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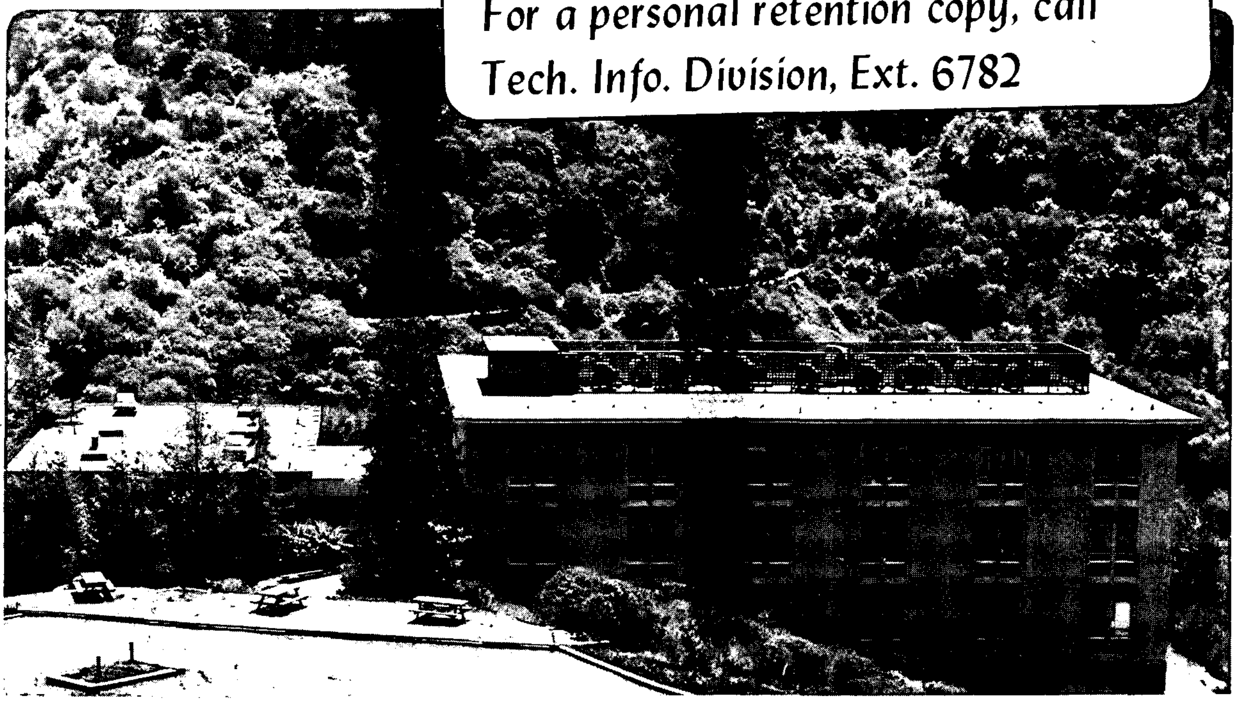

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The Spectrum and Energy Levels of Four-times Ionized Niobium

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ABSTRACT

The $4p^6nl$ spectrum of Nb^{4+} was measured and analyzed. The spectrum was excited in a vacuum sliding spark source with a peak current of 800 amps and a pulse width of 70 μseconds. The analysis of the spectrum has extended the 12 known lines to 84 and the 10 known levels to 30. The ionization energy was estimated to be 407897 cm^{-1}. There is strong evidence that the $4p^54d5s$ configuration interacts strongly with the $4p^6nf$ configuration. In addition, the hyperfine splitting of the $4p^66s$ level has been observed and measured to be 1.1 cm^{-1}.

Introduction

Nb^{4+} is isoelectronic with rubidium, thus its simplest configuration has one active electron. The ground state of Nb^{4+} is the $4p^6 4d$ state unlike rubidium which has a $4p^6 5s$ ground state. The spectrum of the $4p^6 nl$ configuration has now been analyzed beyond the work of Charles[1] and Trawick.[2] Their analysis contained 12 lines and resulted in 10 levels. The current work contains 84 assigned lines and yields 30 levels. The lines range in wavelength from about 300 Å to 5500 Å.

