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## HIGHLY IONIZED ATOMS: THE CONFIGURATIONS $s^2p^n$ ( $n = 1, 2, 4, 5$ )\*

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### ABSTRACT

The energy levels of highly ionized atoms in the configurations  $2s^22p^n$  and  $3s^33p^n$  ( $n = 1, 2, 4, 5$ ) are obtained by a judicious use of laboratory data (for the lower degrees of ionization), of observational data (identified coronal lines and nebular lines), and of theoretical analysis. A list is given of proposed identifications of visible forbidden coronal lines confirmed or suggested by the present work, which were not contained in Edlén's work of 1942. Various identifications are excluded. The tables of energy-level spacings are expected to be helpful in future identifications of forbidden lines from the infrared to the far ultraviolet.

### I. INTRODUCTION

Ever since the famous work by Edlén in 1942 (quoted as "EL"), concerning the identification of the coronal emission lines as forbidden lines of half-stripped atoms, there has been interest in highly ionized atoms. Recent observations of solar emission lines in the ultraviolet (Johnson *et al.* 1958; Violett, Behring, McAllister, and Rense 1958; Violett and Rense 1959; Detwiler *et al.* 1961; Hinteregger 1961), the considerable list of unidentified emission lines in the corona (see, e.g., Aly, 1955), and, last but not least, the great efforts since the war toward better understanding of very hot plasmas call for a more detailed study of highly ionized atoms. Finally, the recent work by Bowen (1955 and 1960) greatly improved the reliability of the observational data available for extrapolation.

The present paper is a study of the energy levels of the ground-state configurations primarily responsible for forbidden emission lines. All coronal emission lines so far identified belong to isoelectronic sequences of the two short periods of the periodic table, i.e., they involve the 2p and 3p shells. We shall investigate these shells in a semiempirical way, making use of as much experimental information as is reasonably well established, but, at the same time, exploit the theory of atomic spectra as fully as possible. Both these lines of attack are necessary to assure sufficient accuracy in the predicted energy levels to be of use in questions of identification. Even then, the accuracy is relatively poor in certain cases.

The general approach is simple: theoretically, the energy levels can be described by a number of atomic parameters characterizing the Coulomb and the spin interactions. These parameters can be computed from laboratory data for low enough degrees of ionization  $q$  (up to about  $q \sim 10$  for a typical sequence). The  $Z$ -dependency of these parameters is known to be hydrogen-like asymptotically. Consequently, extrapolations to higher  $Z$  ( $q \sim 15$ ) can be carried out, and the resultant parameters determine the

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levels of the highly ionized atoms not accessible to detailed spectroscopic analysis in the laboratory.

Such a calculation is quite elaborate and can be carried out only when sufficient experimental data are available to determine the parameters to the desired accuracy. In practice it is, therefore, applicable in a few cases only.<sup>1</sup> The prime example of such calculation are the levels of  $2s^2 2p^2$  in a Ca xv (Garstang 1952; Edlén 1954; Layzer 1954; Rohrlich 1956b).

The most useful approach was found to be a more empirical one: According to theory the energy-level differences in a given configuration are smooth functions of  $Z$  and have an asymptotic behavior (large  $Z$ ) which is at least approximately known. (Relativistic effects are often difficult to take into account.) Furthermore, a number of forbidden lines are by now fairly well established as belonging to highly ionized atoms in the configurations under discussion. These can be used as fixed points in a graphical or numerical extrapolation of the laboratory data of the less ionized atoms, taking account of the asymptotic behavior of the energy-level differences. One thus extrapolates along isoelectronic sequences into higher  $Z$  with a few known points on the way and a fair knowledge of the asymptotic shape of the curves.

Despite this apparent uniformity in approach, each isoelectronic sequence offers different problems and requires variations of the general method, for a number of reasons: the laboratory data vary in accuracy and reliability from one sequence to the next and from one element to the next; in several sequences, identifications of coronal emission lines have been well established, in others no lines are known.

We shall consider the configurations  $s^2 p^n$  in each case for the  $n = 2$  shell, as well as the  $n = 3$  shell. The paper will be concluded by a list of solar coronal lines whose identification is either confirmed or suggested by the present work and which had not been established previously in the well-known 1942 work by Edlén.

The present work is in many ways similar to Edlén's 1942 paper. But, apart from small differences in method, the availability of improved experimental data and the use of his now confirmed identifications of coronal lines warrant a re-examination of this problem.

## II. THE CONFIGURATIONS $2s^2 2p$ AND $3s^2 3p$

These are the ground configurations of the sequences based on B I and Al I, respectively. The configuration  $s^2 p$  has only the two levels  $^2P_{1/2}$  and  $^2P_{3/2}$ , the former being the ground level. The separation is due to spin-orbit interaction, characterized by the parameter  $\zeta$ ,

$$^2P_{3/2} - ^2P_{1/2} = \frac{3}{2} \zeta. \quad (1)$$

Along an isoelectronic sequence,  $\zeta$  approaches asymptotically a  $Z^4$  dependence, as is the case for hydrogen-like atoms. More precisely, if  $\sigma$  is the screening constant,  $\zeta$  will become proportional to  $(Z - \sigma)^4$ . Here, as in the following, "asymptotically" always means "for large  $Z$  along an isoelectronic sequence." Large  $Z$  is equivalent to large  $q$ , where  $q$  is the degree of ionization, i.e., the number of electrons missing from the neutral atom. A plot of  $\sqrt[3]{\zeta}$  versus  $q$  must yield a curve which approaches a straight line asymptotically. Equivalently,  $\Delta\sqrt[3]{\zeta} = \sqrt[3]{\zeta(q)} - \sqrt[3]{\zeta(q-1)}$  as a function of  $q$  must yield a curve which approaches a constant asymptotically. The latter plot permits higher accuracy and the corresponding extrapolation can be carried out graphically to sufficient precision. This forms the basis of our treatment of all doublet configurations, i.e.,  $s^2 p$  and  $s^2 p^5$ .

<sup>1</sup> A method recently proposed by Layzer (1959, 1962) would not yield more accurate results than the method used by us here, unless it were carried through relativistically. This would require a sufficiently elaborate calculation to prohibit as extensive a study as is undertaken here. Heavy reliance on experimental data in our case compensates for the relative crudeness of the theory used.

