

## INDO/S CALCULATIONS ON SIMPLE SILICON COMPOUNDS AND SOME SILICON ORGANIC MOLECULES

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Received May 11th, 1981

The INDO/S method has been extended to silicon-containing systems. On the basis of test calculations for SiH<sub>2</sub>, SiHCl, SiF<sub>2</sub>, SiH, SiN, SiO<sup>+</sup>, SiF and SiO we suggest the following semiempirical parameters:  $\beta_{\text{Si}}^0 = -4$  eV and  $\gamma_{\text{Si}} = 5.5$  eV. Additional molecules treated are SiH<sup>+</sup>, SiS, SiCC, SiCSi, SiCl, SiCl<sub>2</sub>, SiO<sub>2</sub>, HNSi, and vinyl- and phenylsilane. Comparison is made with the corresponding carbon species CH<sub>2</sub>, CF<sub>2</sub>, CCl<sub>2</sub>, CH<sup>+</sup>, CO, CS, CH, CF, CN, CO<sup>+</sup>, CO<sub>2</sub>, C<sub>3</sub> and benzene. The method with the suggested Si parameter set is employed for the investigation of the electronic structure and electronic spectra of unstable molecules of silaethylene, silylmethylene, methylsilylene, disilylene, silylsilylene and silabenzene.

Study of electronic spectra of Si-containing compounds is topical for several reasons. Short-lived low-valent silicon compounds play an important role in reactions at high temperatures and in the interstellar space<sup>1</sup>. For example, SiH has been detected in the solar photosphere and the absorption of some N-type stars in the blue-green region was proved<sup>1</sup> to be due to SiCC. Also a possible existence of SiO<sub>2</sub> in the interstellar space is the subject of interest<sup>2</sup>, though SiO<sub>2</sub> is not known to exist under normal conditions. The problem met in the organo-silicon chemistry is the absence of stable compounds with multiple bonds of the  $p_{\pi}-p_{\pi}$ -type, in spite of considerable effort to synthesize them (for a recent review see ref.<sup>3</sup>). Particularly, the prototype compounds silaethylene and silabenzene were the subject of numerous experimental<sup>4,43,44</sup> and theoretical studies (see papers<sup>5-8</sup> and reference therein). As to silicon-containing solids, silica, silicates and aluminosilicates belong to the most common materials on the earth (actually Si is the second most common element after oxygen) and a lot of spectroscopic and experimental material about their electronic structure has been accumulated (see for example ref.<sup>9</sup>). Moreover materials as SiO<sub>2</sub> and Si became very popular in electronics<sup>10</sup> in the last years. Among the stable organo-silicon compounds we only note the siloxanes because of their wide technical application as polymeric silicones<sup>11</sup>.

Difficulties in obtaining experimental information for short-lived low-valent silicon-containing species and silicon-organic intermediates and also a need for

theoretical interpretation of electronic and photoelectron spectra of stable inorganic and organic compounds resulted in a strong demand for theoretical models in this field. Quantum-chemical all-valence electron methods involving spectroscopic parameters are particularly suitable for this purpose because they provide a link between accurate *ab initio* calculations, which are only feasible for small systems, and  $\pi$ -electron methods which are rather limited in their applicability. All-valence electron methods can be applied without technical difficulties to systems with approximately up to 150 atomic orbitals and 50 atoms (40 heavy atoms). This means that rather large conjugated molecules (silabenzene, phenylsilane) and molecular clusters modelling  $\text{SiO}_2$ , such as  $\text{Si}_6\text{O}_{18}\text{H}_{12}$  or  $\text{Si}(\text{OSi}(\text{OH})_3)_4$ , can be easily treated. Unfortunately within the CNDO/S-INDO/S scheme<sup>12,13</sup> which is still successfully employed for calculations of electronic spectra, photoelectron spectra and nuclear screening constants in NMR spectroscopy parameters are available only for H, C, N, O (ref.<sup>12</sup>), B, F (ref.<sup>14,15</sup>), Al (ref.<sup>16</sup>), S (ref.<sup>17</sup>) and Cl (ref.<sup>15</sup>). We considered it therefore expedient to try to suggest semiempirical parameters for silicon. For this purpose we selected a set of small species for which the electronic transition energies are known from experiment and/or *ab initio* calculations. The set comprises  $\text{SiH}_2$ ,  $\text{SiHCl}$ ,  $\text{SiF}_2$ ,  $\text{SiH}$ ,  $\text{SiN}$ ,  $\text{SiO}^+$ ,  $\text{SiF}$ ,  $\text{SiO}$ . We followed the procedure used previously for adjusting the parameters<sup>16</sup> for Al. That means that the parameters searched for,  $\gamma$  and  $\beta^0$  (one-center repulsion integral and bonding parameter) were varied in a range which is reasonable with respect to parameters for the neighbouring atoms in the periodic system. The parameter set reproducing best the reference data was then applied in calculations to further silicon species:  $\text{SiH}^+$ ,  $\text{SiS}$ ,  $\text{SiC}_2$ ,  $\text{Si}_2\text{C}$ ,  $\text{SiCl}$ ,  $\text{SiCl}_2$ ,  $\text{SiO}_2$ ,  $\text{HNSi}$ , silaethylene, silylmethylene, methylsilylene, disilylene, silylsilylene, silabenzene, and vinyl- and phenylsilane. As in previous treatments of S-containing<sup>17</sup> and Cl-containing<sup>15</sup> systems, the calculations were performed without *d*-functions on silicon. Some authors claim<sup>18,19</sup> that the  $(p-d)_\pi$  overlap is important in silicon chemistry, but recent *ab initio* calculations<sup>20</sup> suggest that its effect in C-Si and O-Si bonds is negligible.

