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Low Even Configurations in the First Spectrum of Rhenium (Re I)

RICHARD E. TREES
National Bureau of Standards, Washington, D. C.

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The theory of intermediate coupling with configuration interaction is used to calculate energy levels and g values in the $5d^56s^2$ and $5d^66s$ configurations of Re I. Fifty-one observed levels are fitted with a mean deviation of ±325 cm^{-1} by using eleven free parameters. The $L(L+1)$ correction is important, as the mean deviation is ±514 cm^{-1} without it; the parameter for this correction ($\alpha=66.8\pm13$) has a value similar to that in first and second long-period spectra. Standard deviations of the parameters are calculated, and within the limits so defined, Slater's parameters are consistent with expectations based on known behavior in first and second long-period spectra. Calculated g values agree with observed values for thirty-seven levels to about ±0.03. Levels not previously assigned from experiment are given designations; the eigenvectors are used to illustrate qualitative features of these designations.

THE experimental analysis of Re I has been carried out by several investigators over the last twenty-five years. Recently, a new description of this spectrum was made, based on an extended homogeneous line list,[1] and the earlier work was revised and extended with this as a basis.[2,3] The calculations in this paper were carried out primarily to provide assignments for levels of the $5d^56s^2$ and $5d^66s$ configurations in this spectrum. These assignments have been published,[2,3] and the present paper gives the complete calculation on which they are based.

As in most spectra of the third long period, an intermediate form of coupling, which includes effects of configuration interaction, is required to describe the observed levels rigorously, but for qualitative descriptions it is customary to assign levels designations based on the LS-coupling notation. In the years that have been devoted to the analysis of Re I, experimental spectroscopists have made such term assignments which contributed greatly to the understanding of this complicated spectrum and helped to bring order out of the forest of levels. But about half the observed levels were not assigned; it was not established, for instance, that only two configurations were present,[4] or that all expected levels in the observable region of the spectrum had been found. The use of theory was indispensable in completing the assignments. The eigenvectors given in the present paper show the degree of approximation involved in making the assignments.[5]

The eigenvectors have also an application in indicating the accuracy obtainable in atomic theory generally when calculations are made for spectra with many close interacting levels. Since the g values have been observed for thirty-seven levels, a simple criterion is available for estimating this accuracy in many instances. Eigenvectors may also be used in the calculation of intensities of radiative transitions, or in the calculation of hyperfine structure splittings, and the signs of the amplitudes are given, along with the percentage composition, for possible use in these applications.

A brief description of this calculation and two similar ones has been given.[6] It is planned to publish later a detailed description of these other results that were obtained while the Standards Eastern Automatic Computer (SEAC) was available. At present, coding is being set up to carry out similar calculations on the IBM 704.

The matrix elements of electrostatic and spin-orbit interactions for these two configurations are taken mainly from work already published, and checks were made to insure the correctness of these results.[7] Subse-

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[1] W. F. Meggers, J. Research Natl. Bur. Standards **49**, 187 (1952).

[2] Klinkenberg, Meggers, Velasco, and Catalán, J. Research Natl. Bur. Standards **59**, 319 (1957).

[3] *Atomic Energy Levels*, C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1958), Vol. III; referred to in the present paper as "AEL".

[4] The results of this paper establish the fact that the fifty-one levels found in the region lower than 35 000 cm^{-1} arise from the two configurations $5d^56s^2$ and $5d^66s$. Evidence is also noted that supports earlier conclusions that the $5d^7$ configuration is present in the region slightly higher than 35 000 cm^{-1}, so that three configurations probably overlap in this region of the spectrum. Since the $5d^7$ configuration has been neglected in the present calculation, partial results that were obtained for predicted levels higher than 35 000 cm^{-1} have been omitted. Three known even levels having a J value of $2\frac{1}{2}$ have been disregarded for similar reasons (i.e., 44 054, 44 903, and 50 973 cm^{-1}).

[5] Eigenvectors have been given for the two-electron configurations of Th III by G. Racah [Physica **16**, 651 (1950)], and for the low even three-electron configuration of Th II by Y. Eisenberg [Physica **18**, 177 (1952)]. They have already noted several qualitative features of assignments. Except for one or two levels, their assignments confirmed ones that had been established by experimental methods. Th II and Th III are close to the limit in complexity that can be handled rigorously with desk computers, but are, of course, much simpler than Re I.

[6] R. E. Trees, Bull. Am. Phys. Soc. Ser. II, **3**, 29 (1958).

[7] The matrices of spin-orbit interaction for the d^4s configuration are given by W. R. Bozman and R. E. Trees [J. Research Natl. Bur. Standards **58**, 95 (1957)]. Those for the d^5 configuration are given by H. Greyber [dissertation, University of Pennsylvania, 1953 (unpublished)]; a few errors were corrected in these results. The matrices of the spin-orbit interaction were checked by calculating the eigenvalues on SEAC, and comparing them with values known from j-j coupling theory. Matrix elements of configuration interaction between d^4s and d^5 are given by G. Racah [Phys. Rev. **63**, 367 (1943)]; he has used a digital computer to check these matrix elements [G. Racah (private communication)]. No independent check insures consistency of our phases for the matrices of spin-orbit interaction and those of electrostatic

quent steps in the calculation were carried out on SEAC and most of the coding has been described.[8,9]