The question of relativistic effects may well be raised at this point. Such effects are expected to yield deviations of  $\lambda^{1/4}$  from a linear  $Z$  dependence of the order of, or possibly exceeding, the attempted accuracy of one part in  $10^4$ . Since a satisfactory computation of these effects does not seem feasible, it was necessary to rely on semiempirical data. In the 2p shell where the Ar xiv line  $\lambda$  4412 is observed, perfect linearity is attained from Si x on, and the smoothness of the curve does not seem to admit deviations from it within our accuracy up to at least Ca xvi. In the 3p shell no relativistic effects can be ascertained either, because the curve goes smoothly through Fe xiv ( $\lambda$  5303) and Ni xvi ( $\lambda$  3601), which are both well established, and does not yet reach perfect linearity even at the next two elements (see Table 2). A uniform decrease of curvature is, however, definitely discernible.

a) The B I Sequence

The basic reference for experimental data is the tables of atomic energy levels prepared by Dr. Sitterly (quoted as "AEL"), supplemented by Bowen's recent work

TABLE 1  
B I SEQUENCE  $2s^2 2p$

ION	OBSERVED (AEL)		EXTRAPOLATED	
	$^2P_{3/2} - ^2P_{1/2}$	$\Delta\lambda$	$\Delta\lambda$	$^2P_{3/2} - ^2P_{1/2}$
B I.....	0.016	0.133	0.133	0.016
C II.....	0.064	.129	.130	0.064
N III.....	0.1745	.129	.1283	0.175
O IV.....	0.387	.127	.1270	0.387
F V.....	0.746	.127	.1262	0.7465
Ne VI.....	1.316	.125	.1258	1.307
Na VII.....	2.139	.125	.1257	2.132
Mg VIII.....	3.30	.126	.1257	3.297
Al IX.....	4.89	.126	.1257	4.884
Si X.....	6.99	.125	.1256	6.985
P XI.....	9.70		.1256	9.698
S XII.....		$\Sigma\Delta\lambda = 0.3774$	.1256	13.134
Cl XIII.....			.1256	17.410
Ar XIV.....	22.657		.1256	22.657
K XV.....			.1256	29.01
Ca XVI.....			.1256	36.61
Sc XVII.....			.1256	45.61
Ti XVIII.....			0.1256	56.18

(1955, 1960). These data go up to  $q = 10$  (P XI). There is also one coronal line identified in this sequence:  $\lambda 4412$  corresponding to 22.657 kK (1 kK =  $10^3 \text{cm}^{-1}$ ) was identified by Edlén (1954) to belong to Ar XIV. An earlier questionable identification of  $\lambda 4359$  with the same transition in Ar XIV was later discarded.

As can be seen from Table 1, this line fits into the sequence in a very satisfactory way and, at the same time, permits a very accurate prediction of the doublet separations for  $10 < q < 13$ . The last two columns in this table were obtained as follows.

A plot of  $\Delta\sqrt{\zeta}$  versus  $q$  was made, and a curve was drawn which gives the best over-all fit and approaches a constant for large  $q$ . The smoothed and extrapolated values of  $\Delta\sqrt{\zeta}$  are read off this curve (4th col.), and the corresponding doublet separation is computed.

Two types of results are thus obtained. First, a comparison of observed and smoothed doublet separations shows that the latter are all within the given accuracy of the observations, with the exception of Ne VI and Na VII. Here the observations seem to be higher by  $9 \text{ cm}^{-1}$  and  $7 \text{ cm}^{-1}$ , respectively. However, closer inspection of the original literature shows that these differences are not inconsistent with the errors involved in these measurements. In view of the general agreement of the other elements, the last column of the table may give more reliable figures than the second column.

The second result is the prediction of doublet separations of heretofore not observed spectra.

The method and results just described, as well as similar extrapolations to be discussed later, must be compared with Edlén's work. In EL,  $\sqrt{\zeta}$  was extrapolated, and it was shown that, for large  $q$ , it approaches a straight line. The coronal lines in question were proved to fit satisfactorily to the doublet separations computed in this way. We extrapolate  $\Delta\sqrt{\zeta}$  rather than  $\sqrt{\zeta}$ , because we feel that we can achieve higher accuracy by numerical work with the former approaching a constant. A disadvantage of this procedure is that an incorrect energy level corresponds to two (rather than one) points which fail to lie on the extrapolation curve. But, on the whole, there are no essential differences in the extrapolation of the doublet configurations.

#### b) The Al I Sequence

Experimental data of the  $3s^23p$  configuration exist up to Sc IX, though the latter yields a doublet separation of no more than three-figure accuracy. But we can base our extrapolation on two well-established coronal lines,  $\lambda 5303$  of Fe XIV and  $\lambda 3601$  of Ni XVI.

The procedure followed is the same as in the B I sequence. However, since the corresponding curves offer a particularly nice demonstration of our method, we are presenting a part of the extrapolation-curve in Figure 1. The results are given in Table 2, which is arranged in the same way as Table 1.

In Figure 1 we have plotted  $\Delta\sqrt{\zeta}(q) = \sqrt{\zeta}(q) - \sqrt{\zeta}(q-1)$  versus  $q$ . The last experimental point is for  $q = 8$ . Then there are two points at  $q = 14$  and  $q = 15$  which are not known individually, but their sum is determined by the two coronal lines. This is sufficient to determine the solid line with very little ambiguity, in view of the fact that it must have a horizontal asymptote. There is no doubt that the points for  $q = 6$  and  $7$  cannot fall on this line. But a check on its correctness is that, if  $q = 5$  and  $8$  do fall on it, the deviations of  $q = 6$  and  $7$  must be equal in magnitude and opposite in sign. We conclude that the doublet separation for K VII should be higher by  $6 \text{ cm}^{-1}$ , a result again not inconsistent with the errors of the original measurements.

A similar situation arises for P III (not shown in Fig. 1), where the curve indicates that the doublet separation should be lowered by about  $3 \text{ cm}^{-1}$ . For the other elements up to Sc IX no significant corrections seem to emerge.

The dashed line in Figure 1 indicates what one would obtain by taking the average  $\Delta\sqrt{\zeta}$  between the known values. This average was given in EL. While, as in this case,

in some sequences the solid curve is a definite improvement over the average, other sequences are such that the difference is insignificant.

