

## CNDO/S AND INDO/S CALCULATIONS ON SMALL ALUMINIUM COMPOUNDS

P. ČÁRSKY and J. MÁLEK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*

*Czechoslovak Academy of Sciences, 121 38 Prague 2 and*

*Institute of Physics,*

*Czechoslovak Academy of Sciences, 180 40 Prague 8*

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An extension of the CNDO/S method is reported which permits the accommodation of second-row elements and the use of the INDO level of approximation. A parameter set for aluminium is suggested. The method is applied to transition energies in AlH, AlH<sup>+</sup>, AlH<sub>2</sub>, AlF, AlCl, AlO, and AlS. Observed states are discussed and predictions are made for some unobserved states.

The stimulus for this study arose from our attempts to calculate the electronic structure of oxygen impurity centres originating in an AlN crystal. In our theoretical approach, an impurity centre is approximated by a finite cluster consisting of 8–26 atoms. The assumed model structure is treated by semiempirical all-valence electron methods. Formally, there is no difference between a treatment of this kind and common semiempirical calculations on ordinary molecules. Since we are interested in transition energies, it was our objective to identify a method and parameter set which will give a good account of transition energies in small aluminium molecules. In our opinion, CNDO/S and INDO/S are the methods most suited for this purpose. With regard to the parameter set for aluminium, we varied the one-centre repulsion integral and the bonding parameter in reasonable ranges to obtain the best agreement of computed transition energies with the energies of unambiguously established non-Rydberg states in AlH, AlH<sup>+</sup>, AlF, and AlO. The method and parameter set were then applied to the additional molecules of AlH<sub>2</sub>, AlCl, and AlS.

### CALCULATIONS

The starting point in developing the computational scheme was the CNDO/S method of Del Bene and Jaffé<sup>1</sup>. Its extension to the second row elements was made in the same way as reported by Pfister-Guillouzo and collaborators<sup>2</sup> for sulphur derivatives of pyranone. Thus, only the *sp* basis set was used. The  $1/2(I_s + A_s)$  and  $1/2(I_p + A_p)$  terms and the effective Slater exponents were taken from the original CNDO/2 parameter set<sup>3</sup>. The resonance integrals were calculated

by the formula

$$H_{\mu\nu} = \frac{1}{2} \kappa K (\beta_A^0 + \beta_B^0) S_{\mu\nu},$$

which is the original expression of the CNDO/S method multiplied by the constant  $K$ . The additional constant  $K$  is unity unless A or/and B are second row elements, in which case it is put equal to 0.75. The two-centre repulsion integrals were evaluated by means of the approximation of Mataga and Nishimoto.

In our previous treatment<sup>4</sup> of small radicals we found that CNDO/S may give a very poor state ordering owing to an inherent shortcoming of the CNDO approximation — the neglect of one-centre integrals. In many cases, several states correspond to one electronic configuration and the respective calculated energies differ by terms containing integrals such as *e.g.*,  $K_{\sigma\pi}$  and  $K_{\pi\pi}$ . Since the latter vanish in the CNDO approximation, the observed energy splittings are not amenable to any CNDO treatment. Therefore, we employed a hybrid method which combines the original INDO and CNDO/S methods. In this approach, subsequently denoted as INDO/S, the one-centre  $J_{pp}$ ,  $J_{pp'}$ ,  $K_{sp}$ , and  $K_{pp'}$  integrals are evaluated as usual in standard INDO calculations. The remaining integrals are evaluated using the approximations involved in the CNDO/S method.

We employed the experimental geometries of ground states reported in the literature: AlH (ref.<sup>5</sup>); AlH<sup>+</sup> (ref.<sup>5</sup>); AlH<sub>2</sub> (ref.<sup>6</sup>); AlF (ref.<sup>7</sup>); AlCl (ref.<sup>5</sup>); AlO (ref.<sup>5</sup>); and AlS (ref.<sup>8</sup>). The species AlH<sup>+</sup>, AlH<sub>2</sub>, AlO, and AlS have nondegenerate doublet ground states and were treated by the half-electron method. The configuration interaction treatment was based upon the virtual orbital approximation and included all types of excited configurations which correspond formally to one-electron spinless promotions among several highest occupied orbitals, the open shell (with radicals, for details see ref.<sup>9</sup>), and several lowest virtual orbitals.

