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## Slater-Condon Parameters for Atoms and Ions of the Second Transition Metal Series

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Received August 5, 1969

Slater-Condon parameters have been determined by least-squares methods, starting from experimental spectroscopic data, for the oxidation numbers 0, +1, and +2 of the elements of the second transition metal series. Particular restrictions have been introduced into the calculation with the aim of obtaining a regular trend of the evaluated parameters with respect to atomic number and oxidation states.

### Introduction

Because of the small number of experimental data existing on the atomic spectra of the elements of the second transition series, little work has been done to evaluate their Slater-Condon parameters (SCP).

Only Charkin and Dyatkina<sup>2</sup> have seriously faced the problem with particular care and accuracy by evaluating the parameters for three different oxidation states—0, +1, +2. However the values of these authors show a trend rather irregular with respect to both the atomic number and the oxidation state (Figure 1). Therefore, as has been explained in a previous paper,<sup>3</sup> such values cannot be used for the evaluation of the one-center quantities which are necessary in the semiempirical molecular orbital theory.

We have reevaluated the parameters of the second transition metal series for the oxidation numbers 0, +1, and +2 by imposing some conditions, as has already been done for the first series,<sup>3</sup> in such a way avoiding the above irregularities.

In the calculation for a given element and for a given oxidation state we have considered all the observed experimental terms, including those belonging to different configurations, *i.e.*,  $d^{n-2}s^2$ ,  $d^{n-1}s$ ,  $d^n$ ,  $d^{n-1}p$ ,  $d^{n-2}p^2$ , and  $d^{n-2}sp$ . The conditions introduced in the calculation were as follows.

(a) Only those terms for which we expected small configurational interaction have been considered.

(b) Terms having the same symmetry and configuration have been excluded.

(c) A linear dependence of the parameters  $F_k$  and  $G_k$  on the atomic number of the element has been assumed. In fact, just as for the first series, the parameters  $F_2(\text{dd})$  and  $G_3(\text{pd})$  evaluated theoretically from SCF atomic orbitals<sup>4</sup> vary in this way (Figure 2).

(d) The ratios  $F_2(\text{dd})/F_4(\text{dd})$  and  $G_1(\text{pd})/G_3(\text{pd})$  are assumed equal to those calculated with Slater atomic orbitals. In fact the values of such ratios differ only slightly from the corresponding ones obtained with SCF atomic orbitals. Moreover, these conditions

avoid the fact that the parameters  $F_4(\text{dd})$  and  $G_3(\text{pd})$ , much smaller than the others, are much more sensitive to the inaccuracy of the calculation scheme. In the calculations of Slater-Condon parameters with no such restrictions the values of  $F_4(\text{dd})$  and  $G_3(\text{pd})$  have a random distribution (sometimes assuming negative values).

### Outline of the Evaluation of the Parameters

The Slater theory of atomic spectra gives expressions for the energies of spectroscopic terms as functions of certain quantities  $F_k$  and  $G_k$ . Once the energies of the spectroscopic terms are known with good accuracy and in sufficient number, one can evaluate such quantities.

In this work, the expression

$$E(\chi, i) = W(\chi) + \sum_k (c_{ik}F_k + d_{ik}G_k) \quad (1)$$

has been used, where  $i$  denotes the term and  $\chi$  the configuration.  $W(\chi)$  is a quantity specific to the configuration. It contains all the quantities which appear with the same coefficients in all terms of the configuration. The energy values have been taken from Moore's tables<sup>5</sup> and introduced into eq 1 after a correction for the spin-orbit coupling as reported in ref 6.

The set of linear equations (eq 1) (one for each term) has been solved by means of the least-squares method and by imposing the above restrictive conditions. The values obtained are reported in Tables I-III.

Unfortunately, because of an insufficiency of spectroscopic data, in some cases, especially where  $5p$  orbitals are involved, it was not possible to evaluate all the parameters and some additional criteria have been introduced: (a) Since it is expected that the  $F_2(\text{pp})$  parameters of the second transition metal series are smaller than the corresponding ones of the first series, they have been assumed to be about 75-80% of those previously assumed by Hinze and Jaffé<sup>7</sup> for the first series. (b) The values of all the other param-

(1) (a) Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR. (b) Università di Padova. (c) Università di Parma.

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(6) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 28.