### Details of Calculations

The theoretical approach used may be viewed as the original CNDO/S method of Del Bene and Jaffé<sup>12</sup> into which the INDO approximation was incorporated<sup>13</sup>. Extension of the method to second row elements was made consistently with our previous paper<sup>16</sup>. In calculations for the determination of  $\beta_{\text{Si}}^0$  and  $\gamma_{\text{Si}}$  parameters we assumed the values of  $-4$ ,  $-5$  and  $-6$  eV for  $\beta_{\text{Si}}^0$  and  $4.5$ ,  $5.5$  and  $6.5$  for  $\gamma_{\text{Si}}$ . The ranges into which a reasonable choice of the two parameters should fall, were guessed from the trends of CNDO/S parameters reported for other elements. The best combination appeared to be  $\beta_{\text{Si}}^0 = -4$  eV and  $\gamma_{\text{Si}} = 5.5$  eV which was then used throughout.

The calculations were performed mostly for the experimental geometries. These were available<sup>1</sup> for  $\text{SiH}^+$ ,  $\text{SiH}$ ,  $\text{SiN}$ ,  $\text{SiO}^+$ ,  $\text{SiO}$ ,  $\text{SiF}$ ,  $\text{SiS}$ ,  $\text{SiCl}$ ,  $\text{SiH}_2$ ,  $\text{SiF}_2$  and  $\text{SiHCl}$ . For  $\text{SiCl}_2$ ,  $\text{SiCC}$  and  $\text{SiCSi}$  we assumed the optimum geometries given by *ab initio* SCF calculations. The basis set used was  $4-31\text{G}^{21,22}$ . The following geometry parameters were obtained (bond lengths in  $10^{-10}$  m, bond angles in degrees):  $\text{SiCC}$ ,  $R(\text{SiC}) = 1.688$ ,  $R(\text{CC}) = 1.266$ ,  $\angle(\text{SiCC}) = 180$ ;  $\text{SiCSi}$ ,  $R(\text{SiC}) = 1.674$ ,  $\angle(\text{SiCSi}) = 180$ ;  $\text{SiCl}_2$ ,  $R(\text{SiCl}) = 2.25$ ,  $\angle(\text{ClSiCl}) = 98.7$ . For the following compounds the *ab initio* optimum geometries were taken from the references given in parenthesis: Vinylsilane (ref.<sup>20</sup>), silaethylene and silabenzene (ref.<sup>6</sup>),  $\text{H}_3\text{CSiH}$  and  $\text{H}_3\text{SiCH}$  (ref.<sup>8</sup>);  $\text{Si}_2\text{H}_4$  and  $\text{H}_3\text{SiCH}$  (ref.<sup>22</sup>),  $\text{SiO}_2$  (ref.<sup>2</sup>) and  $\text{HNSi}$  (ref.<sup>23</sup>). For phenylsilane a standard geometry with  $R(\text{SiC}) = 1.483$ ,  $R(\text{CC}) = 1.397$ ,  $R(\text{SiH}) = 1.48$  and  $R(\text{CH}) = 1.084 \cdot 10^{-10}$  m was used. For the purpose of comparison of the results obtained for Si-containing compounds with the data for the corresponding carbon compounds we also performed the INDO/S calculations for the following systems (for the geometries used see the references in parentheses):  $\text{CH}^+$  (ref.<sup>24</sup>),  $\text{CN}$  (ref.<sup>24</sup>),  $\text{CO}^+$  (ref.<sup>24</sup>),  $\text{CO}$  (ref.<sup>24</sup>),  $\text{CS}$  (ref.<sup>24</sup>),  $\text{CH}_2$  (ref.<sup>25</sup>),  $\text{CF}_2$  (ref.<sup>26</sup>),  $\text{CO}_2$  (ref.<sup>25</sup>),  $\text{CCl}_2$  (ref.<sup>27</sup>),  $\text{C}_3$  (ref.<sup>25</sup>), and benzene (experimental geometry,  $R(\text{CC}) = 1.397$ ,  $R(\text{CH}) = 1.084 \cdot 10^{-10}$  m).