Experimental Details

The spectrum of Nb^{4+} was excited in a vacuum sliding spark connected in series with an LRC circuit. The inductance and resistance were variable which allowed the current pulse shape to be varied from peak currents of 30 amps and pulse widths (full widths at half maximum) of 1000 μsec. to peak currents of 1200 amps and pulse widths of 50 μsec. The details of this light source have been discussed previously by Van Deurzen.[3] Lines belonging to the Nb^{4+} spectrum were identified by their behavior in the spark as the current-pulse shape was varied. The optimum current for the production of Nb^{4+} lines was 800 amps with a pulse width of 70 μsec.

Table I contains data on the spectrographs used at Lawrence Berkeley Laboratory and at the Zeeman Laboratory. Notice that the spectrographs at the Zeeman Laboratory have significantly larger dispersion and thus wavelengths from them were used whenever possible. The wavelength standards depended upon the region of study and are indicated in Table I, as are the type of photographic plates that were used. Typical exposures required 2000 to 10,000 pulses. The plates were measured on a Grant Instruments comparator at Lawrence Berkeley Laboratory and on a Cospinsca semi-automatic comparator at the Zeeman Laboratory.

Analysis and Results

The starting point for the analysis was the isoelectronic data of various authors.[4-8] Simple curve fitting of energy level versus nuclear charge yielded rough estimates of the 6p ^2P and 5f ^2F levels. Combining these estimates with the known levels gave two levels of each angular momentum s,p,d, and f. Using this information and some quantum defect extrapolations as well as core polarization calculations (see Edlen[9]) estimates for higher energy levels were obtained. These estimates varied in accuracy from 100 cm^{-1} to a few thousand wavenumbers.

Table II contains the wavenumber, wavelength, and intensity of the assigned transitions. The intensity is a visual estimate of the darkening of the photographic plate. The b in the intensity column means that the line is blended with another. The uncertainty in these wavelengths varies from 0.011 wavenumbers to 5.8 wavenumbers. This uncertainty is attributed to the statistical uncertainty in the fitting of the standard lines to find the dispersion relation for the plates. The wide variation in uncertainty is caused by the typtical problem of very large wavenumbers for the transitions in the vacuum and by the different dispersions of the spectrographs.

The wavelengths in Table II were least squares fitted to find the energy levels. This fit was weighted by the uncertainty in the wavenumber. The overall uncertainty of this fit was 1.14 cm^{-1}, but this is the relative uncertainty of the entire scheme. Individual levels have substantially less uncertainty with respect to each other. Table III contains these fitted energy levels, while Figure 1 is the grotrian diagram of the energy level scheme.

Ionization Energy

Using the series extrapolation formulae of Edlen,[9] one can estimate the $4p^6$ ionization limit. Table IV contains these estimate for the indicated levels. The best value is most likely the one due to the 5g, 6g, 7g, 6h, 7h, and 7i. This is because these configurations interact very little with the core and are thus the most hydrogen-like. The result is 407897 cm^{-1}. The error in this value is difficult to estimate, but is certainly not larger than 20 cm^{-1}.

Discussion

The anomalous value for the ionization energy that was calculated from the $4p^6nf$ series points to a possible perturbation in that series. This is more dramatically shown by the anomalous fine structure intervals of the $4p^6nf$ series. Table III shows that the $4p^65f$ levels are inverted and the $4p^66f$ levels have an unusually large splitting. The perturbations in this series arise from the configuration mixing of the $4p^6nf$ series and the $4p^54d5s$ levels. This configuration is most likely responsible because it is the lowest energy configuration of the same parity.

In Table III, the hyperfine splitting of the $4p^6 6s$ level is indicated. This splitting was seen in the $6p\ ^2P$ to $6s\ ^2S$ transitions in the visible (4249.237 Å and 4542.078 Å). The dispersion on the plates where these lines were seen was about 0.5 angstroms per millimeter. The hyperfine splitting of the $6p\ ^2P$ levels was not resolvable at this dispersion. Hyperfine splitting was also observed in the transitions $5p\ ^2P$ to $5s\ ^2S$ (1877.378 Å and 1758.393 Å). The splitting was certainly larger than 2 cm^{-1}, but the dispersion of the plate was not sufficient to obtain a more accurate value.

Conclusions

The nearly unperturbed levels of the $4p^6 nl$ configuration have now been mostly found. To continue the analysis of the Nb^{4+} spectrum further requires a complete study of other configurations including the $4p^5 4d5s$ and the $4p^5 5s^2$. Beginning this analysis requires many isoelectronic studies of the rubidium sequence.

