than the values obtained by surface ionization[3] [6.16(6)eV], appearance potential[4] [6.1(1)eV] or from the $5f^57s^2$ - $5f^57s8s$ interval[5] [6.19(12)eV]. The lifetimes of five levels were determined and estimates of transition probabilities were made from emission intensities.[6] For three-step excitation of Rydberg series new high odd levels had to be determined because none were known[7] in the required energy range.

EXPERIMENTAL

The experimental apparatus used has been described in detail[2]. In the experiments, an atomic beam of Np was irradiated sequentially by 2 or 3 tunable pulsed dye lasers that stepwise excited and photoionized the atoms (threshold detection) or populated bound Rydberg levels which were field ionized. The ions formed were detected by channeltron particle multipliers and the output processed by a box car integrator. Ions produced by photoionization were quadrupole mass filtered (threshold experiments) while those produced by field ionization (Rydberg series experiments) were deflected by the ionizing field directly to a channeltron detector.

The Np beam was generated using a resistively heated tungsten tube oven containing a single crystal tantalum crucible[8] loaded with 0.5g of pure ^{237}Np metal. Sufficient vapor density for our experiments was produced by heating the oven to 1900°K or less. Two separate experiments, one to obtain photoionization thresholds, lifetimes and to search for autoionizing Rydberg series and the other to obtain bound Rydberg series and levels in the 33 000 to 37 000 cm^{-1} region were conducted using 0.5g Np metal for each. The ^{237}Np metal was provided by R.N.R. Mulford and S.E. Bronisz of the Los Alamos Scientific Laboratory. Because of the vapor pressure relation between Np and NpO[9] and since no quadrupole filtering was used in the field ionization experiment, it was necessary to eliminate NpO from the source by heating at about 1650°K for approximately 12 hrs.[8] This avoided extraneous signals from photoionized NpO that can absorb at the laser wavelengths used.

Ionization Potential

We first determined the photoionization threshold because it is easy to recognize and it would give us an ionization potential accurate to 30 cm^{-1} that we could use to limit the region of search to find Rydberg series. For the thresholds searches, we used two step photoionization techniques.[2] Our search range determined by the uncertainties and variation in the reported[3-5] IP values was about 2400 cm^{-1} or 430 Å. Fig. 1 shows a photoionization threshold of Np marked by the onset of very strong dense autoionization features.

Autoionizing Rydberg series were searched for but none were found because of the very dense autoionization structure from "valence" levels. To obtain Rydberg series in Np it was necessary to apply ionization techniques [1] where the bound Rydberg levels were ionized by a pulsed field applied several microseconds (5 μs in this case) after the last populating laser was fired. This allowed decay of the shorter lived valence states that would obscure the Rydberg series. Several series were obtained by this technique.

Lifetimes and New High Lying Levels

The lifetimes and new levels were determined using techniques explained in detail elsewhere.[1] Lifetimes were determined from plots of natural logarithm of the ion signal vs. delay time between the photoionizing laser pulse and the populating pulse, see Figure 2.

New high lying even and odd levels were found by multistep photoionization techniques. These new levels were determined to use for three step laser excitation of Rydberg levels. To obtain the levels, laser 1 was fixed at a known wavelength to populate an odd or even level in the 16 000 - 19 000 cm^{-1} range. Laser 2 was scanned over the desired wavelength range and laser 3 was fixed at a wavelength to ionize any levels populated by scan laser 2. Thirty seven even levels and twenty seven odd levels were found but only a few were used in our three step laser excitation studies.

RESULTS AND DISCUSSION

Ionization Potential

The photoionization thresholds obtained are given in the last column of Table I. The populating laser wavelength (λ_1), the transition (lower and upper populated levels) and the threshold wavelength are shown in columns 1 to 3. The excitation wavelengths and transition energies are from Fred, et al.[6,7] Only two step excitation schemes were used for the threshold determinations. The threshold values obtained yield an average value of 50 517(6) cm^{-1} [6.2633(7) eV]. While the precision of the threshold value is very good, it is 19 cm^{-1} below the more accurate ionization potential obtained from Rydberg convergence limits, see Table II. The same approximate difference (15 to 40 cm^{-1}) between the threshold value and the Rydberg convergence value was found for the lanthanides and for uranium. The difference is attributed to an unknown experimental parameter, such as electric fields from ion optics, intense laser radiation and/or collisional effects.