## RESULTS AND DISCUSSION

The INDO/S approach was preferred to the CNDO/S method, because the neglect of one-center exchange integrals in the latter may lead in some instances to equal energies for states of different multiplicity (*e.g.* singlet and triplets belonging to the same electronic configuration). Some restrictive features, however, are inherent to both CNDO/S and INDO/S calculations. Particularly it should be recalled that Rydberg states and doubly excited states cannot be accounted for. Since small molecules can be treated accurately by *ab initio* calculations, the principal utility of semiempirical calculations of the INDO/S type may be found in their applications to larger systems. Having this in mind we performed first a series of calculations for small molecules to test the parameter set adopted and then we performed calculations for larger systems (*vide infra*) for which accurate *ab initio* calculations are hardly feasible.

### *Spectra of Small Molecules and Radicals*

The results are presented in Tables I–VIII. We considered it useful to present also the results for the corresponding carbon (Table V) and aluminum compounds (Table VI) to see whether the differences between the predicted and observed transition energies in the silicon compounds are due to a poor Si parameter set or due to deficiencies in the theoretical approach itself.

Table I shows the results for divalent silicon compounds. With  $\text{SiH}_2$  the transition energy was determined experimentally only for the  $A^1B_1$  state. The greatly overestimated prediction for this transition energy may be partly due to a great change in the bonding angle  $\text{HSiH}$  upon excitation ( $123^\circ \leftarrow 92^\circ$ ). The vertical experimental transition energy may therefore be considerably higher than the  $T_0$

TABLE I  
Transition energies (in  $10^3 \text{ cm}^{-1}$ ) for  $\text{SiH}_2$ ,  $\text{SiF}_2$ ,  $\text{SiHCl}$ , and  $\text{SiCl}_2$