Numerical matrices were obtained by using preliminary parameters estimated by comparison with parameters obtained in other calculations already carried out for spectra of the third long period (the latter parameters are listed in footnote 22 of reference 8). By using the eigenvectors of the numerical matrices, linear formulas were set up for the eigenvalues of the matrices as functions of the parameters. New parameters were then determined by least squares. In calculations with large matrices it is important to estimate good preliminary parameters so that the linear formulas will be accurate. In spectra where theory and experiment agree very closely, it may be necessary to use the first set of parameters obtained by least squares to obtain more accurate linear formulas, but there was no need to do this for Re I.[10]

The differences between calculated and observed energy levels when the $L(L+1)$ correction is omitted are given in the last column, "no α," of Table I. The mean deviation is ±514. The errors are mostly positive for small J values, and negative for the large J values. This systematic behavior shows conclusively that the correction has an over-all importance for all levels of this spectrum. In Ta II, over-all importance could not be demonstrated because only a few levels with large J value (more rigorously, L value) were observed.[8] The results are from linear formulas. Inaccuracy of linear formulas usually leads to an overestimate for the mean deviation, but in this case the effect is negligible. It can be estimated by omitting the errors for the two lowest levels with[10] $J=3\frac{1}{2}$ and regarding the adjustment by least squares as being made to fit forty-five observations rather than forty-seven. The mean deviation would then be reduced from ±514 to ±508 cm^{-1}.

The calculated energy levels and g values obtained using the $L(L+1)$ correction are given in the rest of

TABLE I. Calculated energy levels (in cm^{-1}) and g values in the $5d^66s+5d^56s^2$ configurations of the first spectrum of rhenium (Re I).

		Level			g value			No α
J	Label	Obs.	Calc.	Calc. −Obs.	Obs.	Calc.	Calc. −Obs.	Calc. −Obs.
$\frac{1}{2}$	1	15 166	15 265	99	2.368	2.165	−0.203	692
	2	17 238	17 406	168	2.521	2.785	0.264	263
	3	19 758	19 605	−153	0.983	0.901	−0.082	96
	4	27 385	26 764	−621	···	1.831	···	−126
	5	30 132	30 476	344	···	0.375	···	208
	6	···	34 366	···	···	1.939	···	···
						Sum =	−0.021	
$1\frac{1}{2}$	1	13 826	13 858	32	1.485	1.453	−0.032	···
	2	16 328	16 619	291	1.706	1.760	0.054	312
	3	20 482	20 397	−85	1.451	1.404	−0.047	389
	4	22 423	22 427	4	0.781	0.802	0.021	657
	5	26 132	26 812	680	0.650	0.590	−0.060	621
	6	27 828	27 848	20	0.888	0.958	0.070	595
	7	30 527	30 707	180	···	0.913	···	810
	8	31 461	31 888	427	···	1.373	···	663
	9	···	34 081	···	···	1.054	···	···
	10	···	35 289	···	···	1.058	···	···
						Sum =	0.006	
$2\frac{1}{2}$	1	0	681	681	1.950	1.944	−0.006	···
	2	11 584	11 465	−119	1.278	1.251	−0.027	440
	3	14 621	14 726	105	1.151	1.087	−0.064	152
	4	15 770	15 863	93	1.309	1.421	0.112	43
	5	19 458	19 059	−399	1.361	1.320	−0.041	−2
	6	23 155	23 073	−82	1.189	1.182	−0.007	452
	7	24 425	24 657	232	1.067	1.045	−0.022	122
	8	26 661	26 367	−294	1.32	1.428	0.11	592
	9	28 030	27 643	−387	1.12	1.039	−0.08	−173
	10	29 800	30 219	419	1.17	1.034	−0.14	872
	11	31 186	30 601	−585	1.17	1.131	−0.04	−795
	12	32 435	32 391	−44	···	1.170	···	460
	13	33 282	33 279	−3	···	0.842	···	151
	14	···	34 613	···	···	1.256	···	···
						Sum =	−0.205	
$3\frac{1}{2}$	1	14 217	14 484	267	1.567	1.565	−0.002	614
	2	15 058	14 895	−163	1.153	1.153	0.000	−638
	3	17 331	17 282	−49	1.255	1.260	0.005	−579
	4	21 775	21 750	−25	1.135	1.134	−0.001	−110
	5	24 724	24 746	22	1.03	1.038	0.01	−134
	6	27 141	27 099	−42	1.34	1.152	−0.19	−170
	7	28 542	28 045	−497	···	1.027	···	−913
	8	28 810	29 260	450	0.93	0.972	0.04	−15
	9	···	31 000	···	···	1.205	···	···
	10	31 983	31 405	−578	···	1.215	···	−672
	11	33 824	33 978	154	···	1.027	···	101
	12	···	35 163	···	···	1.378	···	···
						Sum =	−0.138	
$4\frac{1}{2}$	1	11 754	11 882	128	1.545	1.534	−0.011	161
	2	16 619	16 403	−216	1.175	1.171	−0.004	−597
	3	22 160	22 232	72	1.198	1.190	−0.008	−316
	4	27 161	26 880	−280	···	1.117	···	−494
	5	27 514	27 967	453	1.13	1.157	0.03	407
	6	30 645	30 139	−506	···	1.173	···	−597
	7	31 399	31 702	303	···	1.042	···	−35
	8	34 194	33 574	−620	···	1.138	···	−762
	9	···	36 472	···	···	1.101	···	···
						Sum =	0.007	
$5\frac{1}{2}$	1	16 307	15 982	−325	1.242	1.247	0.005	−721
	2	23 956	23 559	−397	0.995	0.988	−0.007	−1214
	3	27 244	27 447	203	1.18	1.173	−0.01	−501
	4	30 560	30 869	309	1.07	1.136	0.07	−520
	5	33 318	33 711	393	···	1.127	···	214
	6	···	36 565	···	···	1.023	···	···
						Sum =	0.057	
$6\frac{1}{2}$	1	26 348	25 796	−552	1.100	1.080	−0.020	···
	2	27 130	27 537	407	1.208	1.217	0.009	···
	3	···	38 724	···	···	1.088	···	···
						Sum =	−0.011	
$A(d^6s)$			36 949	±1080			36 955	
$A(d^5s^2)$			20 033	±1148			19 041	
$B(d^6s)$			470.5	±51			499.7	
$B(d^5s^2)$			498.5	±31			465.4	
$C(d^6s)$			1842.6	±95			2032.5	
$C(d^5s^2)$			1881.6	±95			2125.0	
$\zeta(d^6s)$			2347.1	±104			2277.5	
$\zeta(d^5s^2)$			2425.2	±80			2419.6	
G_2			2954.9	±104			2740.1	
H_2			477.6	±26			541.9	
α			66.8	±13			···	
Mean error			±371				±580	
Mean deviation			±325				±514	