With the fixed points for Fe XIV and Ni XVI, all the interpolated and extrapolated values listed in Table 2 then easily follow from the curve of Figure 1. The accuracy is about 1 in  $10^3$ . Two of the resultant doublet separations coincide with observed coronal lines:

$$\lambda 6535 = 15.30 \text{ kK} \rightarrow 15.29 \text{ kK} = 6540 \text{ \AA Mn XIII,}$$

$$\lambda 4351 = 22.975 \text{ kK} \rightarrow 22.99 \text{ kK} = 4350 \text{ \AA Co XV,}$$

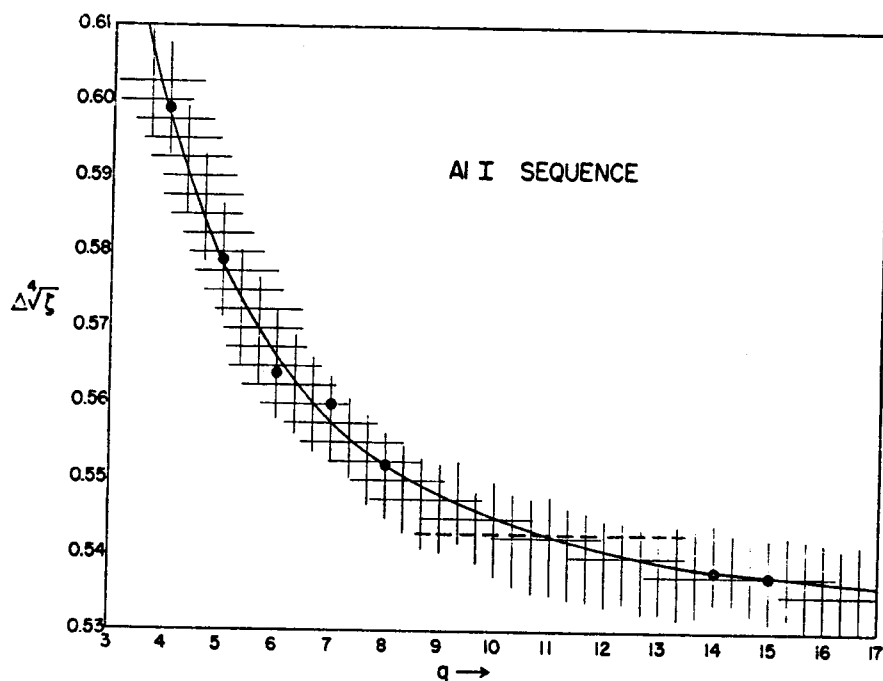


FIG. 1.—The Al I sequence as an example of the method for doublet extrapolation. The two points at  $q = 14$  and  $15$  follow from the known coronal lines  $\lambda 5303$  and  $\lambda 3601$ . The two points at  $q = 6$  and  $7$  deviate from the curve by equal amounts and opposite signs, exhibiting a small error in the adopted experimental value of the doublet separation in K VII. This error is consistent with the accuracy of the measurement. The dashed line indicates how crude the extrapolation would be if it were based on the average difference between the values of  $\sqrt{\xi}$  in Si IX (highest  $q$  observed in the laboratory) and Fe XIV, rather than on a smooth curve. Note that the ordinate is in units of  $\text{K}^{1/4}$ , while the tables are all in kK and  $(\text{kK})^{1/4}$ .

and at the same time confirm the previously made calculations (Edlén 1942; C. Pecker 1958).  $\lambda 6535$  was found by Aly, and  $\lambda 4351$  was first seen by Lyot and Dollfus. The latter also first suggested this identification in 1953.

### III. THE CONFIGURATIONS $2s^22p^5$ AND $3s^23p^5$

Being the conjugate configuration to  $s^2p$ ,  $s^2p^5$  has  $^2P_{3/2}$  as the ground level and  $^2P_{1/2}$  as the excited level. Apart from this, the theoretical arguments and the method used are exactly the same as for  $s^2p$ .

## a) The F I Sequence

Here we can take  $\lambda$  5536 of Ar x and  $\lambda$  3329 of Ca xii as established coronal lines (Edlén 1942, 1954). This gives us data up to Ca xii, beyond which the  $\Delta\sqrt{\zeta}$  curve apparently has reached its constant value (Table 3). From our curve we find two major corrections of experimental data: the separation of S viii should be 49  $\text{cm}^{-1}$  smaller and that of Cl ix about 36  $\text{cm}^{-1}$  larger.

The value of 23.475 kK for K xi, already found in EL, is probably to be identified with  $\lambda$  4256, which yields 23.488 kK, as observed by Aly. This was pointed out earlier (Pecker 1958). The ion of Ti xiv has an ionization potential well exceeding 788 V and is therefore to be found at best in extremely hot regions of the corona, i.e., it would belong to the same class as  $\lambda$  5694 of Ca xv. In addition, Ti is by an order of magnitude less abundant in the sun than Ca is.

In this connection it is worth mentioning that a useful guide to ionization potentials

TABLE 2  
AL I SEQUENCE  $3s^23p$

ION	OBSERVED (AEL)		EXTRAPOLATED	
	$^2P_{3/2}-^2P_{1/2}$	$\Delta\sqrt{\zeta}$	$\Delta\sqrt{\zeta}$	$^2P_{3/2}-^2P_{1/2}$
Al I.....	0.11204			0.11204
Si II.....	0.287	0.1389	0.1389	0.287
P III.....	0.5596	.1201	.1191	0.557
S IV.....	0.9502	.1106	.1116	0.9502
Cl V.....	1.492	.1065	.1065	1.492
Ar VI.....	2.210	.1030	.1030	2.210
K VII.....	3.129	.1003	.1007	3.135
Ca VIII.....	4.305	.0996	.0991	4.305
Sc IX.....	5.76	.0982	.0982	5.76
Ti X.....			.0975	7.54
V XI.....			.0969	9.69
Cr XII.....		$\Sigma\Delta\sqrt{\zeta} = .4831$	.0965	12.23
Mn XIII.....			.0962	15.29
Fe XIV.....	18.8525		.0960	18.8525
Co XV.....		$\Sigma\Delta\sqrt{\zeta} = 0.1914$	.0958	22.99
Ni XVI.....	27.762		.0956	27.762
Cu XVII.....			.0955	33.24
Zn XVIII.....			0.0954	39.494

of highly ionized atoms is the table prepared by means of extrapolation by Finkelnburg and Hunbach (1955).

b) *The CL I Sequence*

The coronal lines  $\lambda$  6374 of Fe X and  $\lambda$  4231 of Ni XII are well known (Edlén 1942). Together with laboratory data, we thus know all doublet separations up to and including Ni XII, though Co XI is only poorly known.