Molecule	State	Main configuration <sup>a</sup>	Calc. INDO/S	Observed <sup>b</sup>	Calc. <i>ab initio</i>	
$\text{SiH}_2$	$X^1A_1$	$4a_1^2 2b_2^2 5a_1^2$	0	0		
	$^3B_1$	$4a_1^2 2b_2^2 5a_1 2b_1$	12.9	—	0	
	$A^1B_1$	$4a_1^2 2b_2^2 5a_1 2b_1$	23.3	15.5	12.0 <sup>c</sup>	
	$^3A_2$	$4a_1^2 2b_2^2 5a_1^2 2b_1$	27.1			
	$^3A_1$	$4a_1^2 2b_2^2 5a_1 6a_1$	28.7			
	$^1A_2$	$4a_1^2 2b_2^2 5a_1^2 2b_1$	29.0			
	$^3B_2$	$4a_1^2 2b_2^2 5a_1 3b_2$	30.3			
	$^1A_1$	$4a_1^2 2b_2^2 5a_1 6a_1$	41.7			
	$^3B_2$	$4a_1^2 2b_2^2 5a_1^2 6a_1$	41.9			
	$^3A_1$	$4a_1^2 2b_2^2 5a_1^2 3b_2$	43.3			
	$^1B_2$	$4a_1^2 2b_2^2 5a_1 3b_2$	45.8			
	$\text{SiF}_2$	$X^1A_1$	$7a_1^2 1a_2^2 5b_2^2 8a_1^2$	0	0	0
		$^3B_1$	$7a_1^2 1a_2^2 5b_2^2 8a_1 3b_1$	17.1	26.3	25.9 <sup>d</sup>
$A^1B_1$		31.1		44.1	47.8 <sup>d</sup>	
$^3A_1$		$7a_1^2 1a_2^2 5b_2^2 8a_1 9a_1$	49.9			
$^3B_2$		$7a_1^2 1a_2^2 5b_2^2 8a_1 6b_2$	50.6		53.3 <sup>d</sup>	
$^3A_2$		$7a_1^2 1a_2^2 5b_2^2 8a_1^2 3b_1$	52.3		70.4 <sup>a</sup>	
$^1A_2$			53.1			
$^3B_2$		$7a_1^2 1a_2^2 5b_2^2 8a_1^2 3b_1$	54.3			
$^1A_1$		$7a_1^2 1a_2^2 5b_2^2 8a_1 9a_1$	58.4			
$^1B_2$		$7a_1^2 1a_2^2 5b_2^2 8a_1^2 3b_1$	59.0		80.9 <sup>d</sup>	
$^3A_1$		$2b_1 7a_1^2 1a_2^2 5b_2^2 8a_1^2 3b_1$	60.5			
$^3B_1$		$7a_1 1a_2^2 5b_2^2 8a_1^2 3b_1$	60.5			
$^1B_1$			62.5			
$^3A_2$		$4b_2 2b_1^2 7a_1^2 1a_2^2 8a_1^2 3b_1$	64.7			
$^1A_2$			65.9			
$^1B_2$	$7a_1 1a_2^2 5b_2^2 8a_1^2 6b_2$	67.6	62.3	79.1 <sup>d</sup>		
$\text{SiCl}_2$	$X^1A_1$	$3b_1^2 2a_2^2 8b_2^2 11a_1^2$	0	0		
	$^3B_1$	$3b_1^2 2a_2^2 8b_2^2 11a_1 4b_1$	15.2			
	$^3A_1$	$3b_1^2 2a_2^2 8b_2^2 11a_1 12a_1$	21.1			
	$^3B_2$	$3b_1^2 2a_2^2 8b_2^2 11a_1 9b_2$	22.3			
	$A^1B_1$	$3b_1^2 2a_2^2 8b_2^2 11a_1 4b_1$	23.4	30.0		
	$^3A_2$	$3b_1^2 2a_2^2 8b_2 11a_1^2 4b_1$	27.6			
	$^1A_2$		28.4	(28.3)		
	$^3B_2$	$3b_1^2 2a_2^2 8b_2 11a_1^2 12a_1$	28.2			
	$^3A_1$	$3b_1^2 2a_2^2 8b_2 11a_1^2 9b_2$	29.0			
	$^3A_2$	$3b_1^2 2a_2^2 8b_2^2 11a_1^2 12a_1$	29.3			
	$^3B_1$	$3b_1 2a_2^2 8b_2^2 11a_1^2 12a_1$	29.5			
	$^1A_1$	$3b_1^2 2a_2^2 8b_2^2 11a_1 12a_1$	30.5			
	$^1B_2$	$3b_1^2 2a_2^2 8b_2 11a_1^2 12a_1$	30.8			

TABLE I  
(Continued)