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interaction, but this is a question of the correct interpretation of Racah's formulas rather than one of numerical error. After setting up matrices of d^4s+d^5, the matrices for $d^6s+d^5s^2$ were obtained formally by use of negative values for the spin-orbit parameters. The orders of the final matrices, followed by the J values in parentheses, are 13(1/2), 19(3/2), 24(5/2), 20(7/2), 14(9/2), 7(11/2), and 3(13/2).

[8] Trees, Cahill, and Rabinowitz, J. Research Natl. Bur. Standards **55**, 335 (1955).

[9] A code used to evaluate standard deviations of the parameters has not been described. Definitions of these deviations, which are given in Table I, must be obtained from books on statistics, since we do not know of any atomic spectra for which they have been calculated previously. The probable errors are two-thirds of the standard deviations. I wish to thank J. M. Cameron for making this code available and discussing its use with me.

[10] No allowance was made for inaccuracy of the linear formulas, as is sometimes done by omitting pairs of levels that are close, or by using an average value. The errors in the linear formulas were less than 100 cm^{-1} for all levels but the ones at 19 758 and 27 141 cm^{-1}, where the errors were about 200 cm^{-1}, and the levels at 14 217 and 15 058 cm^{-1} where the errors were about 450 cm^{-1}. The fact that the mean error of the final calculations is ±371 cm^{-1} is justification for ignoring these inaccuracies. Four levels were omitted from the calculation by least squares to minimize the computer time and the ground level was one of these omissions.

Table I. The mean deviation between calculated and observed energy levels is ±325 cm^{-1}. The errors still show appreciable systematic behavior, being greater the higher the energy. Excluding the ground level, none of the levels lower than 25 000 cm^{-1} have errors in excess of 400 cm^{-1}, but errors of about half the higher levels are greater than this. This is probably because we neglected the $5d^7$ configuration.[4] It is reasonable to expect that the mean deviation would be about half as great if the $5d^7$ configuration were included, so that the agreement would be similar to that obtainable in first and second long-period spectra. It is likely that three high even levels omitted from the calculation[4] originate in the three low even configurations. Our calculation with two configurations does not explain these three levels well. In one instance (for the level observed at 50 973) a discrepancy of 2800 cm^{-1} would have to be accepted, which is outside the probable error, as noted in the next paragraph. This is an indication that there is direct experimental evidence for the position of the $5d^7$ configuration, so that a calculation with three configurations would not have to be made solely on the basis of the relatively small perturbations produced in the levels lower than 35 000 cm^{-1}. (We did not attempt this calculation because the matrices would have been too large for SEAC.)

The error in predicting positions of levels well isolated from the observed region of the spectrum is often not realized, this being the same as the failure to distinguish between interpolation and extrapolation.[11] By using the full statistical matrix,[9] which we omit for the sake of brevity, probable errors can be estimated for any predicted level, but the qualitative behavior can be seen from the standard deviations. The errors in different parameters are correlated so that the effects of the standard deviations, which are additive, are compensated in the well observed regions of the spectrum, but the sign of the correlation will change and be additive for isolated levels. If the errors were random, the mean error of ±371 cm^{-1} might apply for the accuracy of the prediction of, say, the ninth level with a J value of $3\frac{1}{2}$ (calculated position 31 000 cm^{-1}). But in predicting positions of levels by extrapolation, as done for the ground level in this calculation,[10] the standard deviations of about 1000 cm^{-1} in the parameters A would be a better estimate (these two parameters enter into all the linear formulas for eigenvalues with a total coefficient of unity). For this reason, a single isolated level can often be well fitted when it is included in the calculation by least squares without making much change in the mean error, so that this is not a sensitive way to establish the identity of isolated unassigned levels. However, when the level is included, the standard deviations of certain of the parameters will be greatly reduced. Checks on the internal consistency of the parameters, such as those discussed in the next paragraph, then become more critical and provide a better way to establish the identity.