Our extrapolation curve (Table 4) agrees with AEL, except for Mn IX (which we find  $19 \text{ cm}^{-1}$  higher) and Co XI (which we find  $76 \text{ cm}^{-1}$  higher). Both AEL data are based on rough extrapolations. The new value for Co XI excludes the previously suggested identification with Aly's  $\lambda$  5188, which corresponds to  $19.27 \text{ kK}$  (Pecker 1958).

IV. THE CONFIGURATIONS  $2s^22p^2$  AND  $3s^23p^2$

Configurations of the type  $s^2p^2$  contain five levels— $^3P_0$ ,  $^3P_1$ ,  $^3P_2$ ,  $^1D_2$ , and  $^1S_0$ , in that order. Although the three triplet levels are much closer spaced than the singlet levels,

TABLE 3  
F I SEQUENCE  $2s^22p^2$

ION	OBSERVED (AEL)		EXTRAPOLATED	
	$^3P_{1/2}-^3P_{3/2}$	$\Delta\sqrt{I}$	$\Delta\sqrt{I}$	$^3P_{1/2}-^3P_{3/2}$
Fe I.....	0.404			0.404
Ne II.....	0.782	0.130	0.1286	0.779
Na III.....	1.364	.126	.1277	1.365
Mg IV.....	2.226	.128	.1272	2.228
Al V.....	3.44	.126	.1268	3.441
Si VI.....	5.10	.127	.1266	5.091
P VII.....	7.268	.126	.1265	7.271
S VIII.....	10.13	.127	.1263	10.081
Cl IX.....	13.60	.126	.1263	13.636
Ar X.....	18.059	.126	.1263	18.059
K XI.....	23.475	.1262	.1263	23.476
Ca XII.....	30.028	0.1262	.1262	30.029
Sc XIII.....			.1262	37.859
Ti XIV.....			.1262	47.133
V XV.....			.1262	58.02
Cr XVI.....			.1262	70.68
Mn XVII.....			.1262	85.29
Fe XVIII.....			0.1262	102.05

all five levels must be considered simultaneously in any computation that attempts our accuracy. The reason for this situation lies in the spin interactions which couple all levels of equal total angular momentum  $J$ . Thus all calculations must be carried out in intermediate coupling, and this is the more important for highly ionized atoms, since the spin-orbit parameter increases with degree of ionization like  $Z^4$ , whereas the Coulomb interaction parameters (Slater parameters) vary only linearly.

A further complication associated especially with high ionization is the interaction of  $s^2p^2$  with the higher configurations like  $p^4$ . This is not the only configuration with which  $s^2p^2$  interacts, but it is the most important such configuration, because it is the closest and because it is a conjugate configuration. The latter implies that  $p^4$  has exactly the same levels as  $s^2p^2$ , so that each level is directly affected by configuration interaction. This permits one to take into account the interaction with other configurations in an effective way, yielding simply "distorted" sets of interaction parameters. This distortion is larger in the 3p shell because the interaction with configurations other than  $p^4$  is more important there than in the 2p shell.

TABLE 4  
CL I SEQUENCE  $3s^23p^4$

ION	OBSERVED (AEL)		EXTRAPOLATED	
	$^2P_{1/2}-^2P_{3/2}$	$\Delta\sqrt{\zeta}$	$\Delta\sqrt{\zeta}$	$^2P_{1/2}-^2P_{3/2}$
Cl I.....	0.881			0.881
Ar II.....	1.432	0.1131	0.1129	1.432
K III.....	2.162	.107	.1070	2.160
Ca IV.....	3.115	.105	.1050	3.115
Sc V.....	4.328	.102	.1028	4.327
Ti VI.....	5.84	.102	.1011	5.834
V VII.....	7.66	.0986	.0997	7.675
Cr VIII.....	9.90	.0984	.0987	9.897
Mn IX.....	(12.53)	.0982	.0980	12.549
Fe X.....	15.683	.0983	.0975	15.684
Co XI.....	(19.28)	.0952	.0971	19.356
Ni XII.....	23.626	0.0988	.0969	23.626
Cu XIII.....			.0967	28.560
Zn XIV.....			.0966	34.221
Ga XV.....			.0965	40.68
Ge XVI.....			.0965	48.01
As XVII.....			.0965	56.28
Se XVIII.....			0.0964	65.58



For the lower degrees of ionization where configuration interaction is small, the work of Garstang (1951) on the  $s^2p^2$  and  $s^2p^4$  configurations is relevant. The parameters determined there are—within the limits mentioned—fairly accurate. The parameter  $\eta$ , however, is not precisely known because of its smallness.

To attain the accuracy desired, it is also necessary to include the polarization term  $aL(L+1)$ , as well as the spin-other-orbit and spin-spin interactions, characterized by a parameter which varies approximately like  $Z^3$ . The parameter  $a$  may be small when configuration interaction is accounted for satisfactorily.

Thus  $s^2p^2$  is a difficult configuration to compute and requires a good many experimental data to approach it successfully in a semiempirical way. Since the  $Z$ -dependence of the parameters is known, it was generally considered sufficient to carry out such a detailed calculation for only one (highly ionized) atom of each sequence and to obtain the others by inter- and extrapolation.

#### a) The C I Sequence

This sequence contains the coronal lines  $\lambda$  5694 and  $\lambda$  5446 which were only questionably identified in EL with the Ca xv ion. This identification has been confirmed very strongly on semiempirical grounds by Layzer (1954), Edlén (1954), and Rohrllich (1956). The laboratory data in AEL for the C I sequence end with P x, which has poor accuracy.

The method employed consists of a precise calculation of the levels of  $2s^22p^2$  in Ca xv, which involves the determination of the Coulomb parameter  $f$ , the configuration interaction parameter  $G_1(2s^22p^2 - 2p^4)$ , and the spin interactions parameters  $\zeta$  and  $\eta$  for the degree of ionization  $q = 14$ . The polarization parameter  $a$  is negligible.

Once these parameters are determined, they can be related to their values for small  $q$  by means of their known  $Z$ -dependence. The parameters are then known for all elements in the sequence. However, within the accuracy attainable, these parameters can be used only as a check on the extrapolated and interpolated energy levels. In practice, the energy levels can be obtained with higher accuracy graphically, using the data at  $q = 14$  and at  $q \leq 9$ .