The Rydberg convergence limits in Table II were obtained by three step excitation techniques except for one value from two step excitation. A three step scan containing two Rydberg series is shown in Fig. 3. The excitation scheme is shown at the left on the Figure. The 1.3 μs wide field ionization pulse of 7000 V/cm was applied 5 μs after the laser 3 pulse. As indicated on the Figure, one series converges to the $5f^4 6d7s\,^7L_5$ ground state of the ion while the other series converges to the $5f^4 7s^2\,^5I_4$ level 24.27 cm^{-1} above the ground state.[10] For the latter series, the shorter markers are calculated positions obtained from the equation

$$\text{level value} = \text{limit} - [R/(n^*)^2]$$

assuming that the fractional part of the quantum defect $(n-n^*)$ was constant at 0.3. This is the value obtained from the higher members (longer markers) of the series. As can be seen, these two series explain most of the observed features. In addition to the two limits at 0.00 and 24.27 cm^{-1}, Np has a third limit at 83.49 cm^{-1} above the ground state so that many of the unexplained features in the scan could be Rydberg members converging to this limit. The next limits are more than 900 cm^{-1} away.

Values of n^* for the Np series were determined using the equation

$$n^* = [R/\ (\text{assumed limit} - \text{level value})]^{1/2}.$$

The variation in quantum defect $(n-n^*)$ vs. n with change in assumed limit for the two series in Fig. 3 are shown in Figs. 4 and 5. The value of n is not necessarily the principal quantum number but a number chosen close to n^* to evaluate the variation in quantum defect. The series convergence limit (ionization limit) is taken as the assumed limit that gives the most constant quantum defect as a function of n for the high quantum number Rydberg levels.[2] Limits obtained by this technique for nine neptunium Rydberg series are listed in Table II. The uncertainties given in Table II are estimates from the quantum defect plots. They are considerably larger than the standard deviation of the nine values.

Table III is a summary table of the ionization potential determinations for neptunium. Our values are higher but more accurate than the other experimental values and the value obtained by Rajnak and Shore[11] based on regularities in s electron binding energies in $\ell^N s^M$ configurations. The ionization potential derived from Rydberg series is the most accurate value. The surface ionization[3] and appearance potential[4] values are lower than this value beyond their quoted uncertainties. Sugar's value[5] obtained from interpolated f^n7s^2 - f^n7s8s intervals in the actinides agrees within his quoted uncertainty.

Lifetimes and New High Lying Levels

Lifetimes of two even and three odd levels of Np are given in column 2 of Table IV. The transition and its wavelength are listed in columns 3 and 4. The branching ratios (B.R.) in column 5 were estimated from unpublished data of M. Fred, et. al.[6] These branching ratios were used with the equation

$$A = \frac{B.R.}{\tau}$$

to calculate the transition probabilities given in column 6. The uncertainties estimated for the branching ratios and the transition probabilities may be conservative. The uncertainties could be as large as 50 percent of the value.

The high even levels of Np are reported in Table V. Searches were made from three different levels. Their wavelengths, energies and J's are the headings for columns 1, 2 and 3 of the table. Column 4 gives the average energy of the levels found. The estimated uncertainity in the level energy is less than 0.5 cm^{-1} when observed from 2 or more odd levels and about 1 cm^{-1} when observed from only one level. Since the odd levels used have J values of 4.5 and 6.5, the selection rule $\Delta J=0,\pm 1$ can be used to assign J values, see column 5. The only case where an unequivocal assignment can be made is for the value 5.5. Further searches from other levels could improve the J assignment.

High odd levels obtained in a search from the 19 373.87 cm^{-1}, J = 3.5 even level are listed in Table VI. These levels are uncertain by about 1 cm^{-1}. Their J value can be either 2.5, 3.5 or 4.5.

These energy level searchs are by no means a complete coverage of the energy ranges. They were only performed to obtain levels for use in our three-step laser excitation studies. The few levels used in the studies are listed in column 3 of Table II.

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Figure Captions

Figure 1. Neptunium photoionization threshold spectrum. The excitation scheme is shown at the left. The threshold at 4593 Å is marked by the onset of very strong autoionization peaks. It yields an ionization potential of 50 518 cm^{-1} (6.2634 eV).

Figure 2. Plot of neptunium ion signal vs. ionizing pulse delay time for the 28 986 cm^{-1} odd level of neptunium. The transition and excitation wavelength are given in Table III. The wavelength of the ionizing laser was 4310 Å.

Figure 3. Rydberg series in neptunium obtained by field ionization (double arrow) of laser excited levels. The excitation scheme is shown on the figure. The spectrum contains two series, one converging to the $4f^4 6d7s\ ^7L_5$ ground state and the other converging to the $^5I_4$ level at 24.27 cm^{-1} in the ion. For the series converging to the $^5I_4$ level, the Rydberg level positions with n^* less than 40.7 (short markers) are calculated using a constant fractional defect of 0.3.