With the exception of aluminium, all CNDO/S parameters were available in the literature. From the trends in CNDO/2 and CNDO/S parameters, we assumed that  $-\beta_{Al}^0$  and one-centre  $\gamma_{Al}$  should lie in the range 2–5 eV and 2–7 eV, respectively. The two parameters were varied within this range with a grid of 1.0 and their effect on the transition energies was examined. As standards we selected the  $A^1\Pi$  and  $C^1\Sigma^+$  states of AlH, the  $A^2\Pi$  state of AlH<sup>+</sup>, the  $a^3\Pi$ ,  $A^1\Pi$ ,  $b^3\Sigma^+$ , and  $B^1\Sigma^+$  states of AlF, and the  $A^2\Pi$ ,  $B^2\Sigma^+$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Delta$ , and  $F^2\Sigma^+$  states of AlO. The best overall agreement appears to be obtained for  $\beta_{Al} = -4.0$  eV and  $\gamma_{Al} = 4.0$  eV. The complete INDO/S parameter set used is listed in Table I.

## RESULTS AND DISCUSSION

Results are summarized in Tables II–V. To interpret the entries properly, three restrictive features of the theoretical approach should be kept in mind. First, the use of the minimal basis set of valence shell atomic orbitals allows treatment of only non-Rydberg states. Second, the predicted transition energies are not the state energies,  $T_0$ . Instead, they mimic the vertical transition energies from the ground state. Third, some low lying non-Rydberg states may be doubly excited states, which are not accounted for by our calculations.

We now comment in detail on individual molecules. Table II presents data for AlH, AlH<sup>+</sup>, and AlH<sub>2</sub>. At the first glance it may appear that the CNDO/S results

for AlH are superior to those from INDO/S. CNDO/S gives a very good account of the observed states  $A^1\Pi$ ,  $C^1\Sigma^+$ , and  $E^1\Pi$ , but it disregards the singlet-triplet splittings in the  $\Pi$  states. Thus, INDO/S provides a more realistic overall picture, though the INDO/S transition energies for the  $A$  and  $E$  singlet states are overestimated. The other observed<sup>5</sup> states which are not presented in Table II are  $b^3\Sigma^-$ ,  $B^1\Sigma^-$ , and  $D^1\Sigma^+$ . The most probable assignment for the  $b^3\Sigma^-$  state is the doubly excited configuration  $KL 4\sigma^2 2\pi^2$ , which is not amenable to our theoretical treatment. For the  $B^1\Sigma^-$  and  $D^1\Sigma^+$  states, we have no explanation. For  $AlH^+$ , only one excited state is known. The respective transition energy,  $A^2\Pi \leftarrow X^2\Sigma^+$ , is reproduced well by both CNDO/S and INDO/S. Also for  $AlH_2$  only one excited state is known. The calculations support the assignment of experimentalists<sup>6</sup> of the  $A^2B_1$  state. The calculated energies for the  $A^2B_1 \leftarrow X^2A_1$  transition are overestimated. In this case, however, it does not indicate a defect in the theoretical approach, since  $AlH_2$  in the  $A^2B_1$  state is linear<sup>6</sup> and the vertical transition energy from the bent  $X^2A_1$  state must be higher than  $T_0$ . It is interesting to compare the present results for  $AlH^+$  and  $AlH_2$  with our previous CNDO/S results<sup>10,17</sup> on  $BH^+$  and  $BH_2$ . The two boron radicals also have the low lying excited states,  $A^2\Pi$  and  $A^2B_1(\Pi)$ , respectively. A quite different picture was found for higher non-Rydberg states in the B and Al radicals. In the former, the second lowest singlet non-Rydberg states are predicted to lie in the vacuum ultraviolet region, whereas in the latter, several states are predicted to fall in the visible and near ultraviolet region. This may be attributed to different features of the valence shells in B and Al atoms. In Al the  $3s-3p$  energy gap is much lower than the  $2s-2p$  energy gap in B. Experimentally, higher non-Rydberg

TABLE I  
The Parameter Set<sup>a</sup>

Atom	$-\beta_A^0$	$\gamma_A$	$G^1$	$F^2$	Source
H	12	12.85	—	—	<i>b</i>
C	17	11.11	7.285	4.727	<i>b, c</i>
N	26	12.01	9.416	5.961	<i>b, c</i>
O	45	13.00	11.816	7.249	<i>b, c</i>
F	55	13.9	14.485	8.593	<i>c, d</i>
Al	4	4.0	3.359	1.602	<i>e, f</i>
S	15	8.96	3.075	4.537	<i>f, g</i>
Cl	15	11.30	2.864	5.277	<i>h, i</i>