Because B, C, and ζ were adjusted independently in the $5d^56s^2$ and $5d^66s$ configurations, it is possible to check the internal consistency of the calculation from these three pairs of similarly defined parameters. In each pair, the parameter evaluated in the $5d^56s^2$ configuration is expected to be larger by 5 to 15%, from analogy with results obtained in first and second long-period spectra. Since errors in different parameters are correlated, this is more than a check on B, C, and ζ individually. When the $L(L+1)$ correction is included, all three pairs of parameters behave as expected. The standard deviations are rather large, however, and there would not necessarily have been an inconsistency if the parameter in the $5d^56s^2$ configuration had been slightly smaller in one of the three pairs. This happens for the parameter B in the calculation with the $L(L+1)$ correction omitted, but the standard deviations are larger in this calculation, approximately in the ratio of the mean errors, so that this is not improbable from the statistics. However, the parameter $C(d^5s^2)$ changes by 240 cm^{-1} in the two calculations, and a change in excess of 150 cm^{-1} is unlikely [i.e., the standard deviation in C when the $L(L+1)$ correction is omitted]. This discrepancy is present because it is a particularly poor approximation to regard the errors as random when the $L(L+1)$ correction is neglected. For both d^6s and d^5s^2, the parameter C will be systematically too large when the correction is omitted.[12]

Very roughly, calculated g values agree with the observed values to ±0.03, or to about 1% of the range of the Landé g values for the levels in pure LS-coupling. The mean error for the calculation of energy levels is about 1% of the observed range of levels, so a crude correspondence can be established between the accuracy in the two calculations. The somewhat arbitrary figure of ±0.03 is regarded as an upper limit, but based on the consideration that larger errors are always found in pairs (or triples) of relatively close levels, and in these pairs the observed and calculated g sums check to this accuracy, except for three instances where the g value in a nearby level is not observed. Since the sensitivity of calculated g values to the parameters varies greatly for different levels, it is difficult to evaluate the significance of either very good or very bad agreement in

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[11] Extrapolations made by D. S. Bowman [Phys. Rev. **59**, 386 (1941)] and R. E. Trees [Phys. Rev. **83**, 756 (1951)] predict essentially the same positions for levels of the $3d^54s$ configuration in Mn II. Their mean error is about ±250 cm^{-1}, but the error in the predictions increases regularly, the higher the level, and has a magnitude of about 3000 cm^{-1} for the highest levels, as shown by a recent extension of the experimental analysis made by L. Iglesias [J. Opt. Soc. Am. **46**, 449 (1956)]. This may exceed the error normally expected in extrapolation, because eight observations were fitted with five parameters (in Trees' calculation) and statistical assumptions would not apply well with so few observations.

[12] R. E. Trees, Phys. Rev. **84**, 1089 (1951), Table I; **85**, 382 (1952), references 5 and 9.

TABLE II. Composition of the states with $J=1/2$.

LS position	Level Desig.	15 166 a^4P	17 238 a^6D	19 758 a^4D	27 385 a^2S	30 132 b^4D	b^4P	Total
18 936	$(^5D)^6D$	16.0−	**71.4**−	2.2	1.1	1.2	5.1	97.0
19 380	^4P	**47.5**−	9.4	26.5−	8.2	2.2	0.6	94.4
20 868	^4D	18.0−	11.9	**56.2**	0.2	0.4−	2.8	89.5
32 916	$(^3D)^4D$	1.7−		3.8	1.7	38.6−	8.6−	54.4
33 590	^2S	4.5	0.5−	2.9	**36.3**	6.0	17.4−	67.6
33 593	$(^5D)^4D$	1.2−	1.2	5.6	5.0−	**38.1**	10.8−	61.9
34 347	$(4^3P)^4P$	6.7	0.3	1.7		1.6	**37.0**	47.3
39 609	$(2^3P)^4P$	2.1−	4.9−		4.0−	0.1−	**12.8**−	23.9
38 266	$(4^1S)^2S$	1.6−		0.6−	28.0−	2.3−	1.4−	33.9
70 075	$(0^1S)^2S$	0.3	0.1		5.9	0.2	1.8	8.3
42 142	$(4^3P)^2P$				1.5	5.2−		6.7
49 153	$(2^3P)^2P$	0.1−	0.1	0.3	5.3−	4.2	0.4−	10.4
48 952	^2P	0.3	0.1−	0.2−	2.7		1.2−	4.5

TABLE III. Composition of the states with $J=3/2$.

LS position	Level Desig.	13 826 a^4P	16 328 a^6D	20 482 a^4D	22 423 a^2D	26 132 a^4F	27 828 b^4D	30 527 b^4F	31 461 b^4P	b^2D	c^4D	Total
18 232	$(^5D)^6D$	6.5	**79.9**	1.7	1.7	0.1−	2.5	2.2	3.1−	0.4	0.3	98.4
19 380	^4P	**40.2**	1.9−	40.1−	5.7−	0.3	3.2	2.2	2.0−	0.4	0.1−	96.1
20 869	^4D	34.6	6.3−	**38.2**	2.0−	0.3−	1.4−	0.1	2.6−	0.3−	6.9	92.7
26 361	5^2D	2.7	0.7−	3.4−	**41.2**	12.7−	4.3−	2.0−	0.1−	1.1	2.8	71.8
52 911	1^2D	1.0	0.2−	1.6−	**11.5**		3.6−	0.3	0.3	3.2	3.4	25.1
27 525	^4F	1.9	0.8−	1.1	20.1	**46.4**	1.7−	13.6	0.9	3.4−	7.5−	97.4
30 016	$(4^3F)^4F$		0.5−	0.2	3.8	17.3	24.5	**25.6**	0.9−	3.4	5.7	81.9
44 102	$(2^3F)^4F$					1.9−	1.0−	**5.0**		5.1−	0.1−	13.1
31 027	$(4^3P)^4P$	5.1−	1.8−	3.2	0.9	0.7−	0.8	11.8	**20.9**−	6.9	3.5	55.6
41 755	$(2^3P)^4P$	1.0	4.6			0.2	0.3−	2.9−	**16.6**	7.8−	1.8	35.2
32 536	$(^5D)^4D$	2.2	1.2−	5.2	0.1	3.7−	**11.9**	1.5	41.3	1.5	0.6	69.2
33 112	$(^3D)^4D$	3.0	0.6	2.4	0.8−	0.3	13.2−	14.1−		27.8	**26.0**−	88.2
35 269	$(4^3P)^2P$		0.3	0.1−	0.7−	2.5	7.8−	5.0−	0.2−	3.2−	11.3	31.1
53 677	$(2^3P)^2P$		0.2−	0.6	0.3	1.8−	9.0	3.5	0.4	3.8	10.4−	30.0
37 256	3^2D	1.0−	0.3	1.8−	0.5−	3.3	0.7−	5.3	6.6	**26.9**	13.3	59.7
39 748	$(4^1D)^2D$		0.2−	0.1	1.4		8.9	3.3−	3.6−	2.8−	1.9−	22.2
59 240	$(2^1D)^2D$				0.2−		4.2−		0.3	0.3		5.0
41 976	$(^3D)^2D$	0.5	0.2−		8.9	8.3−	0.4	1.5−		1.7−	2.9−	24.4
48 953	^2P			0.3−		0.2	0.7−	0.1−		0.1−	1.4	2.8