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Table I. Various data on the spectrographs

Spectrograph	Location	Wavelengths (Angstroms)	Grating (lines/mm)	Plate Factor (Å/mm)	Plates	Standards
McPherson 247-2.2m Grazing Incidence Vacuum	LBL	200-700	1200	∿1.0	Kodak 10105	SiIV, OIII, OIV
McPherson 241-3m Normal Incidence Vacuum	LBL	600-2800	1200	∿2.8	Kodak SWR	CuII
Jarrell-Ash 3.4m Ebert	LBL	2500-4800	600	∿5.0	Kodak 103a0	ThI, ThII
		4500-7000	600	∿5.0	Kodak 103aF	ThI, ThII
		2500-4550	300	∿0.5*	Kodak 103a0	ThI, ThII
6.65m Normal Incidence Vacuum	ZL	200-700	2400	∿0.6	Kodak SWR	CuIII
		700-1250	2400	∿0.6	Ilford Q2	CuII, CuIII
		1200-2300	1200	∿1.2	Ilford Q2	CuII
Jarrell-Ash 3.4m Ebert	ZL	2000-2800	600	∿2.5**	Ilford Q2	CuII

* 12-23 order

** second order

Table II. The classified lines of Nb^{4+}. The wavenumbers followed by em were from Meinders. The b in the intensity column means blend.

Assignment		Wavenumber (cm^{-1})	Wavelength (Å)	Relative Intensity
Odd	Even			
7p $^2P^o_{1/2}$	- 6d $^2D_{3/2}$	18822.90	5311.200	50
7p $^2P^o_{3/2}$	- 7d $^2D_{3/2}$	18917.69	5284.587	10
7p $^2P^o_{3/2}$	- 7d $^2D_{5/2}$	19066.76	5243.270	70
5f $^2F^o_{5/2}$	- 5g ^2G	19355.80	5164.971	40
7p $^2P^o_{3/2}$	- 6d $^2D_{5/2}$	19362.38	5163.216	60
7p $^2P^o_{3/2}$	- 6d $^2D_{3/2}$	19624.53	5094.243	10
7p $^2P^o_{1/2}$	- 7d $^2D_{3/2}$	19719.20	5069.786	40
5f $^2F^o_{7/2}$	- 5g ^2G	19924.52	5017.542	70
6h $^2H^o$	- 7i ^2I	20345.41	4913.741	100
7h $^2H^o$	- 6g ^2G	20854.77	4793.725	100
6p $^2P^o{}_{1/2}$	- 6s $^2S_{1/2}$	22010.18	4542.078	90
7p $^2P^o_{3/2}$	- 8s $^2S_{1/2}$	23096.14	4328.510	40
6p $^2P^o_{3/2}$	- 6s $^2S_{1/2}$	23527.01	4249.237	100
7p $^2P^o_{1/2}$	- 8s $^2S_{1/2}$	23897.76	4183.313	20
6f $^2F^o_{5/2}$	- 5g ^2G	24170.39	4136.127	30
6f $^2F^o_{7/2}$	- 5g ^2G	25001.61	3998.611	40
6f $^2F^o_{7/2}$	- 7g ^2G	29259.28	3416.74	20
6f $^2F^o_{5/2}$	- 7g ^2G	30090.98	3322.30	10
6f $^2F^o_{5/2}$	- 6d $^2D_{5/2}$	33837.8	2954.40	10
6f $^2F^o_{5/2}$	- 6d $^2D_{3/2}$	34100.64	2931.638	60