Figure 4. Variation in quantum defect $(n-n^*)$ vs. n with charge in assumed ionization limit for the neptunium series in Figure 3 converging to the ground state of the ion. The assumed limit giving the most constant quantum defect is 50 536 cm^{-1} and is taken as the ionization limit.

Figure 5. Variation in quantum defect vs. n with charge in assumed limit for the series in Figure 3 converging to the $^5I_4$ level in the ion. The assumed limit giving the most constant quantum defect is 50 535 cm^{-1} and when corrected by 24.27 cm^{-1} yields the ionization limit of 50 535 cm^{-1} for neptunium.

PHOTOIONIZATION THRESHOLD SPECTRUM FOR N_p

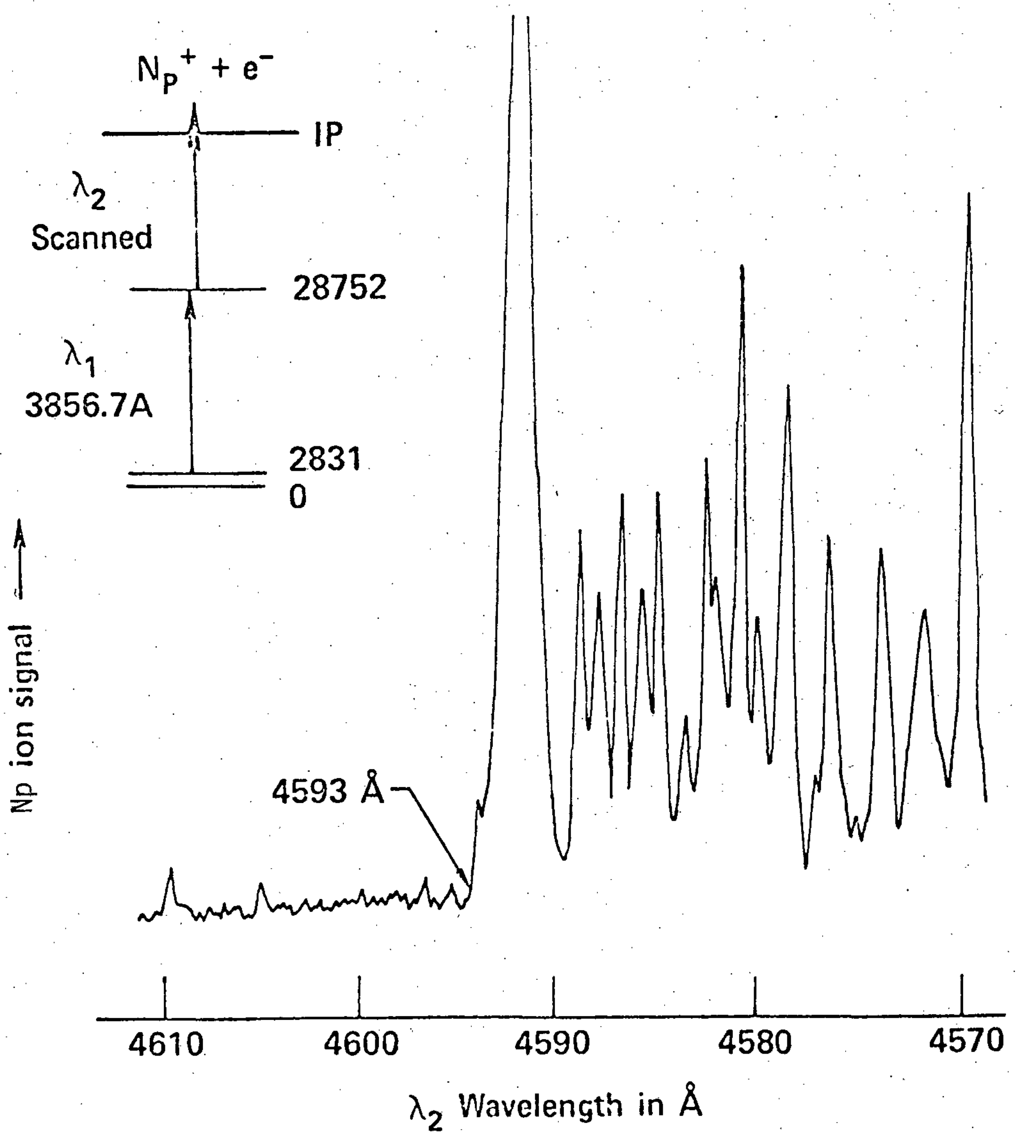

Figure 1

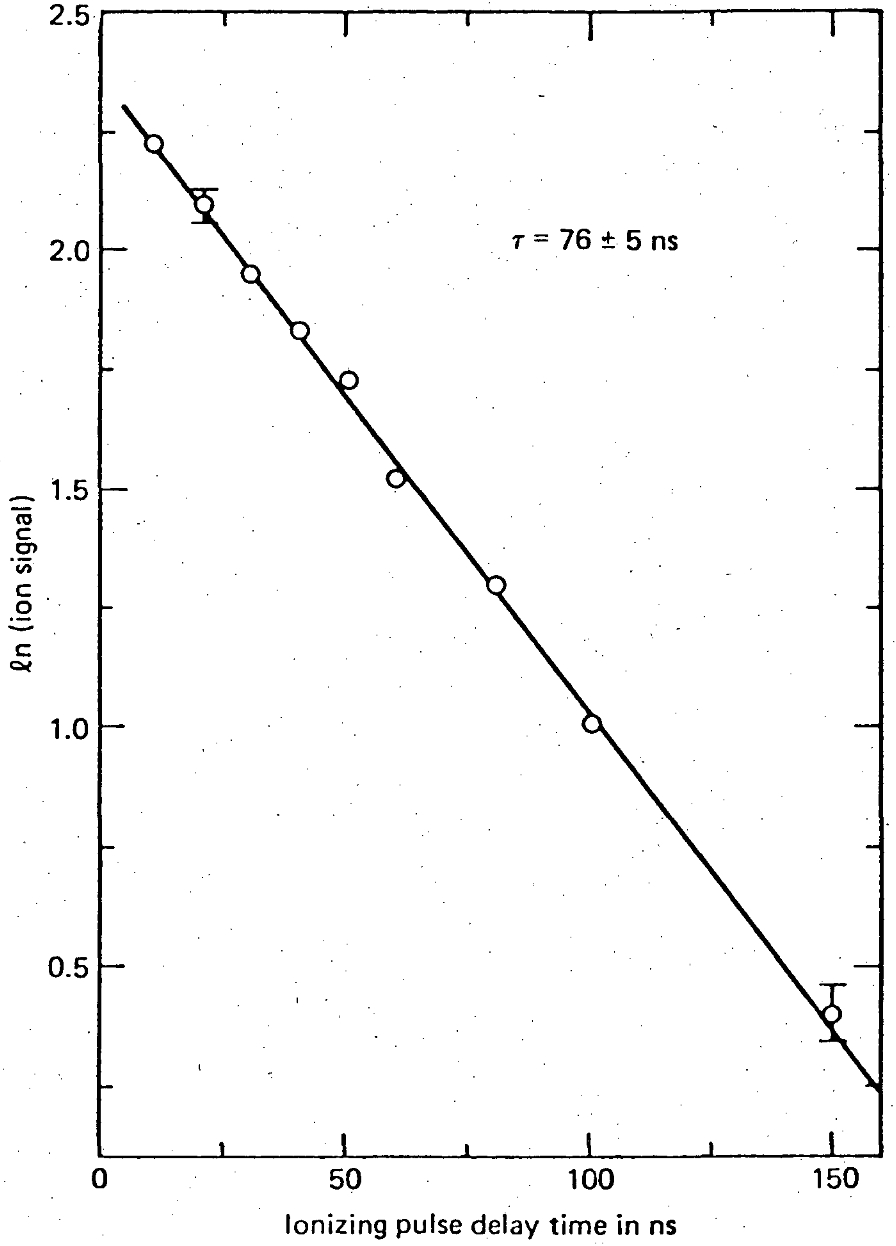
2.5
2.0
1.5
1.0
0.5
ℓn (ion signal)
τ = 76 ± 5 ns
0
50
100
150
Ionizing pulse delay time in ns