Molecule	State	Main configuration <sup>a</sup>	Calc. INDO/S	Observed <sup>b</sup>	Calc. <i>ab initio</i>
	<sup>1</sup> A <sub>2</sub>	3b <sub>1</sub> <sup>2</sup> 2a <sub>2</sub> 8b <sub>2</sub> <sup>2</sup> 11a <sub>1</sub> <sup>2</sup> 12a <sub>1</sub>	31.9		
	<sup>1</sup> B <sub>1</sub>	3b <sub>1</sub> 2a <sub>2</sub> <sup>2</sup> 8b <sub>2</sub> <sup>2</sup> 11a <sub>1</sub> <sup>2</sup> 12a <sub>1</sub>	32.1		
	<sup>3</sup> B <sub>2</sub>	3b <sub>1</sub> <sup>2</sup> 2a <sub>2</sub> 8b <sub>2</sub> <sup>2</sup> 11a <sub>1</sub> <sup>2</sup> 4b <sub>1</sub>	32.1		
	<sup>1</sup> B <sub>2</sub>		32.2		
	<sup>3</sup> A <sub>1</sub>	3b <sub>1</sub> 2a <sub>2</sub> <sup>2</sup> 8b <sub>2</sub> <sup>2</sup> 11a <sub>1</sub> <sup>2</sup> 4b <sub>1</sub>	33.1		
	<sup>1</sup> A <sub>1</sub>		33.2		
SiHCl	X <sup>1</sup> A'	(3a'') <sup>2</sup> (12a') <sup>2</sup> (13a') <sup>2</sup>	0	0	
	<sup>3</sup> A''	(3a'') <sup>2</sup> (12a') <sup>2</sup> 13a'4a''	21.1	21.6	
	A <sup>1</sup> A''		20.7		
	<sup>3</sup> A'	(3a'') <sup>2</sup> (12a') <sup>2</sup> 13a'14a'	22.8		
	<sup>3</sup> A'	(3a'') <sup>2</sup> (12a') <sup>2</sup> 13a'15a'	27.0		
	<sup>3</sup> A''	(3a'') <sup>2</sup> 12a'(13a') <sup>2</sup> 4a''	30.9		
	<sup>1</sup> A'	(3a'') <sup>2</sup> (12a') <sup>2</sup> 13a'14a'	31.3		
	<sup>1</sup> A''	(3a'') <sup>2</sup> 12a'(13a') <sup>2</sup> 4a''	32.2		
	<sup>3</sup> A'	(3a'') <sup>2</sup> 12a'(13a') <sup>2</sup> 14a'	32.8		
	<sup>3</sup> A''	3a''(12a') <sup>2</sup> (13a') <sup>2</sup> 14a'	34.5		
	<sup>3</sup> A'	3a''(12a') <sup>2</sup> (13a') <sup>2</sup> 4a''	34.7		
	<sup>1</sup> A'	3a''(12a') <sup>2</sup> (13a') <sup>2</sup> 4a''	35.7		
	<sup>1</sup> A''	3a''(12a') <sup>2</sup> (13a') <sup>2</sup> 14a'	37.1		
	<sup>3</sup> A''	11a'(3a'') <sup>2</sup> (12a') <sup>2</sup> (13a') <sup>2</sup> 4a''	37.5		
	<sup>1</sup> A''		38.4		

<sup>a</sup> Inner shells accounted for; <sup>b</sup> T<sub>0</sub> from ref.<sup>1</sup>; <sup>c</sup> <sup>1</sup>B<sub>1</sub> - <sup>3</sup>B<sub>1</sub> difference, ref.<sup>28</sup>; <sup>d</sup> ref.<sup>29</sup>; essentially double zeta basis set.

energy. The data for CH<sub>2</sub> show the same trend (Table V) which suggests that the overestimation of the A <sup>1</sup>B<sub>1</sub> ← X <sup>1</sup>A<sub>1</sub> transition energy for SiH<sub>2</sub> is not due to a poor Si parameter set. Determination of the spin multiplicity of the ground state of SiH<sub>2</sub> is difficult. As with CH<sub>2</sub>, it may be profitable<sup>28</sup> for this purpose to know the <sup>1</sup>B<sub>1</sub> - <sup>3</sup>B<sub>1</sub> energy difference. Our prediction is 10 400 cm<sup>-1</sup>, in good agreement with the result of *ab initio* calculations<sup>28,29</sup> (12 000 cm<sup>-1</sup>). Also the INDO/S result for the AlH<sub>2</sub> (Table VI) may be noted, since in both SiH<sub>2</sub> and AlH<sub>2</sub> the 2b<sub>1</sub> ← 5a<sub>1</sub> transition is involved. A somewhat lower transition energy of 20 500 cm<sup>-1</sup> predicted<sup>16</sup> for AlH<sub>2</sub> corresponds well to a somewhat lower experimental value for AlH<sub>2</sub> with upper limit of 15 200 cm<sup>-1</sup>. For SiF<sub>2</sub> three excited states are experimentally known. Their assignment and the order of transition energies are supported by the present calculations. The difference between the predicted and observed <sup>1</sup>B<sub>1</sub> ← <sup>1</sup>A<sub>1</sub> transitions

(13 000  $\text{cm}^{-1}$ ) is large but it is also met with  $\text{CF}_2$  (7 300  $\text{cm}^{-1}$ , see Table V). As with  $\text{SiH}_2$ , the singlet-triplet splitting is well reproduced. The predicted value is 14 100  $\text{cm}^{-1}$ , compared to the observed one of 17 800  $\text{cm}^{-1}$ . The only state of  $\text{HSiCl}$  observed spectroscopically is  $A^1A''$ . Its transition energy is well reproduced by our calculations. For  $\text{SiCl}_2$  two excited states were observed in emission in the region at 30 000  $\text{cm}^{-1}$ . The assignment of  $A^1B_1$  to one of them is confirmed by our calculation, though the transition energy is somewhat underestimated. (This is also the case with  $\text{Si}_2\text{F}_2$  and  $\text{CF}_2$ , see Table V.) The  $^1B_1 - ^3B_1$  splitting is predicted to be 8 200  $\text{cm}^{-1}$  INDO/S gives for this silylene a large number of low-lying states. Eight triplet states