Table II. Continued

Assignment Odd Even	Wavenumber (cm^{-1})	Wavelength (Å)	Relative Intensity
6h $^2H^o$ - 5g ^2G	34413.01	2905.026	100
6f $^2F^o_{7/2}$ - 6d $^2D_{5/2}$	34670.58	2883.444	90b
6p $^2P^o_{3/2}$ - 6d $^2D_{3/2}$	35140.21	2844.906	50
6p $^2P^o_{3/2}$ - 6d $^2D_{5/2}$	35402.38	2823.838	90
6p $^2P^o_{1/2}$ - 6d $^2D_{3/2}$	36657.09	2727.177	80
6p $^2P^o_{1/2}$ - 5d $^2D_{3/2}$	38812.56	2575.714	70
6p $^2P^o_{3/2}$ - 5d $^2D_{5/2}$	39784.94	2512.757	90
6p $^2P^o_{3/2}$ - 5d $^2D_{3/2}$	40328.9em	2478.862	40
6p $^2P^o_{3/2}$ - 7s $^2S_{1/2}$	42712.7em	2340.507	40
6p $^2P^o_{1/2}$ - 7s $^2S_{1/2}$	44229.5em	2260.235	20
5p $^2P^o_{1/2}$ - 5s $^2S_{1/2}$	53265.7em	1877.378	80
5p $^2P^o_{3/2}$ - 5s $^2S_{1/2}$	56870.1em	1758.393	100
5f $^2F^o_{7/2}$ - 5d $^2D_{5/2}$	64931.1em	1540.093	50
5f $^2F^o_{5/2}$ - 5d $^2D_{5/2}$	65496.5em	1526.799	30b
5f $^2F^o_{5/2}$ - 5d $^2D_{3/2}$	66041.8em	1514.193	40
4f $^2F^o_{5/2}$ - 6d $^2D_{3/2}$	71903.0	1390.76	10
4f $^2F^o_{7/2}$ - 6d $^2D_{5/2}$	72023.4	1388.44	40
6p $^2P^o_{3/2}$ - 7d $^2D_{5/2}$	73828.8	1354.49	20
5f $^2F^o_{7/2}$ - 7g ^2G	74182.9	1348.02	10
7p $^2P^o_{1/2}$ - 6s $^2S_{1/2}$	77485.7	1290.56	3
6p $^2P^o_{3/2}$ - 8s $^2S_{1/2}$	77856.2	1284.42	6
7p $^2P^o_{3/2}$ - 6s $^2S_{1/2}$	78288.4	1277.33	6

Table II. Continued

Assignment Odd	 Even	Wavenumber (cm^{-1})	Wavelength (Å)	Relative Intensity
5p $^2P^o_{3/2}$	- 5d $^2D_{3/2}$	78892.8em	1267.543	50
6p $^2P^o_{1/2}$	- 8s $^2S_{1/2}$	79370.7	1259.91	3
5p $^2P^o_{3/2}$	- 5d $^2D_{3/2}$	79437.4em	1258.853	90
4f $^2F^o_{7/2}$	- 5g ^2G	81697.0em	1224.035	70
4f $^2F^o_{5/2}$	- 5g ^2G	81835.0em	1221.971	60
5p $^2P^o_{1/2}$	- 5d $^2D_{3/2}$	82498.6em	1212.142	80
7p $^2P^o_{1/2}$	- 5d $^2D_{3/2}$	94294	1060.51	15
7p $^2P^o_{3/2}$	- 5d $^2D_{5/2}$	94548	1057.66	20
5p $^2P^o_{3/2}$	- 6s $^2S_{1/2}$	95696.1em	1044.975	70
5p $^2P^o_{1/2}$	- 6s $^2S_{1/2}$	99301.6em	1007.033	90b
6f $^2F^o_{5/2}$	- 5d $^2D_{5/2}$	109029	917.19	10
6f $^2F^o_{5/2}$	- 5d $^2D_{3/2}$	109569.7em	912.661	20
6f $^2F^o_{7/2}$	- 5d $^2D_{5/2}$	109857.5em	910.270	30
4f $^2F^o_{7/2}$	- 6g ^2G	115520.1em	865.650	10
4f $^2F^o_{5/2}$	- 6g ^2G	115658.2em	864.617	5
5p $^2P^o_{1/2}$	- 4d $^2D_{3/2}$	129195.0em	774.024	90
5p $^2P^o_{3/2}$	- 4d $^2D_{5/2}$	130932.7em	763.751	100
5p $^2P^o_{3/2}$	- 4d $^2D_{3/2}$	132800.2em	753.011	70
4f $^2F^o_{7/2}$	- 7g ^2G	135957.9em	735.522	6
4f $^2F^o_{5/2}$	- 7g ^2G	136097.6em	734.767	3
5p $^2P^o_{3/2}$	- 6d $^2D_{3/2}$	154365.3em	647.814	5
5p $^2P^o_{3/2}$	- 6d $^2D_{5/2}$	154627.4em	646.716	20