<sup>a</sup> All entries are in eV; <sup>b</sup>  $\beta_A^0$  and  $\gamma_A$  taken from ref.<sup>1</sup>; <sup>c</sup>  $G^1$  and  $F^2$  taken from ref.<sup>3</sup>; <sup>d</sup>  $\beta_A^0$  and  $\gamma_A$  taken from ref.<sup>10</sup>; <sup>e</sup>  $\beta_A^0$  and  $\gamma_A$  adjusted (see text); <sup>f</sup>  $G^1$  and  $F^2$  taken from ref.<sup>11</sup>; <sup>g</sup>  $\beta_A^0$  and  $\gamma_A$  taken from ref.<sup>2</sup>; <sup>h</sup>  $\beta_A^0$  and  $\gamma_A$  taken from ref.<sup>12</sup>; <sup>i</sup>  $G^1$  and  $F^2$  taken from ref.<sup>21</sup>.

states in  $\text{BH}^+$ ,  $\text{BH}_2$ ,  $\text{AlH}^+$ , and  $\text{AlH}_2$  are not known. Our calculations suggest that they would be difficult to detect for  $\text{BH}^+$  and  $\text{BH}_2$  but that there is a chance for finding some higher non-Rydberg states for  $\text{AlH}_2$  and possibly also for  $\text{AlH}^+$ .

In Table III, we present results for  $\text{AlF}$  and  $\text{AlCl}$ . Our calculations give a reasonable account of the observed non-Rydberg states, except for the typical overestimation of transition energies for high lying states. For the region above the  $b^3\Sigma^+$  state

TABLE II  
Transition Energies (in  $10^{-3} \text{ cm}^{-1}$ ) in  $\text{AlH}$ ,  $\text{AlH}^+$ , and  $\text{AlH}_2$

	State	Main configuration <sup>a</sup>	CNDO/S	INDO/S	Observed <sup>b</sup>
AlH	$X^1\Sigma^+$	$4\sigma^2 5\sigma^2$	0	0	0
	$a^3\Pi$	$4\sigma^2 5\sigma 2\pi$	23.7	11.0	
	$A^1\Pi$	$4\sigma^2 5\sigma 2\pi$	23.7	25.6	23.8
	$^3\Sigma^+$	$4\sigma^2 5\sigma 6\sigma$	34.9	26.0	
	$C^1\Sigma^+$	$4\sigma^2 5\sigma 6\sigma$	46.7	41.4	44.7
	$^3\Pi$	$4\sigma 5\sigma^2 2\pi$	56.2	55.1	
	$E^1\Pi$	$4\sigma 5\sigma^2 2\pi$	56.2	65.2	53.4
AlH <sup>+</sup>	$X^2\Sigma^+$	$4\sigma^2 5\sigma$	0	0	0
	$A^2\Pi$	$4\sigma^2 2\pi$	27.8	31.1	27.6
	$^2\Sigma^+$	$4\sigma 5\sigma^2$	30.1	32.8	
	$^2\Sigma^+$	$4\sigma^2 6\sigma$	43.8	50.0	
	$^4\Pi$	$4\sigma 5\sigma 2\pi$	57.8	54.3	
	$^4\Sigma^+$	$4\sigma 5\sigma 6\sigma$	63.2	60.5	
		$^2\Pi$	$4\sigma 5\sigma 2\pi$	57.8	68.1
AlH <sub>2</sub>	$X^2A_1$	$4a_1^2 2b_2^2 5a_1$	0	0	0
	$A^2B_1$	$4a_1^2 2b_2^2 2b_1$	17.6	20.5	<15.2 <sup>c</sup>
	$^2B_2$	$4a_1^2 2b_2 5a_1^2$	24.6	28.2	
	$^2A_1$	$4a_1^2 2b_2^2 6a_1$	27.6	31.2	
	$^4A_2$	$4a_1^2 2b_2 5a_1 2b_1$	43.0	39.8	
	$^2B_2$	$4a_1^2 2b_2^2 3b_2$	38.5	41.8	
	$^4B_2$	$4a_1^2 2b_2 5a_1 6a_1$	47.8	45.8	
	$^2A_2$	$4a_1^2 2b_2 5a_1 2b_1$	43.0	46.1	
	$^2A_1$	$4a_1 2b_2^2 5a_1^2$	48.2	52.1	
	$^4A_1$	$4a_1^2 2b_2 5a_1 3b_2$	55.2	52.5	
	$^2A_2$	$4a_1^2 2b_2 5a_1 2b_1$	54.7	58.4	
	$^2B_2$	$4a_1^2 2b_2 5a_1 6a_1$	60.3	62.9	
	$^4B_1$	$4a_1 2b_2^2 5a_1 2b_1$	65.7	63.0	