The details of the Ca xv calculations are given in the quoted papers. Suffice it to say here that, while  $^3P_1$  and  $^3P_2$  are given by the coronal lines, the position of  $^1D_2$  and especially of  $^1S_0$  are not very accurately known, since the theoretical work is limited to a precision of, at most, four significant figures.

The calculation for Ca xv (Rohrllich 1956b) was repeated with improved numerical methods for the diagonalization of the matrices involved, permitting more iterations. The results are as follows: taking  $^3P_0$  as zero, we have  $^3P_1 = 17.60$  kK,  $^3P_2 = 35.99$  kK,  $^1D_2 = 109.08$  kK,  $^1S_0 = 189.58$  kK.

The computed wavelengths for  $^3P_1 - ^3P_0$  (17.60 kK = 5682 Å) and  $^3P_2 - ^3P_1$  (18.39 kK = 5438 Å) are in satisfactory agreement with the coronal lines  $\lambda$  5694 and  $\lambda$  5446, respectively.

Using Ca xv as a fixed point, the interpolations (and extrapolations) can now be carried out with high accuracy.<sup>2</sup> The results are presented in Table 5 in brackets. Level spacings based on computed levels are indicated by parentheses.

The results for the two lowest excited states,  $^3P_1$  and  $^3P_2$ , in Ar XIII through Ti XVII should be compared with the work by Layzer and Zirin (1955), who used slightly different parameters and a somewhat different method. The agreement is within the expected accuracy of their method, i.e., a few per cent.

■ Our results clearly indicate that the singlets in Na VI and Mg VII should be displaced relative to the triplets by +0.12 and -0.54 kK, respectively. This result was independently arrived at in Edlén's laboratory (private communication), where +0.120 and -0.538 were obtained.

<sup>2</sup> Here, as in the following sequences, the graphical part of the extra- and interpolations consisted of plots for  $(E_{SLJ} - E_{S'L'J'}) / (q + a)^n$ , where  $n = 1$  (except  $n = 4$  when  $S = S'$  and  $L = L'$ ) and  $a$  was chosen to give highest possible accuracy.

Similarly, the levels of Si IX and P X as given in AEL seem to require revision. Most of the levels given there are based on extrapolation rather than measurement. In particular, the position of the  $^1S$  level is difficult to ascertain. Our curve is based on the above Ca XV calculation and is consistent with the asymptotic value of the  $^1S - ^1D$  difference, as obtained by Layzer (1959). The  $^1S - ^1D$  differences in AEL are not consistent with this asymptotic behavior.

As an immediate application of Table 5, the coronal line  $\lambda$  6740 given by Aly (14.83 kK) can be tentatively identified with the transition  $^3P_2 - ^3P_1$ , in K XIV. Its ionization potential is 717 V. Similarly, the coronal line  $\lambda$  8475.66 given by Wlerick and Fehrenbach (1961) is tentatively identified with  $^3P_2 - ^3P_1$  in Ar XIII (ionization potential is 620 V).

TABLE 5\*  
C I SEQUENCE  $2s^22p^2$

Ion	$^3P_1 - ^3P_0$	$^3P_2 - ^3P_1$	$^1D_2 - ^3P_2$	$^1S_0 - ^1D_2$
C I.....	0.0164	0.0271	10.1502	11.4547
N II.....	0.0491	0.0819	15.1856	17.3727
O III.....	0.114	0.1930	19.9671	22.9125
F IV.....	0.2252	0.3871	24.6223	28.303
Ne V.....	0.414	0.6981	29.1813	33.606
Na VI.....	0.698	1.160	[33.660]	38.916
Mg VII.....	1.127	[1.812]	[38.074]	44.188
Al VIII.....	1.740	2.70	42.25	49.480
Si IX.....	2.590	[3.85]	46.50	[54.4]
P X.....	[3.78]	[5.30]	[50.75]	[59.0]
S XI.....	[5.34]	[7.08]	[55.1]	[63.5]
Cl XII.....	[7.39]	[9.23]	[59.5]	[68.1]
Ar XIII.....	[10.04]	[11.79]	[64.0]	[72.3]
K XIV.....	[13.38]	[14.83]	[68.6]	[76.5]
Ca XV.....	17.566	18.355	(73.16)	(80.5)
Sc XVI.....	[22.73]	[22.40]	[78.0]	[84.7]
Ti XVII.....	[29.0]	[27.80]	[82.8]	[88.8]

\* Energy-level differences in units kK =  $10^3 \text{ cm}^{-1}$ . The parentheses indicate computed values, the brackets indicate interpolated values.

#### b) The S I Sequence

Although there are apparently quite a few coronal lines in the  $3s^23p^2$  sequence, we shall consider only the Fe XIII lines ( $\lambda\lambda$  3388, 10798, 10747) and the Ni XV lines ( $\lambda$  8024 and  $\lambda$  6072) as established. The AEL tables go up to Ti IX, but the  $^1S$  level is known only up to Cl IV. The S I sequence therefore differs from the C I sequence in two respects: fewer laboratory data, but more coronal lines. The latter is a great asset, because it permits one to do better by semiempirical methods. In particular, all levels of Fe XIII are known from coronal lines except the  $^1S$  level.

This situation suggests strongly carrying out a detailed calculation for Fe XIII to determine the atomic parameters for this ion to good accuracy and establishing a "fixed point" in the extrapolation also for the  $^1S$  level.

The computation for the  $3s^23p^2$  configuration of Fe XIII was carried out in intermediate coupling, following the lines of the computation of  $3s^23p^2$  in Ca XV. Since the observed coronal emission lines of Fe XIII give all but the  $^1S_0$  level, this computation yielded an estimate of this level as well as an estimate of the various relevant atomic parameters. After a somewhat laborious successive approximation procedure, the following parameter values (in the notation of Rohrlich 1956b) were obtained:  $f = 15.1$ ,  $\zeta = 12.02$ ,  $\eta = 0$ ,  $L = 500$ ,  $\phi = G_1 = 34$ . All values<sup>3</sup> are in kK =  $10^3 \text{ cm}^{-1}$ .

<sup>3</sup> In this calculation the sensitivity of the four known levels of Fe XIII with respect to the five parameters was computed, and, by successive iteration, those parameters were found which fit these levels, as well as extrapolation estimates for these parameters along the isoelectronic sequence.