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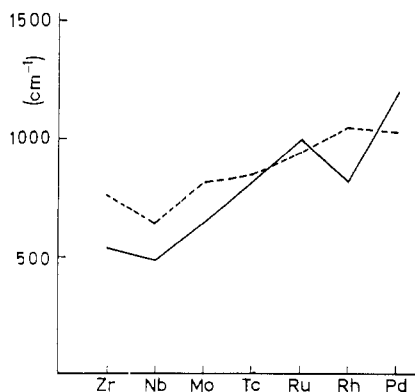


Figure 1.—Charkin and Dyatkina  $F_2(dd)$  parameter: —,  $q = 0$ ; - - -,  $q = +1$ .

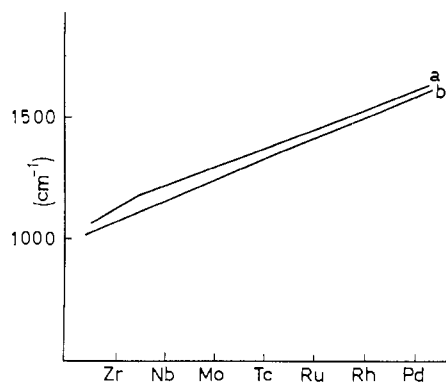


Figure 2.— $F_2(dd)$  parameter theoretically evaluated: a, Basch and Gray AO; b, Burns AO.

eters which could not be calculated on the basis of spectroscopic data (*e.g.*,  $G_1(sp)$  for many positive ions  $M^{II}$ ) have been evaluated by assuming a linear behavior with respect to the atomic number and a slope equal to that of the corresponding parameters of the first series. (c) Whenever the corresponding configurations are not reported in the tables by Moore, the values of  $W(d^{n-2}p^2)$  have been approximated as

$$W(d^{n-2}p^2) \simeq 2W(d^{n-2}sp) - W(d^{n-2}s^2)$$

(d) Finally the values of the parameters  $W(d^n)$ ,  $W(d^{n-1}s)$ , and  $W(d^{n-1}p)$  for  $Tc^{III}$  and  $W(d^n)$  for  $Tc^I$  have been interpolated on the basis of the trend of the values of the other metals.

### Discussion

Several comparisons have been made in order to test the goodness of the values of the parameters calculated in this work with regard to the accuracy in evaluating the spectroscopic term energies. With respect to the  $W(\chi)$  values plotted against the atomic number of the metals (Figure 3), our trend is analogous to that obtained by Charkin and Dyatkina.<sup>2</sup> The values of  $F_2(dd)$  increase regularly with oxidation number (Figure 4) and are smaller than those theoretically evaluated (Watson effect).<sup>8</sup> The values of the pa-

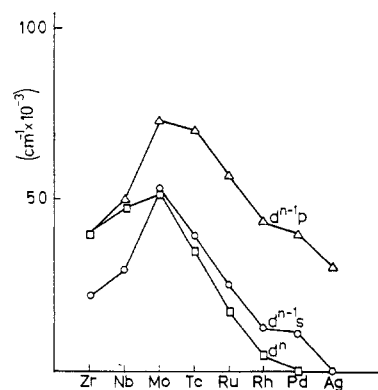


Figure 3.—Plot of neutral atom  $W(d^n)$ ,  $W(d^{n-1}s)$ , and  $W(d^{n-1}p)$  values evaluated in this work.

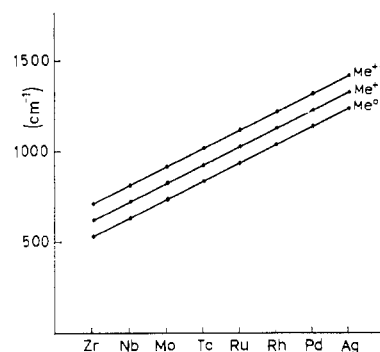


Figure 4.— $F_2(dd)$  parameter, evaluated in this work.

rameters  $F_2(dd)$  and  $F_4(dd)$  obtained in this work agree with those determined by Shadmi<sup>9</sup> for monovalent positive ions with configurations  $4d^n$  and  $4d^{n-1}5s$ . In Table IV a comparison concerning the Racah parameter  $B = F_2(dd) - 5F_4(dd)$  is reported together with the values given by the Jørgensen formula

$$B(4d) = 472 + 28q + 50Z_0 - \frac{500}{Z_0}$$

where  $q$  is the number of the valence electrons and  $Z_0$  the ion charge always increasing by a unit. In both the latter comparisons a good agreement is evident. Only for the neutral atom values of  $B$  is there some difference. We think that in this case the values given by the Jørgensen equation are particularly low.