<sup>a</sup> Inner shells accounted for; <sup>b</sup>  $T_e$  from refs.<sup>5,6</sup>; <sup>c</sup> The head of the band is at  $6584 \cdot 10^{-10} \text{ m}$  and the absorption expands to longer wavelengths.

and below the ionization limit, our calculations predict a series of non-Rydberg states that arise from the  $2\pi^33\pi$  and  $6\sigma3\pi$  configurations. However So and Richards<sup>13</sup> conclude from the *ab initio* Hartree-Fock calculations that all states from the  $2\pi^33\pi$

TABLE III

Transition Energies (in  $10^{-3} \text{ cm}^{-1}$ ) in AlF and AlCl

	State	Main configuration <sup>a</sup>	CNDO/S	INDO/S	<i>ab initio</i> <sup>b</sup>	Observed <sup>c</sup>	
AlF	$X^1\Sigma^+$	$6\sigma^22\pi^47\sigma^2$	0	0	0	0	
	$a^3\Pi$	$6\sigma^22\pi^47\sigma3\pi$	31.7	25.6	20.2	27.2	
	$A^1\Pi$	$6\sigma^22\pi^47\sigma3\pi$	31.7	39.5	42.8	43.9	
	$b^3\Sigma^+$	$6\sigma^22\pi^47\sigma8\sigma$	62.0	54.2	45.0	44.8	
	$^3\Sigma^+$	$6\sigma^22\pi^37\sigma^23\pi$	65.0	60.0			
	$^3\Delta$	$6\sigma^22\pi^37\sigma^23\pi$	65.0	60.8			
	$^3\Sigma^-$	$6\sigma^22\pi^37\sigma^23\pi$	65.0	61.6			
	$^1\Sigma^-$	$6\sigma^22\pi^37\sigma^23\pi$	65.0	61.6			
	$^1\Delta$	$6\sigma^22\pi^37\sigma^23\pi$	65.0	62.3			
	$B^1\Sigma^+$	$6\sigma^22\pi^47\sigma8\sigma$	62.4	64.4		54.2	
	$^3\Pi$	$6\sigma2\pi^47\sigma^23\pi$	70.7	66.6			
	$^1\Pi$	$6\sigma2\pi^47\sigma^23\pi$	70.7	69.6			
	$^1\Sigma^+$	$6\sigma^22\pi^37\sigma^23\pi$	73.1	72.3			
	AlCl	$X^1\Sigma^+$	$8\sigma^23\pi^49\sigma^2$	0	0		0
		$^3\Pi$	$8\sigma^23\pi^49\sigma4\pi$	27.4	23.4		
$^3\Sigma^+$		$8\sigma^23\pi^49\sigma10\sigma$	34.7	32.1			
$A^1\Pi$		$8\sigma^23\pi^49\sigma4\pi$	27.4	32.2		38.2	
$^3\Sigma^+$		$8\sigma^23\pi^39\sigma^24\pi$	42.0	39.2			
$^3\Delta$		$8\sigma^23\pi^39\sigma^24\pi$	42.0	39.5			
$^1\Sigma^+$		$\left\{ \begin{array}{l} 8\sigma^23\pi^39\sigma^24\pi (67\%) \\ 8\sigma^23\pi^49\sigma10\sigma (33\%) \end{array} \right\}^d$	38.6	39.7			
$^3\Sigma^-$		$8\sigma^23\pi^39\sigma^24\pi$	42.0	39.8			
$^1\Sigma^-$		$8\sigma^23\pi^39\sigma^24\pi$	42.0	39.8			
$^1\Delta$		$8\sigma^23\pi^39\sigma^24\pi$	42.0	40.1			
$^3\Pi$		$8\sigma^23\pi^39\sigma^210\sigma$	43.1	42.1			
$^1\Pi$		$8\sigma^23\pi^39\sigma^210\sigma$	43.1	44.1			
$^3\Pi$		$8\sigma3\pi^49\sigma^24\pi$	49.5	48.5			
$^1\Sigma^+$		$\left\{ \begin{array}{l} 8\sigma^23\pi^49\sigma10\sigma (67\%) \\ 8\sigma^23\pi^39\sigma^24\pi (33\%) \end{array} \right\}^d$	47.9	51.0			
$^3\Sigma^+$		$8\sigma3\pi^49\sigma^210\sigma$	56.6	54.0			
$^1\Pi$		$8\sigma3\pi^49\sigma^24\pi$	49.5	57.2			
$^1\Sigma^+$		$8\sigma3\pi^49\sigma^210\sigma$	66.4	69.6			