With these parameters the computed wavelengths of the forbidden lines in the  $3s^23p^2$  configuration in Fe XIII agree to four figures with the coronal emission lines ( $\lambda$  3388,  $\lambda$  10747). This gives an estimate of the  $^1S$  level which is now estimated at 87.247 kK. This value is larger than Edlén's estimate of 82 kK (cf. AEL).

With the knowledge of the estimated  $^1S$  and the observed  $^3P_{0,1,2}$  and  $^1D_2$  levels of Fe XIII, together with the observed  $^3P_1$  and  $^3P_2$  levels of Ni XV (from  $\lambda$  6702 and  $\lambda$  8024), a graphical extrapolation and interpolation is now carried out. The results are given in Table 6.

While the extrapolation of the level spacings  $^3P_1-^3P_0$ ,  $^1D_2-^3P_1$ , and  $^1D_2-^3P_2$  offer no serious difficulty, the extrapolation of the  $^1S_0-^1D_2$  spacing involves various problems, and the results of that column in Table 6 should not be taken too seriously. They are offered here more as a guide to future work than as a proposed estimate. The problems involved are these: if Bowen's (1960) value of  $^1S_0-^1D_2$  in Ar V, 21.6131 kK, is adopted, the extrapolated curve (a) is very far from the computed  $^1S$  value of Fe XIII and (b) does not tend toward a straight line (linear in  $Z$ ), as would be expected from the irregular doublet law.

TABLE 6\*

SI I SEQUENCE  $3s^23p^2$ 

Ion	$^3P_1-^3P_0$	$^3P_2-^3P_1$	$^1D_2-^3P_2$	$^1D_2-^3P_1$	$^1S_0-^1D_2$
Si I.....	0.07715	0.14616	6.0755	6.2217	9.0954
P II.....	0.1666	0.3042	8.4136	8.7178	12.6938
S III.....	0.2972	0.5353	10.4883	11.0236	15.8383
Cl IV.....	0.491	0.8499	12.4257	13.2756	18.7802
Ar V.....	0.765	1.2653	14.2702	15.5355	[21.54]
K VI.....	1.131	1.793	16.049	17.842	[24.14]
Ca VII.....	1.627	[2.46]	[17.78]	[20.24]	[26.61]
Sc VIII.....	2.28	[3.27]	19.50	[22.77]	[28.96]
Ti IX.....	[3.12]	[4.22]	[21.25]	[25.47]	[31.19]
V X.....	[4.18]	[5.31]	[23.07]	[28.38]	[33.32]
Cr XI.....	[5.54]	[6.53]	[25.01]	[31.54]	[35.36]
Mn XII.....	[7.21]	[7.86]	[27.13]	[34.99]	[37.31]
Fe XIII.....	9.3025	9.2585	29.507	38.766	(39.18)
Co XIV.....	[11.86]	[10.73]	[32.19]	[42.92]	[40.97]
Ni XV.....	14.9172	12.4589	[35.02]	[47.48]	[42.7]

\* See also note to Table 5.

On the other hand, if this value is not adopted, both difficulties are removed. The results of the latter choice are given in Table 6. However, the theoretical estimate of  $^1S$  is probably not accurate to four figures (an improved estimate is very difficult), so that the numbers given should be regarded with suitable suspicion. The reason for this inaccuracy lies both in the fact that this highest level of the configuration is more susceptible to configuration interaction and in that it is an S-level and therefore more susceptible to the atomic core structure.

Comparison of the results for the Si I sequence with observed coronal lines confirms the following identifications by Edlén (1955) of  $\lambda$  3998, and by Pecker (1958) of  $\lambda$  3170 and  $\lambda$  3685:

$$\lambda 3170 = 31.54 \text{ kK: } ^1D_2 - ^3P_1 \text{ Cr XI,}$$

$$\lambda 3685 = 27.13 \text{ kK: } ^1D_2 - ^3P_2 \text{ Mn XII,}$$

$$\lambda 3998 = 25.01 \text{ kK: } ^1D - ^3P_2 \text{ Cr XI.}$$

Furthermore, the Ca VII prediction is apparently to be identified with  $\lambda$  5620 found by Aly:

$$\lambda 5620 = 17.78 \text{ k} : {}^1\text{D}_2 - {}^3\text{P}_2 \text{ Ca VII}.$$

This is a new identification. Finally, it should be noted that the identifications of  $\lambda$  3534 and  $\lambda$  4311 or  $\lambda$  4349 with V X lines found in the literature are not confirmed. The predictions here are 28.38 kK = 3523 Å for  ${}^1\text{D}_2 - {}^3\text{P}_1$ , and 23.07 kK = 4337 Å for  ${}^1\text{D}_2 - {}^3\text{P}_2$ , respectively.

#### V. THE CONFIGURATIONS $2s^22p^4$ AND $3s^23p^4$

The  $s^2p^4$  configuration interacts about equally strong with several configurations simultaneously. Little would be gained in attempting a description of this configuration interaction. On the one hand, these configurations are only incompletely known experimentally and, even if completely known, would require very laborious calculations. On the other hand, comparable accuracy can be achieved by permitting a certain latitude in the intermediate coupling description, which will now be explained.

The main effect of configuration interaction in addition to intermediate coupling is a change in the diagonal elements of the energy matrices for each value of  $J$ . Since we have only  $2 \times 2$  matrices (for  $J = 0$  and 2), this effect can be taken into account satisfactorily by permitting the Slater parameter  $f = 3F_2$  to depend on  $J$ . Thus we shall write  $f$  for  $J = 2$  and  $f'$  for  $J = 0$ . Since the configuration interaction elements often contain larger coefficients for  $J = 0$  and, furthermore, since the  $J = 0$  levels are higher than the  $J = 2$  levels, it is reasonable to expect that the latter are less affected by configuration interaction. Therefore,  $f$  will be closer than  $f'$  to the value extrapolated from cases where configuration interaction is neglected completely. We shall assume it to be equal to that value.

Edlén (1954) has also taken into account configuration interaction in an effective way. He permitted the values of  $\zeta$  determining the  ${}^3\text{P}_2 - {}^3\text{P}_1$  and the  ${}^3\text{P}_1 - {}^3\text{P}_0$  spacings to differ. We feel that our method approximates the theoretical situation at least equally well.

It is obvious that the proposed method precludes consideration of the polarization term, which is also partially taken into account. As was observed by various authors, the inclusion of the polarization term without also including configuration interaction leads to worse results than without both.