Table II. Continued

Assignment Odd - Even	Wavenumber (cm^{-1})	Wavelength (Å)	Relative Intensity
$5p\ ^2P^o_{1/2} - 6d\ ^2D_{3/2}$	157969.8em	633.032	15
$5p\ ^2P^o_{3/2} - 7s\ ^2S_{1/2}$	161936.8em	617.525	10
$5p\ ^2P^o_{1/2} - 7s\ ^2S_{1/2}$	165541.1em	604.080	5
$6p\ ^2P^o_{1/2} - 5s\ ^2S_{1/2}$	174578em	572.807	15
$6p\ ^2P^o_{3/2} - 5s\ ^2S_{1/2}$	176094em	567.879	20
$4f\ ^2F^o_{5/2} - 4d\ ^2D_{5/2}$	213391em	468.623	50
$4f\ ^2F^o_{7/2} - 4d\ ^2D_{5/2}$	213530em	468.318	100
$4f\ ^2F^o_{5/2} - 4d\ ^2D_{3/2}$	215258em	464.559	90
$6p\ ^2P^o_{3/2} - 4d\ ^2D_{5/2}$	250157em	399.749	50
$6p\ ^2P^o_{1/2} - 4d\ ^2D_{3/2}$	250508em	399.189	40
$6p\ ^2P^o_{3/2} - 4d\ ^2D_{3/2}$	252024em	396.788	20
$5f\ ^2F^o_{7/2} - 4d\ ^2D_{5/2}$	275301em	363.239	50
$5f\ ^2F^o_{5/2} - 4d\ ^2D_{5/2}$	275871em	362.488	20
$5f\ ^2F^o_{5/2} - 4d\ ^2D_{3/2}$	277737em	360.052	80b
$7p\ ^2P^o_{3/2} - 4d\ ^2D_{5/2}$	304922	327.953	20
$7p\ ^2P^o_{1/2} - 4d\ ^2D_{3/2}$	305989	326.809	10
$7p\ ^2P^o_{3/2} - 4d\ ^2D_{3/2}$	306794	325.952	1
$6f\ ^2F^o_{5/2} - 4d\ ^2D_{3/2}$	319397	313.090	10
$6f\ ^2F^o_{7/2} - 4d\ ^2D_{5/2}$	320222	312.283	50
$6f\ ^2F^o_{5/2} - 4d\ ^2D_{5/2}$	321255	311.279	50

All wavelengths over 2000 Å are given in air at 15°C and 760 Torr.

Table III. The $4p^6nl$ Levels of Nb^{4+}

Level	Energy (cm^{-1})	Interval (cm^{-1})
4d $^2D_{3/2}$	– 0 –	1867.4
4d $^2D_{5/2}$	1867.4	
5s $^2S_{1/2}$	75929.6	
5p $^2P^o_{1/2}$	129195.2	3604.8
5p $^2P^o_{3/2}$	132800.0	
5d $^2D_{3/2}$	211694.0	544.4
5d $^2D_{5/2}$	212238.4	
4f $^2F^o_{5/2}$	215259.1	138.4
4f $^2F^o_{7/2}$	215397.5	
6s $^2S_{1/2}$ (F=4)	228495.7	
6s $^2S_{1/2}$	228496.3	1.1
6s $^2S_{1/2}$ (F=5)	228496.8	
6p $^2P^o_{1/2}$	250506.5	1516.8
6p $^2P_{3/2}$	252023.3	
5f $^2F^o_{7/2}$	277169.7	-568.6
5f $^2F^o_{5/2}$	277738.3	
6d $^2D_{3/2}$	287163.6	262.0
6d $^2D_{5/2}$	287425.6	
7s $^2S_{1/2}$	294736.0	
5g ^2G	297094.2	
7p $^2P^o_{1/2}$	305986.5	801.6
7p $^2P^o_{3/2}$	306788.1	

Table III. Continued

Level	Energy (cm^{-1})	Interval (cm^{-1})
6f $^2F^o_{5/2}$	321264.4	831.5
6f $^2F^o_{7/2}$	322095.9	
7d $^2D_{3/2}$	325705.7	149.1
7d $^2D_{5/2}$	325854.8	
8s $^2S_{1/2}$	329884.2	
6g ^2G	330917.5	
6h $^2H^o$	331507.2	
7g ^2G	351355.3	
7h $^2H^o$	351772.2	
7i ^2I	351852.6	

Table IV. Estimates of the Ionization Energy of Nb^{4+}

Levels used for calculation	Ionization Energy (cm^{-1})
6s, 7s, 8s	407613
5p, 6p 7p	407469
5d, 6d, 7d	407554
4f, 5f, 6f	431515
5g, 6g, 7g	407863
6h, 7h, 7i	407886
5g, 6g, 7g, 6h, 7h, 7i	407897*

*Calculated by the core polarization method, all others found from quantum defect extrapolation.