<sup>a</sup> Inner shells accounted for; <sup>b</sup>  $T_e$  taken from Hartree-Fock calculations<sup>13</sup>; <sup>c</sup>  $T_e$  taken from ref.<sup>14</sup> for AlF and from ref.<sup>5</sup> for AlCl; <sup>d</sup> Weights from INDO/S calculations.

configuration are repulsive and therefore cannot be observed. So and Richards also give a qualitative explanation for this finding. The electron population analyses indicate that AlF in the  $2\pi^33\pi$  configuration has the energetically unfavourable structure  $\text{Al}^{\delta-}\text{F}^{\delta+}$ . Our calculations also suggest that the  $6\sigma \rightarrow 3\pi$  excitation gives rise to the  $\text{Al}^{\delta-}\text{F}^{\delta+}$  structure and hence the predicted  ${}^3\Pi$  and  ${}^1\Pi$  states should also be repulsive. With regard to the states observed<sup>14</sup> above the  $B^1\Sigma^+$  state, So and Richards<sup>13</sup> identified the observed  $D^1\Delta$  and  ${}^3\Delta$  states with the Rydberg  $7\sigma1\delta$  states. Experimentalists<sup>14</sup> also favour the assignments to Rydberg states of all states observed above the  $B^1\Sigma^+$  state. For AlCl only one excited state,  $A^1\Pi$ , is known<sup>5</sup>. The red shift observed on going from AlF to AlCl is reproduced well by INDO/S. Compared with AlF, the predicted  $S-T$  splitting for this  $\Pi$  state of AlCl is smaller and hence the  $a^3\Pi$  state of AlCl may be expected to lie at about  $26000\text{ cm}^{-1}$ . A prediction for the  $B^1\Sigma^+$  state is difficult because of considerable mixing of the bound  $9\sigma10\sigma$  configuration with the repulsive  $3\pi^34\pi$  configuration. New types of states, not found with AlF below the ionization limit, are due to the  $3\pi^310\sigma$  and  $8\sigma10\sigma$  configurations. The former however gives rise to a structure  $\text{Al}^{\delta-}\text{Cl}^{\delta+}$  and hence the  ${}^1,{}^3\Pi3\pi^310\sigma$  states are most likely repulsive. With the  $8\sigma10\sigma$  configuration, the charge transfer from Cl to Al is smaller and we are not able to decide whether the respective  ${}^3\Sigma^+$  and  ${}^1\Sigma^+$  states are repulsive or bound.