By comparing  $B$  values obtained in this work with the corresponding ones of the first transition series (Table V), the former ones are seen to be smaller. This is due to the higher screening effect of the inner electrons on the  $4d$  electrons. On the basis of this fact Jørgensen and Schaeffer<sup>10</sup> have concluded that the ratio  $B(4d)/B(3d) = 0.66$  holds. Such a ratio varies within the range 0.66–0.74 if calculated with the values of this work and of our previous work<sup>3</sup> concerning the first transition series.

Finally we think that the values of the Slater-Condon parameters in this work are particularly well suited for evaluation of the semiempirical quantities

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(9) Y. Shadmi, *Bull. Res. Council Israel*, **F**, **9**, 141 (1961).

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TABLE I

SLATER-CONDON PARAMETERS (IN  $\text{cm}^{-1}$ ) FOR NEUTRAL ATOMS OF THE SECOND TRANSITION PERIOD

	Zr <sup>I</sup>	Nb <sup>I</sup>	Mo <sup>I</sup>	Tc <sup>I</sup>	Ru <sup>I</sup>	Rh <sup>I</sup>	Pd <sup>I</sup>	Ag <sup>I</sup>
$W(d^n)$	40,250	47,700	51,480	(35,000)	17,070	4,250	0	...
$W(d^{n-1}s)$	21,400	29,060	52,970	39,470	24,690	12,100	10,900	0
$W(d^{n-1}p)$	40,370	50,000	73,300	70,810	56,910	43,510	41,110	30,160
$W(d^{n-2}s^2)$	4,590	14,350	40,060	49,420	41,610	34,770	37,740	32,230
$W(d^{n-2}sp)$	29,800	41,340	70,540	82,380	86,560	(88,730)	84,640	72,890
$W(d^{n-2}p^2)$	55,670	(68,330)	(101,020)	(115,340)	(131,510)	(142,690)	(131,540)	(113,550)
$F_2(pp)$	(160)	(180)	(200)	(220)	(240)	(260)	(280)	(300)
$F_2(pd)$	400	425	450	475	500	525	550	575
$F_2(dd)$	530	635	740	845	950	1,055	1,160	1,265
$F_4(dd)$	39	47	55	63	71	79	87	95
$G_1(pd)$	260	286	312	338	364	390	416	442
$G_3(pd)$	10	11	12	13	14	15	16	17
$G_2(sd)$	1,650	1,700	1,750	1,800	1,850	1,900	1,950	2,000
$G_1(sp)$	1,900	2,000	2,100	2,200	2,300	2,400	2,500	2,600
$\Delta^a$	1,007	1,281	1,095	966	1,055	1,169	1,678	390

<sup>a</sup> Standard deviation (see Appendix).

TABLE II

SLATER-CONDON PARAMETERS (IN  $\text{cm}^{-1}$ ) FOR SINGLY CHARGED POSITIVE IONS

	Zr <sup>II</sup>	Nb <sup>II</sup>	Mo <sup>II</sup>	Tc <sup>II</sup>	Ru <sup>II</sup>	Rh <sup>II</sup>	Pd <sup>II</sup>	Ag <sup>II</sup>
$W(d^n)$	15,380	24,600	46,760	37,100	19,600	8,960	0	0
$W(d^{n-1}s)$	9,300	24,350	51,710	66,960	54,590	46,660	40,950	43,070
$W(d^{n-1}p)$	38,260	54,310	83,200	101,513	100,880	93,100	87,500	86,850
$W(d^{n-2}s^2)$	13,600	...	...	...	95,270	...	...	108,640
$W(d^{n-2}sp)$	45,660	...	...	...	...	...	...	...
$W(d^{n-2}p^2)$	(77,720)	...	...	...	...	...	...	...
$F_2(pd)$	430	445	480	505	530	555	580	605
$F_2(dd)$	620	725	830	935	1,040	1,145	1,250	1,355
$F_4(dd)$	46	54	62	70	78	86	94	102
$G_1(pd)$	350	376	402	428	454	480	506	532
$G_3(pd)$	13	14	15	16	17	18	19	20
$G_2(sd)$	1,850	1,900	1,950	2,000	2,050	2,100	2,150	2,200
$G_1(sp)$	2,200	(2,300)	(2,400)	(2,500)	(2,600)	(2,700)	(2,800)	(2,900)
$\Delta^a$	2,700	2,327	1,418	1,658	1,472	1,250	1,276	2,701

<sup>a</sup> Standard deviation (see Appendix).