Figure 2

NEPTUNIUM RYDBERG SERIES

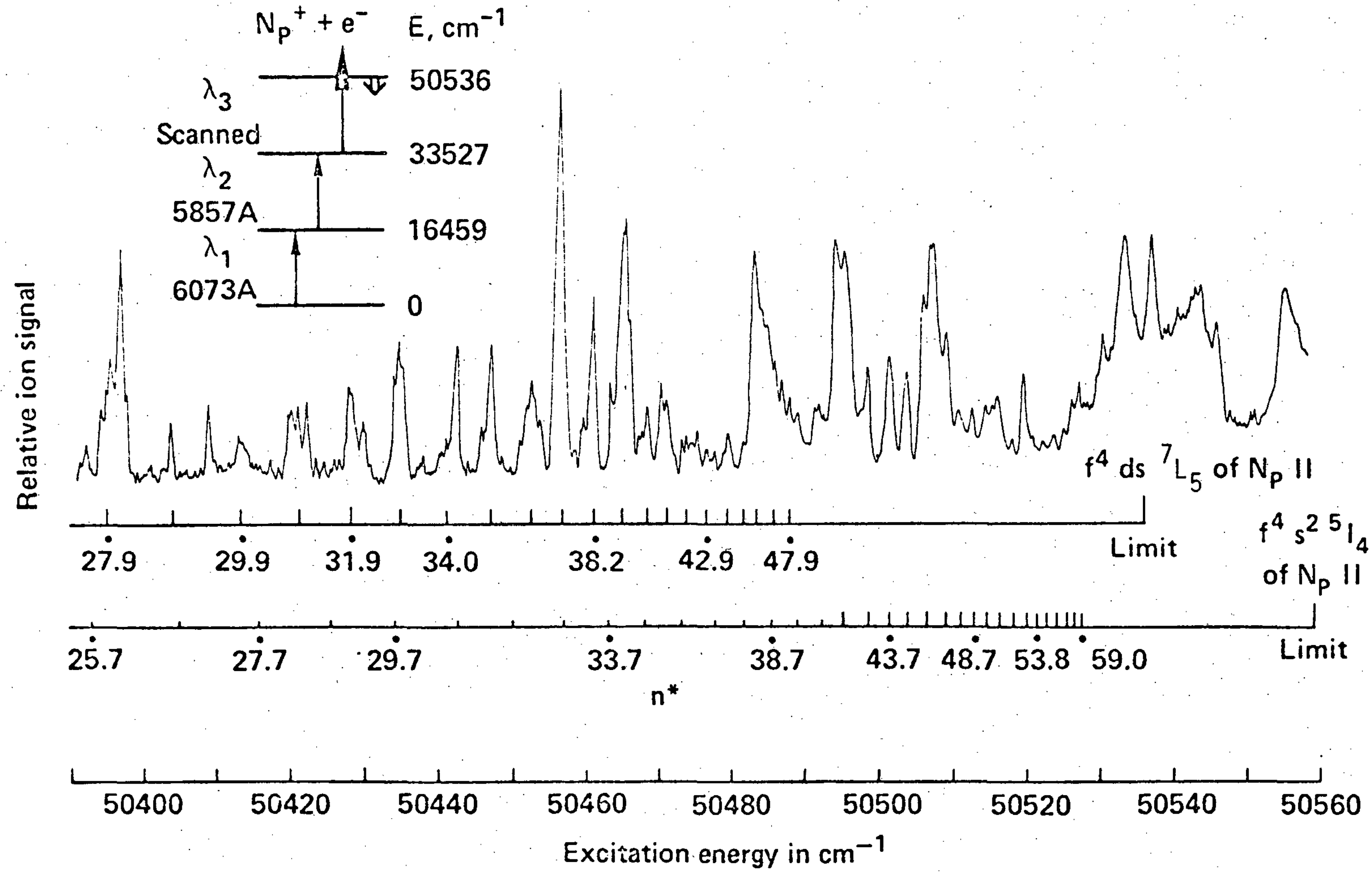

Figure 3

VARIATION IN QUANTUM DEFECT (n-n*) VS n WITH CHANGE IN ASSUMED LIMIT FOR N_p

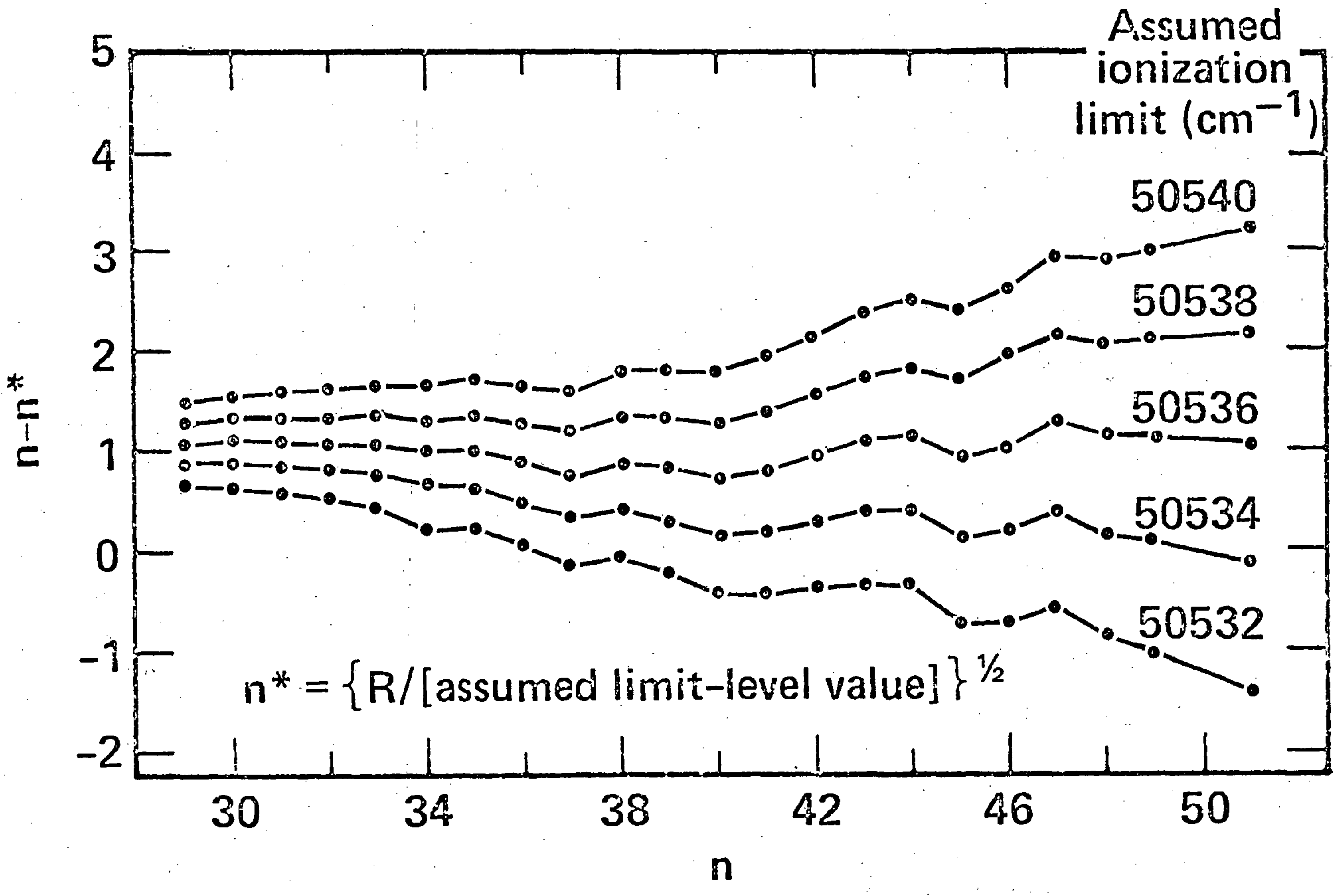

Figure 4

VARIATION IN QUANTUM DEFECT (n-n*) VS n WITH CHANGE IN ASSUMED LIMIT FOR N_p

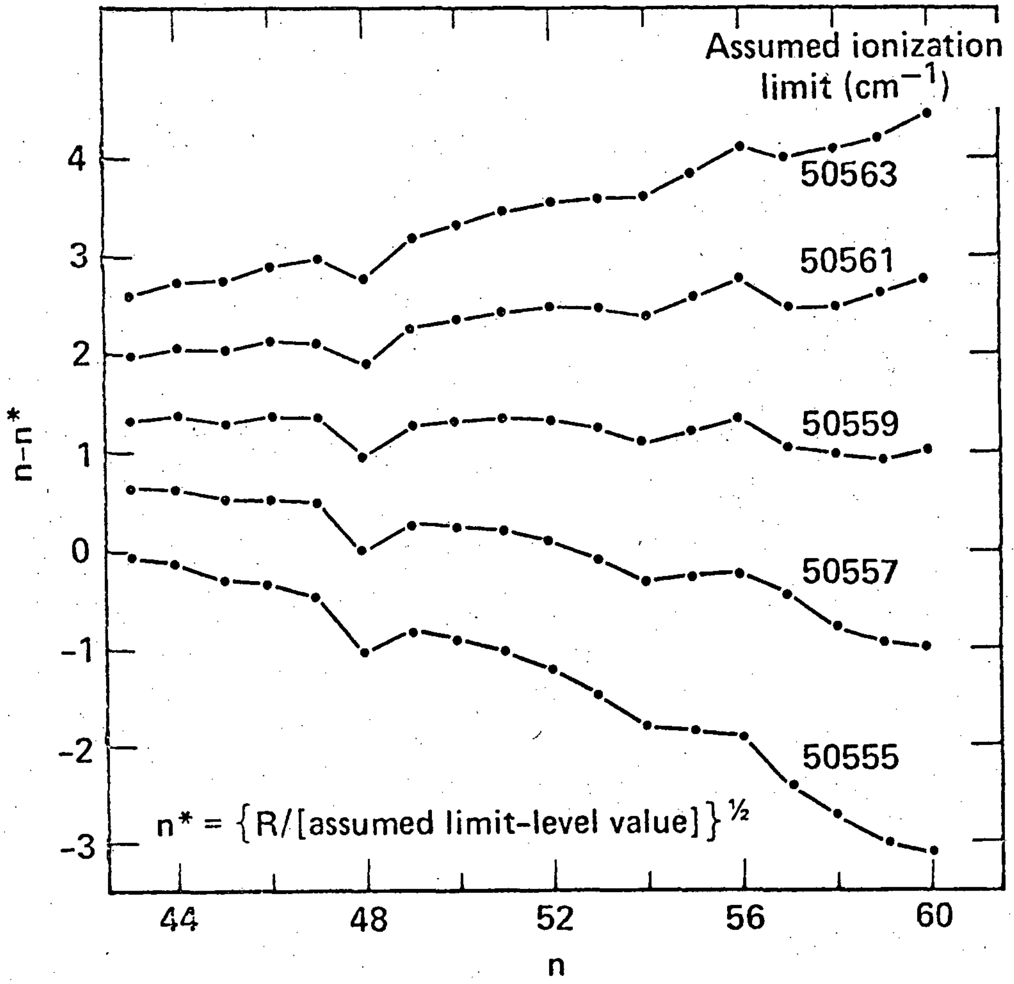

Figure 5

Table I. Photoionization thresholds obtained for neptunium by two-step laser excitation.

Excitation[a] Wavelength (Å)	Transition and Excited Level Used[a] cm^{-1}		λ_2 Wavelength at Threshold (Å)	Ionization Threshold cm^{-1}
	Odd	Even		
3806.36	26264.37-	0.00	4122.6	50514(3)
3822.22	2831.10-	28986.45	4637	50516(5)
3849.42	25970.58-	0.00	4072.7	50517(3)
3856.75	2831.10-	28752.39	4593	50518(5)
3876.23	27824.89-	2033.94	4406	50514(5)
3888.47	27743.72-	2033.94	4389	50521(5)
				50517(6) [6.2633(7)] eV [b]

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[a] Wavelengths, transitions and energy levels from Reference 6.

[b] Uncertainty is three times standard deviation. The conversion factor 1 eV = 8065.479 cm^{-1} was used.