The theoretical expressions for the energy levels, then, are

$$\left. \begin{aligned} {}^3\text{P}_0 \\ {}^1\text{S}_0 \end{aligned} \right\} = A + 2.5f' + 0.5\zeta + \eta \mp [(2.5f' + 0.5\zeta + \eta)^2 - 5f'(\zeta + 2\eta) + 2\zeta^2]^{1/2},$$

$${}^3\text{P}_1 = A + 0.5\zeta + 5\eta, \quad (2)$$

$$\left. \begin{aligned} {}^3\text{P}_2 \\ {}^1\text{D}_2 \end{aligned} \right\} = A + f - 0.25\zeta - 1.7\eta \mp [(f - 0.25\zeta - 1.7\eta)^2 + 2f(0.5\zeta + 3.4\eta) + 0.5\zeta^2]^{1/2}.$$

The parameter  $A$  is so chosen that  ${}^3\text{P}_2 = 0$ .

In determining the parameters, the established coronal lines play the dominant role, but the interpolation between laboratory data (AEL) and the ions identified in the corona involves the theoretical  $Z$ -dependence, as well as the dependence of these parameters on the configuration. The latter point was analyzed for  $f$  and  $G_1$  in an earlier paper (Rohrlich 1956a) and will be studied for  $\zeta$  in the following papers. In any case, the determination of these parameters depends on the coronal lines, which are well-established, and therefore differs from sequence to sequence.

#### a) The O I Sequence

Only the Ca XIII line  $\lambda$  4086 is known in the  $2s^22p^4$  sequence. This makes the parameter determination very difficult. The four parameters  $f, f', \zeta, \eta$ , for Ca XIII must be so deter-

mined that the energy levels computed by means of formulae (2) fit the above coronal line for  $^3P_1-^3P_2$  and fit smoothly on the (not uniquely) extrapolated curves for all five levels of the configuration. At the same time, the extrapolation-curves for the parameters themselves must follow the known  $Z$ -dependence. Thus a trial-and-error calculation is called for, where the final parameters are overdetermined within certain limits and therefore require a good deal of judgment throughout the work.

Garstang's work (1951) gives values for  $f = 3F_2$  which agree very well with those from other configurations and are linear to very good approximation (Rohrlich 1956a). His values for  $\zeta$  are very accurately fitted by  $\sqrt{\zeta} = aZ + b$ ;  $\eta$  can be only crudely estimated from his work. Fitting  $\lambda 4086$  then yielded, as the best set of parameters for Ca XIII,

$$f = 36.40, \zeta = 21.51, \eta = 0.03 \text{ kK.}$$

A study of the  $J = 0$  levels then leads to  $f' = 31.69 \text{ kK.}$

TABLE 7\*  
O I SEQUENCE  $2s^2 2p^4$

Ion	$^3P_1-^3P_2$	$^1D_2-^3P_2$	$^1D_2-^3P_1$	$^1D_2-^3P_0$	$^1S_0-^1D_2$
O I.....	0.1583	15.8678	15.7095	15.7095	17.9247
F II.....	0.3418	20.873	20.531	20.382	24.046
Ne III.....	0.6429	25.8408	25.1979	24.914	29.909
Ne IV.....	1.1055	30.839	29.733	29.263	35.662
Mg V.....	1.780	35.92	34.14	33.40	41.364
Al VI.....	[2.730]	41.14	[38.41]	37.31	47.07
Si VII.....	[4.03]	46.55	[42.52]	40.98	52.78
P VIII.....	[5.76]	[52.35]	[46.59]	[44.52]	58.52
S IX.....	[8.01]	[58.65]	[50.64]	[48.02]	[64.35]
Cl X.....	[10.88]	[65.5]	[54.6]	[51.27]	[70.32]
Ar XI.....	[14.50]	[72.8]	[58.3]	[54.45]	[76.4]
K XII.....	[18.97]	[80.6]	[61.6]	[57.5]	[82.8]
Ca XIII.....	24.465	(89.0)	(64.5)	(60.3)	(89.5)

\* See also note to Table 5.

The resultant Ca XIII level spacings are given in parenthesis in Table 7 and the inter- and extrapolated level spacings are shown in brackets. As a check, Cl X was studied along lines similar to Ca XIII with satisfactory results.

The extrapolation relies heavily on the smoothness of the curves and on the computed Ca XIII levels, since only one coronal line is known. This fact makes the extrapolation of the O I sequence definitely the least reliable of the present study. The recently observed intercombination lines in Si VII which fixes  $x$  (see AEL) as  $-0.45 \text{ kK}$  (private communication by Professor Edlén) plays an important role in the graphical procedure used. The resultant curves determine the relative position of the singlet and triplet systems and thus permit an estimate of the remaining uncertainties  $x$  of this sequence in AEL. For P VIII, S IX, and Cl X we find the estimates  $-0.10$ ,  $+0.65$ , and  $+4.5 \text{ kK}$ .

The  $^3P_1-^3P_2$  spacings lead to a prediction of about  $6892 \text{ \AA}$  for Ar XI. The value  $6919 \text{ \AA}$  (quoted in AEL) is not consistent with the smoothness of our curves.

Finally, we want to caution that the  $^1S_0$  level is, by its nature, less accurately determined than the other levels.

#### b) The S I Sequence

This sequence is much easier to analyze than the O I sequence. Both Fe XI and Ni XIII have each two known coronal lines,  $\lambda 7892$ ,  $\lambda 3987$ , and  $\lambda 5116$ ,  $\lambda 3643$ , respectively, cor-

responding to the  $^3P_1-^3P_2$  and  $^1D_2-^3P_1$  transitions. Furthermore, Fe XI was studied in the laboratory (cf. AEL).

Proceeding similarly as in the O I sequence, we find

$$\text{Fe XI: } f = 14.57, f' = 14.02, \zeta = 10.73, \eta = 0.047 \text{ kK,}$$

$$\text{Ni XIII: } f = 16.52, f' = 15.86, \zeta = 15.83, \eta = 0.103 \text{ kK.}$$

The corresponding levels agree within the expected accuracy with Edlén's results (cf. AEL); the latter are given in Table 8. The estimate for  $x$  in Cr IX and Mn X are  $\sim 0$  and  $\sim 0.2$  kK.