TABLE IV. Composition of the states with $J=5/2$.

LS position	Level Desig.	0 a^6S	11 584 a^4P	14 621 a^4G	15 770 a^6D	19 458 a^4D	23 155 a^2D	24 425 a^2F	26 661 b^4P	28 030 b^4F	29 800 a^4F	31 186 b^4D	32 435 b^2F	33 282 b^4G	Total
2586	^6S	**87.4**	6.7	1.1	0.7−	1.8−	0.8−	0.4	0.7	0.1					99.7
17 058	$(^5D)^6D$		1.4	23.9	**60.0**	0.9	5.1		3.1	3.0	1.0−	0.6	0.3−		99.2
18 315	^4G		13.1	**40.2**−	14.4	4.2	12.6−	2.0	0.6	0.8	0.6−	1.3	4.4	3.5	97.7
19 380	^4P	10.8−	**18.0**	5.7	4.3−	16.4−	10.9−	7.1	13.9	2.1	1.1−	0.4−	1.5−	0.4	92.6
20 869	^4D	0.6	19.2	5.8	9.7−	**37.0**		5.6−	3.3	0.3−	0.2	0.7−	0.1−	1.0−	83.5
25 241	$(4^3P)^4P$	0.3	3.0−	4.7−	0.7−	1.8	12.1	1.6−	**23.9**	3.8		0.3	0.1	2.3	54.6
45 584	$(2^3P)^4P$		0.8	2.8	2.0	0.2−	5.3−	0.2	**21.9**−	2.5−	0.3	0.1	2.1	0.4−	38.5
26 361	5^2D	0.5−	10.2	0.2−	0.3−	15.7−	**14.7**	2.4−	0.6−		1.1	6.3	10.3	0.1	62.5
52 911	1^2D	0.3−	4.8		0.2−	4.4−	**4.6**	0.1−	0.1−		0.8	0.2	0.9	0.1	16.4
27 188	3^2F	0.1	11.9−	9.9	1.7−	1.3	7.7−	9.8	1.6	1.8	3.3	19.6	**19.1**	1.3	89.1
27 525	^4F		3.6	0.2−	0.5−	4.8	8.4	20.5	5.0−	11.5	**34.2**	0.1−	3.4−	0.3	92.5
30 112	$(4^3F)^4F$			0.1−	1.2−	0.4	1.0	4.5	7.2−	**24.8**	19.6−	0.2−	1.9	15.7−	76.5
43 680	$(2^3F)^4F$				0.4	0.1−			2.3	**4.0**−	4.6	2.2	2.8−	0.3	16.7
30 776	$(^5D)^4D$		1.5	0.5	1.7−	3.8	0.4−	5.2−	7.2−	0.9	6.1−	**33.0**	6.4−	8.2	74.9
31 401	5^2F		0.4−		0.1	1.1−	8.3−	**25.2**−	0.2	23.6	6.4		0.7	4.5−	70.5
32 905	$(^3G)^4G$		0.4−	1.6	0.9−	0.1−	1.3		2.3−	4.2	7.3−	11.2−	0.3	**45.0**	74.6
33 438	$(^3D)^4D$		1.5	2.4	0.3	2.3	0.4−	0.9−	1.8−	1.1−	0.8	12.0−	35.1		58.5
37 256	3^2D		1.2−	0.2−	0.6	2.2−	1.9−	0.4−	0.1−	6.0	3.7	1.3−	2.4−	0.9	21.0
39 028	$(4^3F)^2F$					0.1	0.8	8.6	0.7	5.7−	1.3−	0.6	0.4	2.2−	20.5
52 558	$(2^3F)^2F$		0.1−	0.1	0.1−		0.3−			1.7		0.2		1.5	4.0
39 748	$(4^1D)^2D$			0.1−	0.2−		1.2	1.0	1.0	0.2	6.0−	0.9	0.1	5.4−	16.1
59 240	$(2^1D)^2D$		0.2	0.1				0.4−	0.7−	0.7−	1.2	0.2−	1.3	1.0	5.8
42 896	$(^1F)^2F$		0.1−	0.2		0.2		2.8		0.2−	0.3−		1.5	6.0	11.4
44 628	$(^3D)^2D$		1.5		0.1−	1.1−	2.0	1.2−	1.6−	0.8−	0.3	8.7	5.1		22.2

Table V. Composition of the states with $J=7/2$.