Table II. Rydberg series limits determined by stepwise laser excitation techniques for Np and ionization potentials derived.

λ_1[a] Å	λ_2 Å	Transition and Excited Level[b] cm^{-1}		Number of Members	Convergence Limit[c] (cm^{-1})	Convergence Level in Ion[d] (cm^{-1})	First Ionization Potential[c] (cm^{-1})
		Odd	Even				
6073.897	5857.3	16 459.34-	33 527.4	22 18	50 536(4) 50 559(4)	0.00 24.27	50 536(4) 50 535(4)
6073.897	5868.2	16 459.34-	33 495.5	19	50 537(3)	0.00	50 537(3)
6073.897	5885.5	16 459.34-	33 445.5	23 14	50 536(4) 50 559(5)	0.00 24.27	50 536(4) 50 535(5)
6073.897	5911.2	16 459.34-	33 371.7	35	50 536(4)	0.00	50 536(4)
6073.897	5924.4	16 459.34-	33 333.8	23	50 536(4)	0.00	50 536(4)
6188.594	5766.3	16 154.29-	33 491.6	14	50 536(4)	0.00	50 536(4)
3877.537	–	25 782.26-	0.00	17	50 559(6)	24.27	50 535(6)
							50 536(4) [6.2657(5) eV][e]

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[a] All first step transitions are from the ground state of Np I. Wavelengths are from Ref. 6.

[b] High even levels determined by laser spectroscopy. The levels are accurate to about ± 0.5 cm^{-1}. Odd level values are from Ref. 7.

[c] Uncertainties in parenthesis are estimates from quantum defect plots, see Figs. 4 and 5.

[d] Levels in the ion are from Ref. 10.

[e] The conversion factor 1 eV = 8065.479 cm^{-1} was used.

Table III. First ionization potentials of neptunium determined by various techniques.

Ionization Potential (cm^{-1})	(eV)	Method	Reference
49 685(480)	6.16(6)	Surface ionization	3
49 200(610)	6.1(1)	Appearance potential	4
49 930(970)	6.19(12)	$f^5 7s^2$-$f^5 7s8s$ interval interpolated	5
49 950	6.193	Semi-emperical	11
50 517(25)[a]	6.2633(30)[a]	Photoionization threshold	This work.
50 536(4)	6.2657(5)	Rydberg series	This work.

[a] Uncertainty based on observed differences between photoionization thresholds and Rydberg series limits in uranium and the lanthanides (Refs. 1 and 2).

Table IV. Lifetimes of five excited states of neptunium and estimated branching ratios and transition probabilities.