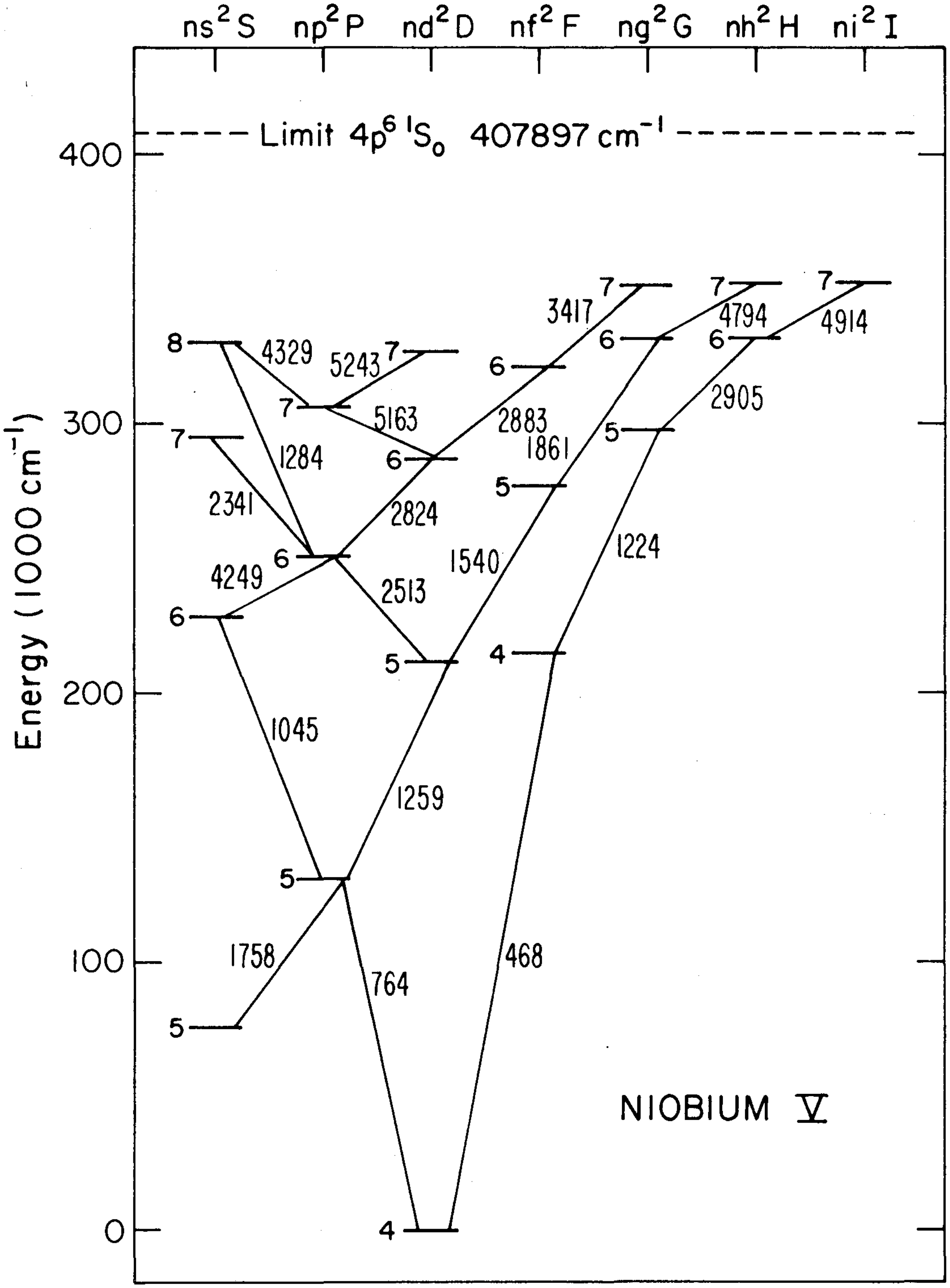

Figure 1. Grotrian diagram for Nb^{4+}.

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