LS position	Level Desig.	14 217 a^6D	15 058 a^4G	17 331 a^4D	21 775 a^2F	24 724 b^4F	27 141 b^2F	28 542 a^2G	28 810 a^4H	a^4F	31 983 b^4D	33 824 b^4G	c^4D	Total
15 415	$(^5D)^6D$	**93.3**	0.4−	0.2		2.1	0.3−	0.3−	1.3			0.1−	1.5−	99.5
18 315	^4G	0.4	**48.7**	32.3−	1.6	2.6	3.5	1.8−	1.3−	3.5	0.3	2.8	0.4−	99.2
20 869	^4D	0.1	24.5	**45.5**		5.3−	0.3	1.4	6.0−	0.3	4.8	0.2	10.9−	99.3
27 188	3^2F	0.1	12.3−	0.4	17.5	1.5	**25.8**	10.2−	3.6−	0.2−	18.9	0.3	0.9−	91.7
27 525	^4F		6.6	1.3	24.7	1.0	12.3−		5.8	**33.4**−	2.4	0.9	8.6	97.0
28 312	$(^5D)^4D$	0.4−	3.5	10.8	1.5−	5.0	19.7	11.8−	6.7	1.3−	**29.0**−	0.1−	1.1	90.9
29 645	$(4^3F)^4F$	2.7−	0.2	0.7	1.6	**10.6**	7.1−	3.5−	14.4	8.4	2.9	17.3−	11.6−	81.0
43 690	$(2^3F)^4F$	1.2		0.5−		**4.4**−	1.6	0.5	3.2−	9.4−	0.7−	0.9	0.2−	22.6
29 941	5^2G		0.1−	0.2	10.3	9.9	7.9	**51.1**	0.4	0.8	1.9−	0.3		82.9
30 868	$(^3H)^4H$			0.1−	0.2	14.2−	5.6		**45.9**	1.6	4.4	6.2		78.2
31 401	5^2F				**27.4**−	5.0	2.4	4.8	1.9	2.1−	24.8	0.2	0.2	68.8
32 084	$(^3G)^4G$	0.2−	1.8−	2.9	0.1−	8.0	9.7−	1.0−	0.1−	9.3	0.2−	**60.0**		93.3
33 894	$(^3D)^4D$	1.3	1.0	3.7		0.1−	0.1	0.1−	0.8−	17.8	3.5	3.0−	**61.6**	93.0
37 975	$(4^3F)^2F$		0.3−	0.3−	7.4	6.9−	0.7−		1.4−	3.6	0.4−	0.7−	2.1−	23.8
52 699	$(2^3F)^2F$	0.1−		0.3	0.1	3.7	1.8	1.9−		1.2−	0.1	1.2	0.1−	10.5
41 183	$(^3G)^2G$				1.7	0.2−	0.6	5.5	1.8	3.4	0.6−	0.8−	0.1−	14.7
41 680	3^2G		0.2−	0.1	1.9	1.0−		1.3	0.6	1.2	4.9−	0.1		11.3
42 896	$(^1F)^2F$		0.2−	0.2	3.6		0.5	1.9−	0.8−	2.0		0.2	0.4	9.8
43 842	$(4^1G)^2G$			0.2		12.3		2.7	2.1−			0.2−		17.5
50 492	$(2^1G)^2G$				0.2	6.0−	0.2	0.1−	1.8	0.4	0.1−	4.6		13.4

Table VI. Composition of the states with $J=9/2$.

LS position	Level Desig.	11 754 a^6D	16 619 a^4G	22 160 a^2G	27 161 a^4H	27 514 a^4F	30 645 b^4F	31 399 a^2H	34 194 b^4G	b^2G	Total
13 303	$(^5D)^6D$	**90.7**		3.6	1.9	0.2	2.7		0.3		99.4
18 315	^4G		**84.6**−	2.8−	5.9	1.0−	0.3	0.4−	4.5−	0.2	99.7
27 525	^4F	0.2	5.3−	18.4	0.2	**47.7**	13.8−	8.8	0.4		94.8
28 800	$(4^3F)^4F$	5.1−		9.8	11.2	3.4	**23.5**	0.2	10.4	0.2	63.8
43 949	$(2^3F)^4F$	3.3		4.0−	5.4−		**11.9**−			1.3−	25.9
29 886	^2H		3.1−	4.2	9.2−	25.8−	0.3	**46.6**	8.0	0.2−	97.4
29 941	5^2G		1.4−	**31.4**	20.0−	2.9−	1.7−	13.9−	4.8−		76.1
30 164	$(^3H)^4H$		0.1−	2.4−	**24.5**−	10.7	38.7	1.6	11.4−	8.1−	97.5
31 027	$(^3G)^4G$	0.2−	4.9	7.1	16.0	2.7−	0.1−	11.4	**52.6**−	0.3−	95.3
39 070	$(^3G)^2G$			2.7	2.9−	0.1−	3.3	3.1−	0.8−	**43.3**	56.2
39 264	$(^3H)^2H$			1.2−	0.1	1.6	2.0−		0.2−	0.9−	6.0
41 680	3^2G		0.4−	0.7−	0.1−	0.6		2.4	0.1−	33.2	37.5
43 842	$(4^1G)^2G$	0.2−		9.3	0.5	2.7−	0.7	8.5−		6.2−	28.1
50 492	$(2^1G)^2G$	0.1		2.5−	2.0−	0.6	0.9−	3.1	6.5−	5.9	21.6

Table VII. Composition of the states with $J=11/2$.