TABLE III

SLATER-CONDON PARAMETERS (IN  $\text{cm}^{-1}$ ) FOR DOUBLY CHARGED POSITIVE IONS

	Zr <sup>III</sup>	Nb <sup>III</sup>	Mo <sup>III</sup>	Tc <sup>III</sup>	Ru <sup>III</sup>	Rh <sup>III</sup>	Pd <sup>III</sup>	Ag <sup>III</sup>
$W(d^n)$	6,860	16,620	32,360	47,000	39,800	25,380	11,010	0
$W(d^{n-1}s)$	22,120	36,530	58,910	82,000	104,910	99,760	88,600	82,400
$W(d^{n-1}p)$	58,970	75,480	101,630	126,000	149,970	157,730	147,500	140,160
$F_2(pd)$	460	485	510	535	560	585	610	635
$F_2(dd)$	710	815	920	1,025	1,130	1,235	1,340	1,445
$F_4(dd)$	53	61	69	77	85	93	101	109
$G_2(pd)$	440	466	492	518	544	570	596	622
$G_3(pd)$	16	17	18	19	20	21	22	23
$G_2(sd)$	2,050	2,100	2,150	2,200	2,250	2,300	2,350	2,400
$\Delta^a$	1,921	269	302	...	1,101	2,712	2,544	2,606

<sup>a</sup> Standard deviation (see Appendix).

TABLE IV

COMPARISON BETWEEN THE PARAMETER  $B$  EVALUATED BY JØRGENSEN (J) AND IN THIS WORK<sup>a</sup>

	M <sup>I</sup>		M <sup>II</sup>		M <sup>III</sup>	
	J	This work	J	This work	J	This work
Zr	134	335	406	390	511.3	445
Nb	162	400	434	455	539.3	510
Mo	190	465	462	520	567.3	575
Tc	218	530	490	585	595.3	640
Ru	246	595	518	650	623.3	705
Rh	274	660	546	715	651.3	770
Pd	302	725	574	780	679.3	835
Ag	330	790	602	845	707.3	900

<sup>a</sup> The values are in  $\text{cm}^{-1}$ .

TABLE V

COMPARISON BETWEEN  $B$  VALUES FOR THE FIRST AND SECOND TRANSITION SERIES ELEMENTS<sup>a</sup>

	Ti-Zr	V-Nb	Cr-Mo	Mn-Tc	Fe-Ru	Co-Rh	Ni-Pd	Cu-Ag
M <sup>I</sup> <sup>b</sup>	490 335	622.5 400	655 465	737.5 530	820 595	902.5 660	985 725	1,067.5 790
M <sup>II</sup> <sup>b</sup>	560 390	642.5 455	725 520	807.5 585	890 650	972.5 715	1,055 780	1,137.5 845
M <sup>III</sup> <sup>b</sup>	675 445	751.5 510	828 575	905 640	981.5 705	1,058.5 770	1,135 835	1,212 900

<sup>a</sup> The values are in  $\text{cm}^{-1}$ . <sup>b</sup> First row relative to I series; second row relative to II series.