For AlO the following states are known:  $X^2\Sigma^+$ ,  $A^2\Pi$ ,  $B^2\Sigma^+$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Delta$ , and  $F^2\Sigma^+$ . In Table IV, we compare the transition energies given by CNDO/S, INDO/S and *ab initio* calculations<sup>15</sup>. The best agreement with experiment is obtained with INDO/S transition energies. CNDO/S is poor in this instance. Note that it yields a single value of  $47900\text{ cm}^{-1}$  for all states which arise from the  $KKL5\sigma^22\pi^36\sigma^27\sigma3\pi$  configuration. In the *ab initio* transition energies calculated by Schamps<sup>15</sup> configuration mixing was disregarded. However, we have found large mixing between the  ${}^2\Sigma^+KKL5\sigma^22\pi^36\sigma^27\sigma3\pi$  and  ${}^2\Sigma^+KKL5\sigma^22\pi^46\sigma^28\sigma$  configurations, for example. This neglect of configuration mixing is the probable reason why the  $D^2\Sigma^+ - F^2\Sigma^+$  separation given by Schamps is greatly overestimated. The second feature of these *ab initio* calculations, which is useful for judging the semiempirical results, is the predicted incorrect ordering of the  $X^2\Sigma^+$  and  $A^2\Pi$  states. A failure of this type was also reported for the CNDO/S (ref.<sup>17</sup>) and *ab initio*<sup>18,19</sup> calculations on  $\text{N}_2^+$  and was assigned to correlation effects. Schamps attempted to introduce correlation effects in a semiempirical way. In his opinion, the estimated correlation energy difference for the  $A-X$  transition is underestimated, but the trend is correct. With CNDO/S and INDO/S, the situation is more complex, since these methods do not provide  $T_e$  but only mimic vertical transition energies. From the shapes of the potential curves<sup>15,20</sup> for the  $X^2\Sigma^+$  and  $A^2\Pi$  states of  $\text{N}_2^+$  and AlO, it is seen that the vertical  $A^2\Pi \leftarrow X^2\Sigma^+$  transition energy depends strongly on the internuclear distance and becomes negative at distances slightly longer than the equilibrium bond length in the ground state. For AlS, only one excited state,  $A^2\Sigma^+$ , is known<sup>8</sup>. The results

of our calculations are summarized in Table V. The observed  $A^2\Sigma^+ - X^2\Sigma^+$  transition energy is reproduced well. However, the calculations suggest that the upper state should be called the  $B^2\Sigma^+$  state, in full analogy to AIO. With regard to the incorrect ordering of the two lowest states of AIS, the same arguments hold as in the discussion for AIO.

TABLE IV  
Transition Energies (in  $10^{-3} \text{ cm}^{-1}$ ) in AIO

State	Main configuration <sup>a</sup>	CNDO/S	INDO/S	<i>ab initio</i>		Observed <sup>d</sup>
				SCF <sup>b</sup>	correlated <sup>b,c</sup>	
$X^2\Sigma^+$	$2\pi^4 6\sigma^2 7\sigma$	0	0	0	0	0
$A^2\Pi$	$2\pi^3 6\sigma^2 7\sigma^2$	- 1.0	0.1	- 6.9	- 3.6	5.4
$B^2\Sigma^+$	$2\pi^4 6\sigma 7\sigma^2$	33.1	30.2	9.2	12.6	20.7
$^4\Sigma^+$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	33.0	11.2	21.3	
$C^2\Pi$	$2\pi^4 6\sigma^2 3\pi$	26.8	34.0	39.1	39.0	33.1
$^4\Delta$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	34.1	12.6	22.7	
$^4\Pi$	$2\pi^4 6\sigma 7\sigma 3\pi$	40.8	34.4	24.7	34.8	
$^4\Sigma^-$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	35.1	14.0	24.1	
$^4\Pi$	$2\pi^3 6\sigma^2 7\sigma 8\sigma$	42.2	36.3	38.8	48.9	
$^2\Sigma^-$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	37.8	15.9	26.0	
$^2\Delta$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	38.7	15.6	25.7	
$D^2\Sigma^+$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	38.8	40.8	23.4	33.5	40.3
$E^2\Delta$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	43.9	40.0	50.1	45.3 <sup>e</sup>
$F^2\Sigma^+$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	44.0	43.9	54.0	47.2 <sup>e,f</sup>
$^4\Sigma^+$	$2\pi^4 6\sigma 7\sigma 8\sigma$	52.4	44.4	49.6	59.7	
$^2\Sigma^-$	$2\pi^3 6\sigma^2 7\sigma 3\pi$	47.9	44.8	41.0	51.1	
$^2\Pi$	$2\pi^3 6\sigma^2 7\sigma 8\sigma$	42.2	46.3	43.3	53.4	
$^2\Pi$	$2\pi^4 6\sigma 7\sigma 3\pi$	40.8	48.3	38.0	48.0	
$^2\Sigma^+$	$\left\{ \begin{array}{l} 2\pi^4 6\sigma 7\sigma 8\sigma \\ 2\pi^4 6\sigma^2 8\sigma \end{array} \right\}$	55.9	59.6			
$^2\Pi$	$2\pi^3 6\sigma^2 7\sigma 8\sigma$	74.7	64.2	54.7	64.8	
$^2\Pi$	$2\pi^4 6\sigma 7\sigma 3\pi$	52.8	66.3	60.1	70.2	
$^2\Sigma^+$	$2\pi^4 6\sigma 7\sigma 8\sigma$	69.8	74.0	62.5	72.6	
$^2\Sigma^+$	$2\pi^4 6\sigma 7\sigma 8\sigma$	80.2	81.2	73.8	83.9	