LS position	Level Desig.	16 307 a^4G	23 956 a^2I	27 244 a^4H	30 560 b^4G	33 318 a^2H	b^2I	b^2H
18 315	^4G	**82.3**−	5.7−	3.6	0.1	8.2	0.1−	
25 928	^2I	2.0−	**70.4**	2.8−	7.6−	13.5	3.7−	
29 304	$(^3H)^4H$	0.2−	0.7−	**61.8**−	22.0	8.8	6.3	0.1−
29 736	$(^3G)^4G$	5.2	3.1	30.8	**33.9**	22.3	3.9	0.7
29 886	^2H	10.3−	19.3	0.1	14.3	**44.9**−	9.5	1.5
37 543	$(^3H)^2H$		0.4−		14.4−	1.8	33.8	**49.5**
37 843	$(^1I)^2I$		0.4−	0.9−	7.7	0.4−	**42.5**−	48.1

individual instances. On an absolute basis, the calculated g values are in exceptionally poor agreement with experiment for the three lowest levels with a J value of one half. But the eigenvectors show that the range of Landé g values is several times as great for these three levels as it is in other close levels, so that the disagreement is not exceptional on a percentage basis.

The percentage compositions of the eigenvectors are given in Tables II to VIII inclusive. In the left-hand column, "*LS*-position," are given the positions of the levels as they would be in pure *LS* coupling with configuration interaction and second-order spin-orbit

Table VIII. Composition of the states with $J=13/2$.

LS position	Level Desig.	26 348 a^2I	27 130 a^4H	b^2I
25 927	^2I	**96.6**	2.7	0.7
28 287	$(^3H)^4H$	1.9−	**91.1**	7.0−
37 843	$(^1I)^2I$	1.5−	6.2	**92.3**

TABLE IX. Alternate classifications given in AEL.

J	Level	Assignment	
		This paper	AEL
11/2	30 560	b^4G	a^2H
	33 318	a^2H	b^4G
7/2	24 724	b^4F	a^2G
	28 542	a^2G	a^4F
	27 141	b^2F	b^4D
	31 983	b^4D	b^2F
5/2	28 030	b^4F	a^4F
	29 800	a^4F	b^4D
	31 186	b^4D	b^4F
3/2	30 527	b^4F	b^4P
	31 461	b^4P	b^4F

effects omitted. Excepting some of the duplicated terms, these are simply the diagonal elements of the matrices. In the second column the LS-coupling names of the vector components are given in the scheme with Racah's seniority number diagonal. The configuration $5d^66s$ or $5d^56s^2$ is implied by the presence or absence of a parent term, respectively. These names correspond, of course, to the diagonal matrix elements given in the left-hand column already described. The top row, "level," lists the experimentally observed levels. The second row, "designation," gives the assignments of the levels in the abbreviated LS-coupling notation customary in experimental work and used in AEL. The full assignment requires, in addition, a configuration and, possibly, a parent term; this is obtained from the second column opposite the boldface component for that level.

Some assignments may be arbitrary choices between equally good alternatives, and it is also possible that we have overlooked possibilities that would be slightly better than the ones given. No assignments will insure that every level has a high purity for the particular LS component specified, or that the latter will correspond to the dominant component of the vector, or indicate the particular vector that contains most of that component. As an example, the assignment of 27 828 cm^{-1} as $5d^6(^5D)6s\ b^4D_{\frac{3}{2}}$ is one where all three criteria are invalid. By using the sum of the purities as a criterion, it would be slightly better to make a cyclic interchange of the three assignments $b^4D_{\frac{3}{2}}$, $b^4P_{\frac{3}{2}}$, and $b^4F_{\frac{3}{2}}$; the total purity for the three levels would be increased from 80.0%, as given, to 81.5% but the assignment of 30 527 cm^{-1} as $5d^6(a^3P)6s\ b^4P_{\frac{3}{2}}$ is then one where all three criteria are invalid. This change should not be made however, because it is desirable to consider the LS character of the levels, apart from the particular configuration and parent. When this is done, the purities of the $b^4F_{\frac{3}{2}}$ and $b^4D_{\frac{3}{2}}$ are both greater by about 13%, while the corresponding effects in the alternate assignment would be about 2%. From this viewpoint, it follows that strong configuration interactions that are present in this spectrum tend to stabilize the assignments to a greater extent than indicated by the purities. The assignment of the level[13] at 27 385 cm^{-1} [13] as $5d^56s^2\ a^2S_{\frac{1}{2}}$ is definitely established by the presence of strong configuration interaction, but the configuration should not be taken too seriously, since the level contains a nearly equal amount of $5d^6(a^1S)6s\ ^2S_{\frac{1}{2}}$.