TABLE VI

Atoms and ions	Configurations					
	$d^{n-2s^2}$	$d^{n-1s}$	$d^n$	$d^{n-1p}$	$d^{n-2p^2}$	$d^{n-2sp}$
Zr <sup>I</sup>	<sup>3</sup> F, <sup>1</sup> D, <sup>3</sup> P, <sup>1</sup> G	<sup>5</sup> F, <sup>3</sup> G, <sup>5</sup> P, <sup>3</sup> F, <sup>3</sup> P, <sup>1</sup> H	<sup>5</sup> D	<sup>5</sup> G, <sup>5</sup> F, <sup>3</sup> I	<sup>5</sup> G	<sup>5</sup> G, <sup>5</sup> F, <sup>5</sup> D, <sup>3</sup> G
Zr <sup>II</sup>	<sup>2</sup> D	<sup>4</sup> F, <sup>2</sup> F, <sup>2</sup> D, <sup>2</sup> G, <sup>2</sup> P, <sup>4</sup> P	<sup>2</sup> G, <sup>4</sup> P, <sup>2</sup> P, <sup>4</sup> F, <sup>2</sup> H, <sup>2</sup> F	<sup>4</sup> G, <sup>2</sup> F, <sup>2</sup> G, <sup>2</sup> S, <sup>4</sup> F, <sup>2</sup> H	...	<sup>4</sup> D, <sup>2</sup> D, <sup>2</sup> F, <sup>4</sup> P
Zr <sup>III</sup>	...	<sup>3</sup> D, <sup>1</sup> D	<sup>3</sup> F, <sup>1</sup> D, <sup>3</sup> P, <sup>1</sup> G	<sup>3</sup> D, <sup>1</sup> D, <sup>3</sup> F, <sup>1</sup> F, <sup>3</sup> P, <sup>1</sup> P	...	...
Nb <sup>I</sup>	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> H, <sup>2</sup> G, <sup>2</sup> P	<sup>6</sup> D, <sup>4</sup> G, <sup>4</sup> H, <sup>2</sup> H, <sup>2</sup> G	<sup>6</sup> S	<sup>6</sup> P, <sup>6</sup> F, <sup>6</sup> D, <sup>4</sup> I	...	<sup>6</sup> G, <sup>6</sup> F
Nb <sup>II</sup>	...	<sup>5</sup> F, <sup>5</sup> P, <sup>3</sup> G, <sup>3</sup> H, <sup>1</sup> F	<sup>5</sup> D, <sup>3</sup> G, <sup>3</sup> H, <sup>3</sup> D, <sup>1</sup> F, <sup>1</sup> I	<sup>5</sup> G, <sup>5</sup> F, <sup>5</sup> D, <sup>3</sup> I	...	...
Nb <sup>III</sup>	...	<sup>4</sup> F	<sup>4</sup> F	<sup>4</sup> F, <sup>4</sup> G	...	...
Mo <sup>I</sup>	<sup>5</sup> D, <sup>3</sup> H, <sup>3</sup> G	<sup>7</sup> S, <sup>5</sup> S, <sup>5</sup> G, <sup>3</sup> G, <sup>5</sup> P, <sup>5</sup> D, <sup>3</sup> P, <sup>3</sup> I, <sup>5</sup> F	<sup>5</sup> D	<sup>7</sup> P, <sup>5</sup> H	...	<sup>7</sup> D, <sup>7</sup> F, <sup>7</sup> P, <sup>5</sup> I
Mo <sup>II</sup>	...	<sup>6</sup> D, <sup>4</sup> G, <sup>4</sup> H, <sup>2</sup> I, <sup>2</sup> H	<sup>6</sup> S, <sup>4</sup> G, <sup>4</sup> F, <sup>4</sup> P, <sup>4</sup> D, <sup>2</sup> I, <sup>2</sup> H, <sup>2</sup> S	<sup>6</sup> F, <sup>6</sup> D, <sup>6</sup> P, <sup>4</sup> I	...	...
Mo <sup>III</sup>	...	<sup>5</sup> F	<sup>5</sup> D	<sup>5</sup> G, <sup>5</sup> F	...	...
Tc <sup>I</sup>	<sup>6</sup> S	<sup>6</sup> D, <sup>4</sup> G, <sup>4</sup> D	...	<sup>6</sup> F, <sup>6</sup> D, <sup>6</sup> P	...	<sup>6</sup> P
Tc <sup>II</sup>	...	<sup>7</sup> S, <sup>5</sup> G, <sup>5</sup> S	<sup>5</sup> D	<sup>7</sup> H, <sup>5</sup> H, <sup>5</sup> G	...	...
Tc <sup>III</sup>	...	...	...	...	...	...
Ru <sup>I</sup>	<sup>6</sup> D, <sup>3</sup> H, <sup>3</sup> G, <sup>3</sup> D	<sup>6</sup> F, <sup>5</sup> P, <sup>3</sup> H, <sup>3</sup> G, <sup>1</sup> H, <sup>1</sup> G	<sup>3</sup> F	<sup>5</sup> G, <sup>5</sup> F, <sup>3</sup> I, <sup>1</sup> I	...	<sup>7</sup> F, <sup>7</sup> D, <sup>7</sup> P