<sup>a</sup> The configurations refer to the INDO/S and *ab initio* calculations; in CNDO/S wave functions for some  $^2\Sigma^+$  states, the main configurations are different; inner shells accounted for. <sup>b</sup>  $T_e$  from ref.<sup>15</sup>. <sup>c</sup> SCF results corrected semiempirically for correlation energies; ref.<sup>15</sup>. <sup>d</sup>  $T_e$  values, for citations see ref.<sup>15</sup>. <sup>e</sup> Value of  $T_0$  instead of  $T_e$ . <sup>f</sup> ref.<sup>16</sup>.

TABLE V  
Transition Energies (in  $10^{-3} \text{ cm}^{-1}$ ) in AIS

State	Main configuration <sup>a</sup>	CNDO/S	INDO/S
$X^2\Sigma^+$	$8\sigma^2 3\pi^4 9\sigma$	0	0
$^2\Pi$	$8\sigma^2 3\pi^3 9\sigma^2$	- 2.3	- 1.0
" $A^2\Sigma^+$	$8\sigma 3\pi^4 9\sigma^2$	26.7	24.9 (23.4) <sup>b</sup>
$^4\Sigma^+$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	25.1
$^2\Pi$	$8\sigma^2 3\pi^4 4\pi$	20.5	25.5
$^4\Delta$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	26.0
$^4\Sigma^-$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	26.8
$^2\Sigma^-$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	29.0
$^2\Delta$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	29.9
$^4\Pi$	$8\sigma^2 3\pi^3 9\sigma 10\sigma$	35.2	31.7
$^2\Sigma^+$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	32.4
$^2\Delta$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	32.6
$^2\Sigma^-$	$8\sigma^2 3\pi^3 9\sigma 4\pi$	33.5	33.5
$^2\Sigma^+$	$\left\{ \begin{array}{l} 8\sigma^2 3\pi^3 9\sigma 4\pi \\ 8\sigma^2 3\pi^4 10\sigma \end{array} \right\}$	32.8	34.2
$^4\Pi$	$8\sigma 3\pi^4 9\sigma 4\pi$	40.9	36.9
$^2\Pi$	$8\sigma^2 3\pi^3 9\sigma 10\sigma$	35.2	37.4
$^2\Pi$	$8\sigma 3\pi^4 9\sigma 4\pi$	40.9	48.9
$^4\Sigma^+$	$8\sigma 3\pi^4 9\sigma 10\sigma$	55.6	49.5
$^2\Sigma^+$	$8\sigma^2 3\pi^4 10\sigma$	49.5	52.8
$^2\Pi$	$8\sigma^2 3\pi^3 9\sigma 10\sigma$	57.4	53.6
$^2\Pi$	$8\sigma 3\pi^4 9\sigma 4\pi$	50.7	60.0
$^2\Sigma^+$	$8\sigma 3\pi^4 9\sigma 10\sigma$	67.5	71.2
$^2\Sigma^+$	$8\sigma 3\pi^4 9\sigma 10\sigma$	74.3	76.4

<sup>a</sup> Inner shells accounted for. <sup>b</sup> Observed  $T_e$ ; ref.<sup>8</sup>.

## CONCLUSION

INDO/S gives reasonable results for the known non-Rydberg states of the aluminium compounds studied. CNDO/S is applicable only to cases, where the retention of one-centre integrals is not crucial in accounting for singlet-triplet and doublet-quartet splittings (*e.g.* in the  $A^2\Pi$  state in  $\text{AlH}^+$ ). Unsatisfactory points in the results are the overestimated energies of high lying states and the underestimated energies of the lowest  $^2\Pi$  states in  $\text{AlO}$  and  $\text{AIS}$ . However, this may be attributed to shortcomings of the whole theoretical approach rather than the suggested parameter set of aluminium. We believe that very little would be gained by a more thorough optimization of the  $\text{Al}$  parameter set.



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