Excited level[a], (cm^{-1})	Lifetime, (ns)	Transition,[a] (cm^{-1}) odd	even	Wavelength,[a] (Å)	Branching,[b] ratio BR	Transition probability, A, ($10^6\ \mathrm{s}^{-1}$)
26 264.37	108 ± 10	0 -	26 264	3806.4	0.5 ± 0.2	4.2 ± 2
27 824.89	37 ± 3	2033 -	27 824	3876.2	0.7 ± 0.1	19 ± 3
28 752.40	40 ± 3	28 752 -	2831	3856.7	0.8 ± 0.1	20 ± 3
28 986.45	76 ± 5	28 986 -	2831	3822.2	0.9 ± 0.1	12 ± 1.4
29 023.76	288 ± 25	29 023 -	2831	3816.8	0.9 ± 0.1	3 ± 0.4

[a] Level energy, transition assignment and wavelength from Ref. 6.

[b] Branching ratio estimated from intensities in Ref. 6.

Table V. High even levels of neptunium observed from the three odd levels given as headings for the first three columns (excitation wavelength, energy and J value).

λ_1 Wavelength (Å)	6188.59	6120.49	6073.89		
Odd level (cm^{-1})	16 154.29	16 334.00	16 459.34		
Odd level J	4.5	6.5	4.5		
	Observed level energy in cm^{-1}			Even level[a] energy (cm^{-1})	Even level J
	No search made	33 128.4	No search made	33 128.4	5.5,6.5,7.5
		33 162.7		33 162.7	" " "
		33 176.3		33 176.3	" " "
		33 273.8		33 273.8	" " "
	33 364.6			33 364.6	3.5,4.5
	33 367.7			33 367.7	3.5,4.5
	33 372.5	33 372.2	33 371.7	33 372.2	5.5
	33 435.4	33 434.3		33 434.8	5.5
	33 445.3	33 445.0	33 445.0	33 445.1	5.5
		33 454.5		33 454.5	6.5,7.5
	33 476.0		33 476.3	33 476.2	3.5,4.5
		33 487.8		33 487.8	6.5,7.5
	33 491.1		33 491.7	33 491.4	3.5,4.5
	33 495.7	33 495.8	33 495.7	33 495.7	5.5
	33 527.7	33 527.6	33 527.7	33 527.7	5.5
		33 538.4		33 538.4	6.5,7.5
	33 548.5		33 548.1	33 548.3	3.5,4.5
	33 556.5			33 556.5	3.5,4.5
	33 569.6			33 569.6	3.5,4.5
	33 582.7	33 582.3	33 582.4	33 582.5	5.5
	33 584.0	33 585.2		33 584.6	5.5
		33 608.4		33 608.4	6.5,7.5
			33 634.2	33 634.2	3.5,4.5
			33 641.5	33 641.5	3.5,4.5
	33 652.7	33 652.7	33 652.5	33 652.6	5.5
	33 673.4	33 673.3	33 673.2	33 673.3	5.5
	No search made	33 679.5		33 679.5	6.5,7.5
			33 684.9	33 684.9	3.5,4.5
		33 703.3	33 704.1	33 703.7	5.5
			33 712.5	33 712.5	3.5,4.5
			33 717.7	33 717.7	3.5,4.5
			33 729.4	33 729.4	3.5,4.5
		33 736.0	33 736.2	33 736.1	5.5
			33 742.3	33 742.3	3.5,4.5
			33 761.0	33 761.0	3.5,4.5
		33 770.4	33 770.3	33 770.4	5.5
		33 774.0		33 774.0	6.5,7.5

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[a] The uncertainty is ±0.5 cm^{-1} for levels with two or more observed values and ±1 cm^{-1} for the others.

Table VI. High odd levels of Np obtained from the 19 373.87 cm^{-1}, J=3.5 even level populated by λ_1 at 6043.282A (2831-19 373). The J of the upper levels observed could be 2.5, 3.5 or 4.5.

λ_2 (Å)	Level[a] (cm^{-1})	λ_2 Å	Level[a] cm^{-1}
5939.95	36204.4	5804.95	36595.8
5926.35	36243.0	5803.21	36600.9
5896.15	36329.4	5769.67	36701.1
5890.00	36347.1	5764.26	36717.3
5874.97	36390.5	5764.01	36718.1
5861.74	36428.9	5757.35	36738.1
5849.38	36465.0	5755.02	36745.2
5846.52	36473.3	5753.15	36750.8
5844.35	36479.7	5742.77	36782.3
5831.24	36518.1	5736.25	36802.0
5827.39	36529.4	5735.00	36805.8
5819.69	36552.2	5723.63	36840.5
5806.88	36590.1	5713.06	36782.8
		5700.63	36910.9

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[a] Level uncertainty is about ±1 cm^{-1}.