Ru <sup>II</sup>	<sup>6</sup> S	<sup>6</sup> D, <sup>4</sup> H, <sup>4</sup> G, <sup>2</sup> I, <sup>2</sup> H	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> H, <sup>2</sup> G, <sup>2</sup> F, <sup>2</sup> P	<sup>6</sup> F, <sup>6</sup> D, <sup>6</sup> P, <sup>4</sup> I	...	...
Ru <sup>III</sup>	...	<sup>7</sup> S, <sup>5</sup> S	<sup>5</sup> D	<sup>7</sup> P	...	...
Rh <sup>I</sup>	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> G	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> G, <sup>2</sup> F, <sup>2</sup> D, <sup>2</sup> P	<sup>2</sup> D	<sup>4</sup> G, <sup>4</sup> F	...	...
Rh <sup>II</sup>	...	<sup>5</sup> F, <sup>5</sup> P, <sup>3</sup> F	<sup>3</sup> F, <sup>3</sup> P	<sup>5</sup> G, <sup>5</sup> F, <sup>3</sup> G, <sup>3</sup> F	...	...
Rh <sup>III</sup>	...	<sup>6</sup> D, <sup>4</sup> H, <sup>4</sup> G, <sup>4</sup> D, <sup>2</sup> I, <sup>2</sup> H, <sup>2</sup> G	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> H, <sup>2</sup> G	<sup>6</sup> F, <sup>6</sup> D, <sup>6</sup> P, <sup>4</sup> I	...	...
Pd <sup>I</sup>	<sup>3</sup> F	<sup>3</sup> D, <sup>1</sup> D	<sup>3</sup> F, <sup>3</sup> D, <sup>3</sup> P, <sup>1</sup> F, <sup>1</sup> D, <sup>1</sup> P	...	...	<sup>1</sup> G, <sup>1</sup> F, <sup>1</sup> D
Pd <sup>II</sup>	...	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> G, <sup>2</sup> F, <sup>2</sup> D, <sup>2</sup> P	<sup>2</sup> D	<sup>4</sup> G, <sup>4</sup> F	...	...
Pd <sup>III</sup>	...	<sup>5</sup> F, <sup>5</sup> P, <sup>3</sup> G, <sup>3</sup> F, <sup>3</sup> P	<sup>3</sup> F, <sup>3</sup> P	<sup>5</sup> G, <sup>5</sup> F	...	...
Ag <sup>I</sup>	<sup>2</sup> D	<sup>2</sup> S	...	<sup>2</sup> P	...	<sup>4</sup> F, <sup>4</sup> D, <sup>4</sup> P
Ag <sup>II</sup>	<sup>3</sup> F, <sup>3</sup> P, <sup>1</sup> G, <sup>1</sup> D	<sup>3</sup> D, <sup>1</sup> D	<sup>1</sup> S	<sup>3</sup> F, <sup>3</sup> D, <sup>3</sup> P, <sup>1</sup> F	...	...
Ag <sup>III</sup>	...	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> G, <sup>2</sup> F, <sup>2</sup> D	<sup>2</sup> D	<sup>4</sup> G, <sup>4</sup> F	...	...

which are necessary in "semiempirical molecular orbital theory."<sup>11</sup> The values reported give the energies of the spectroscopic terms with good accuracy even when belonging to different configurations, and they exhibit a regular trend with respect to the atomic number.

**Acknowledgments.**—This work has been supported by CNR (Italian National Research Council) and by NATO Contract No. 403.

(11) L. Oleari, L. Di Sipio, and G. De Michelis, *Mol. Phys.*, **10**, 97 (1966).

### Appendix

The standard deviation  $\Delta$  is defined as

$$\Delta = \left| \frac{\sum_i d_i^2}{n-1} \right|^{1/2}$$

where  $d_i$  indicates the individual deviation between the  $i$ th energy term calculated by the SCP's and the experimental  $i$ th one, and  $n$  indicates the number of calculated energy terms. The configurations used for this calculation are reported in Table VI.