Complicated criteria could be set up so that the vectors would define the assignments uniquely, but this would not be worthwhile unless the probable accuracy with which the vectors represent the true composition of the levels were also calculated and taken into account. An analysis of this accuracy has not been made, but a comparison of these vectors with those obtained from the preliminary parameters indicates that there would not have been much difference in the assignments if the latter had been used. Inaccuracy would be most important in levels higher than 25 000 cm^{-1}, since here there are eight pairs of levels where either the observed or calculated separation is less than 1000 cm^{-1}, and in five of these pairs the observed and calculated separations differ by a factor of two or more. The neglect of the $5d^7$ configuration may be a factor which is also important for these levels.[14] It was felt, therefore, that assignments for these higher levels should be regarded as indications of what would be reasonable, and that some interchanges suggested by experimental criteria should be accepted. To prevent confusion, and also indicate generally the degree of uncertainty that we consider might arise from inaccuracy in the theory, we list in Table IX the differences between the assignments in this paper and the assignments finally accepted and given in AEL.[3,15]

It is expected that in some instances pairs of vectors can be changed greatly by making small changes in the parameters, even when the corresponding levels are separated by more than 1000 cm^{-1}. This is the basis for considering that the interchange of assignments for the

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[13] In reference 2 this level is classified differently on the basis of a single pattern for the g value, but this pattern has since been rejected as unreliable. Large isotope and hyperfine structure splittings in this spectrum often caused trouble in interpreting the experimental data. For instance, in the early literature the level at 27 385 cm^{-1} was regarded as two levels with a separation of 0.8 cm^{-1}. As noted by Meggers in reference 1, many of the hyperfine structure patterns were fully resolved with a grating and it was not always possible to average these patterns out in making the line list. By increasing the tolerance to allow for this, we have found a few lines listed in reference 1 that are hyperfine structure components of classified lines given in reference 2.

[14] Only the lowest pair of levels with $J=\frac{7}{2}$ are as close as this below 25 000 cm^{-1}, and this could account for the systematic behavior of the errors, rather than neglect of the $5d^7$ configuration. This explanation indicates that the accuracy of calculations made in spectra where LS coupling is applicable, is generally better than that for calculations made in spectra with a strong breakdown of coupling. Calculations that have been made in intermediate coupling often lead to closer agreement as noted by G. Racah [Physica **16**, 651 (1950)], but they have been made for spectra with relatively few allowed levels, so this agreement is not conclusive evidence.

[15] Some changes were suggested by Charlotte E. Moore so that the g values, line intensities, or term groupings would agree better with what was expected in LS coupling.

two levels $a^2H_{11/2}$ and $b^4G_{11/2}$ given in AEL should be made, as indicated by the g value observed for one of them, even though the observed and calculated separations of the two levels are large and agree well (i.e., 2758 cm^{-1} and 2842 cm^{-1}, respectively). Our qualitative criteria for admitting the possibility of a critical dependence on the parameter values in this instance, are that the pure LS levels are nearly degenerate, as can be seen from the left-hand column in Table VII, and there is no direct interaction between the pure levels to stabilize the composition.[16]

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[16] This critical dependence of eigenvectors on the parameters is illustrated for a third-order matrix with a single parameter by E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 39.

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Photodetachment of O_2^-†

D. S. Burch,* S. J. Smith, and L. M. Branscomb
Atomic Physics Section, National Bureau of Standards, Washington, D. C.

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The cross section for photodetachment of O_2^- has been measured for the range of photon energies 0.5 to 3.0 ev. No onset energy is discovered in this range but analysis of the data gives an extrapolated threshold at 0.15 ± 0.05 ev. The curve is found to rise gradually with increasing slope, reaching a value of 2.4×10^{-18} cm^2 at 3.0 ev photon energy. Comparison of the data with the predictions of threshold law theory and the results of previous experiments results in an interpretation in terms of assumed potential curves for O_2^-.

I. INTRODUCTION

A GLANCE at the history of molecular-negative-ion research reveals a great many experiments which have been performed giving valuable information on their rates of production and destruction as well as their behavior under various circumstances. Most of these experiments have been necessarily of the swarm type involving mixtures of electrons, atoms, molecules, and ions with various distributions of energy. Unfortunately, the observations have seldom been unequivocally interpretable in terms of the microscopic character of the ions. The weakness of the forces which maintain negative ions causes them to be very delicate, which fact mitigates against their assembly in sufficiently high densities to permit spectroscopic research of the conventional types. Further, molecular ions have complicated structures, and this has hampered theoretical investigation of their nature. Thus, the mechanics of formation, the energy of binding, and the energy-level schemes have still not been established for any molecular negative ion.

Many different kinds of diatomic negative ions are now known to exist and among the most diligently studied of these has been the ion of oxygen, O_2^-. It is readily formed in gas discharges containing oxygen. The presence of small amounts of the gas in devices such as counters tubes can seriously affect their behavior by capture of electrons from the ionized plasma.[1] Also, the possibility that O_2^- may form in the D region of the ionosphere makes it of interest to several fields of study.[2]

The configuration of electrons in the ground state of O_2^- is believed to consist of the orbitals of O_2 plus an extra electron in the antibonding ($\pi_g 2p$) orbital.[3,4] Formation of the ion may take place by direct radiative attachment although the cross section for this process is expected to be very much smaller than is required to explain the copious production observed in gas discharges. Bloch and Bradbury[5] proposed that the electron capture leaves the ion in an excited vibrational level which is then stabilized by collision. This explanation also requires a cross section for the stabilizing collision considerably larger than is supposed likely.[6] It has also been suggested[7] that the ions may be formed in electron- or ion-exchange collisions of O_2 with O^-.

Published values of the binding energy of the extra electron of O_2^- range from 0.07 ev[5] to 0.9 ev.[8] The low binding energy allows the ion to be destroyed easily by collisional detachment in discharges at high E/p.[9] It is also possible[7] that they may be destroyed in discharges by charge exchange in collisions with other types of molecules. Further, they may be destroyed by the

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* Now at Department of Physics, Oregon State College, Corvallis, Oregon.

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