TABLE 8\*  
S I SEQUENCE  $3s^23p^4$

Ion	$^3P_1-^3P_2$	$^1D_2-^3P_2$	$^1D_2-^3P_1$	$^1D_2-^3P_0$	$^1S_0-^1D_2$
Si I.....	0.3968	9.2390	8.8422	8.6654	12.9424
Cl II.....	0.697	11.652	10.955	10.656	16.235
Ar III.....	1.1121	14.0100	12.8979	12.440	19.2557
K IV.....	1.673	16.3840	14.711	14.062	22.1622
Ca V.....	2.406	18.8301	16.424	15.554	25.016
Sc VI.....	3.352	21.397	18.045	16.944	27.841
Ti VII.....	4.54	24.12	19.58	18.22	[30.73]
V VIII.....	[6.01]	[27.06]	[21.05]	[19.45]	[33.62]
Cr IX.....	[7.81]	[30.27]	[22.46]	[20.67]	[36.57]
Mn X.....	[10.00]	[33.78]	[23.78]	[22.0]	[39.56]
Fe XI.....	12.668	37.743	25.075	23.3	42.57
Co XII.....	[15.83]	[42.12]	[26.29]	[24.8]	[45.6]
Ni XIII.....	19.541	46.984	27.443	[26.3]	[48.7]
Cu XIV.....	[23.82]	[52.39]	[28.57]	.....	[51.8]
Zn XV.....	[28.8]	[58.4]	[29.64]	.....	[55.0]

\* See also note to Table 5.

A discrepancy was noted in Mn X. On the basis of our curve,  $^3P_0$  should be at least 11.80 kK instead of 11.70 kK as listed in AEL. Closer examination of the original paper (Edlén 1937) confirms this correction. As is evidence from Table 8, the  $^3P_0$  level is by far the most uncertain of the configuration. The  $^3P_0$  and  $^3P_1$  levels approach each other for high  $Z$ , making the extrapolation especially difficult.

On the basis of Table 8 the previous identification of  $\lambda 3801$  is tentatively confirmed as  $^1D_2-^3P_1$  transition in Co XII; the agreement is not very good. The previously suggested identifications (Pecker 1958) of  $\lambda 4467$  and  $\lambda 4221$  are definitely excluded by our analysis.

## VI. CONCLUSIONS

The semiempirical methods employed here for the determination of the energy levels in certain ground-state configurations give more accurate results for the doublet configurations  $s^2p$  and  $s^2p^5$  than for the five-level configurations  $s^2p^2$  and  $s^2p^4$ . Identification of coronal lines on the basis of these computations must therefore be considered with corresponding caution. The Tables 1 through 8 indicate very roughly the estimated accuracy by the number of significant figures shown.

Even the agreement of an observed line with a very accurately computed level difference cannot be considered conclusive. A comparison of observed and computed intensities is extremely desirable, though beset, in general, by more uncertainties than the level comparison. Wherever possible, additional experimental and theoretical data should be brought to bear on each identification before it is considered established. "Wavelength

coincidences," as the results of the present paper may be called (they are not much more), are only a first step toward the classification of lines.

For convenience of reference, we summarize in Table 9 all 15 wavelength coincidences of coronal lines in the visible found and confirmed since Edlén's work. Except for Ca xv, these classifications are tentative in many cases and should in no way be considered as certain.

They also include one line each of the configurations  $3s^2 3p^3$ ,  $3s3p$ , and  $2s2p$ , respectively, which were not analyzed in the present work but are included here for completeness. These lines ( $\lambda\lambda$  3010, 5774, and 5974) agree with the corresponding extrapolated values within the latter's high accuracy. The association of  $\lambda$  4744 with the  $3s3p$  configuration (Ni xvii) as suggested at one time (Pecker 1958) was found to be inadmissible.

TABLE 9  
CORONAL EMISSION LINES: SUPPLEMENT TO EDLÉN (1942)

$\lambda$	Vac. ( $\text{kK}$ )	Transition	Config.	Ion	I.P.
3010.....	33.22	$^2P_{1/2} \rightarrow ^2D_{3/2}$	$3s^2 3p^3$	Fe XII	291
3170.....	31.54	$^1D_2 \rightarrow ^1P_1$	$3s^2 3p^2$	Cr XI	246
3685.....	27.13	$^1D_2 \rightarrow ^1P_2$	$3s^2 3p^2$	Mn XII	288
3800.8?.....	26.303	$^1D_2 \rightarrow ^1P_1$	$3s^2 3p^4$	Co XII	306
3998.....	25.01	$^1D_2 \rightarrow ^1P_2$	$3s^2 3p^2$	Cr XI	246
4256.4.....	23.488	$^2P_{3/2} \rightarrow ^2P_{1/2}$	$2s^2 2p^5$	K XI	504
4351.4.....	22.975	$^2P_{3/2} \rightarrow ^2P_{1/2}$	$3s^2 3p$	Co XV	412
4412.....	22.66	$^2P_{3/2} \rightarrow ^2P_{1/2}$	$2s^2 2p$	Ar XIV	687
5446.....	18.355	$^3P_2 \rightarrow ^3P_1$	$2s^2 2p^2$	Ca XV	820
5620.....	17.78	$^1D_2 \rightarrow ^1P_2$	$3s^2 3p^2$	Ca VII	109
5694.....	17.556	$^3P_1 \rightarrow ^3P_0$	$2s^2 2p^2$	Ca XV	820
5774.....	17.314	$^3P_2 \rightarrow ^3P_1$	$3s 3p$	Co XVI	444
5974.....	16.734	$^3P_2 \rightarrow ^3P_1$	$2s 2p$	Ar XV	754
6535.....	15.298	$^2P_{3/2} \rightarrow ^2P_{1/2}$	$3s^2 3p$	Mn XIII	315
6740.....	14.83	$^3P_2 \rightarrow ^3P_1$	$2s^2 2p^2$	K XIV	717
8475.7.....	11.799	$^3P_2 \rightarrow ^3P_1$	$2s^2 2p^2$	Ar XIII	620

In conclusion we wish to express our thanks to Professor Edlén for his criticism of a preliminary draft of this paper and for communication of unpublished results and to Mr. Ted Laetsch and to Mr. John Edie for their help in the numerical work.

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	I.P.
III	291
II	246
III	288
I	306
I	246
I	504
V	412
IV	687
V	820
III	109
V	820
VI	444
I	754
III	315
V	717
II	620

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