TABLE II

Transition energies (in  $10^3 \text{ cm}^{-1}$ ) in  $\text{SiO}$  and  $\text{SiS}$

Molecule	State <sup>a</sup>	Main configuration <sup>b</sup>	Calc. INDO/S	Observed <sup>c</sup>	<i>ab initio</i>	
					<i>d</i>	<i>e</i>
SiO	$X^1\Sigma^+$	$6\sigma^2 2\pi^4 7\sigma^2$	0	0	0	0
	$a^3\Sigma^+$	$6\sigma^2 2\pi^3 7\sigma^2 3\pi$	22.0	33.4	27.6	38.0
	$b^3\Pi_r$	$6\sigma^2 2\pi^4 7\sigma 3\pi$	21.1	33.9	31.8	36.0
	$d^3\Delta_r$	$6\sigma^2 2\pi^3 7\sigma^2 3\pi$	25.3	36.5	30.7	42.0
	$e^3\Sigma^-$	$6\sigma^2 2\pi^3 7\sigma^2 3\pi$	28.5	38.3	32.5	43.5
	$C^1\Sigma^-$	$6\sigma^2 2\pi^3 7\sigma^2 3\pi$	28.5	38.6	33.4	45.0
	$D^1\Delta$	$6\sigma^2 2\pi^3 7\sigma^2 3\pi$	31.6	38.8	33.1	45.7
	$A^1\Pi$	$6\sigma^2 2\pi^4 7\sigma 3\pi$	27.8	42.8	40.9	45.4
				(43.7) <sup>f</sup>		
	$E^1\Sigma^+$	$6\sigma^2 2\pi^4 7\sigma 8\sigma$	52.4	52.9	61.8	
	$^3\Pi_r$	$6\sigma 2\pi^4 7\sigma^2 3\pi$	47.3	—	53.9	
	$^3\Sigma^+$	$6\sigma^2 2\pi^4 7\sigma 8\sigma$	57.0	57.5	58.5	
	$c^3\Pi_i$	$6\sigma^2 2\pi^3 7\sigma^2 8\sigma$	59.2	59.3	59.8	
	SiS	$X^1\Sigma^+$	$8\sigma^2 3\pi^4 9\sigma^2$	0	0	
$^1\Sigma^-$		$8\sigma^2 3\pi^3 9\sigma^2 4\pi$	14.9			
$D^1\Pi$		$8\sigma^2 3\pi^4 9\sigma 4\pi$	16.5	34.9		
				(32.4) <sup>f</sup>		
$^1\Delta$		$8\sigma^2 3\pi^3 9\sigma^2 4\pi$	16.7			
$E^1\Sigma^+$		$8\sigma^2 3\pi^4 9\sigma 10\sigma$	25.1	41.7		
$^1\Pi$		$8\sigma^2 3\pi^3 9\sigma^2 10\sigma$	28.6			

<sup>a</sup> For SiO see ref.<sup>30</sup>; <sup>b</sup> Inner shells accounted for; <sup>c</sup>  $T_e$  for SiO from ref.<sup>30</sup>,  $T_0$  for SiS from ref.<sup>1</sup>; <sup>d</sup> ref.<sup>30</sup>; <sup>e</sup> From ref.<sup>31</sup>, values include corrections based upon the adaption of calculated values to experimental data for CO; <sup>f</sup> In parenthesis the energy is given which is corrected by the difference between the experimental energy for the  $A^1\Pi$  state of CO and the INDO/S calculation (see also Fig. 1).

are predicted to lie below  $30\,000\text{ cm}^{-1}$ . Among the singlet states, the  ${}^1A_2$  and  ${}^1A_1$  states lie very close to the observed second state.

Table II presents the results for the diatomic molecules SiO and SiS. The experimental data available for SiO have already been analyzed in detail by means of *ab initio* calculations<sup>30</sup>. A comparison made in the cited paper<sup>30</sup> is supplemented in Table V for our INDO/S results. The overall order of the states in SiO is well reproduced. Particularly, the predicted locations of low-lying triplet states  $a\ {}^3\Sigma^+$ ,  $b\ {}^3\Pi$  and  $d\ {}^3\Delta$  agree well with the experimental and *ab initio* data. The next three states,  $e\ {}^3\Sigma^-$ ,  $C\ {}^1\Sigma^-$  and  $D\ {}^1\Delta$ , are predicted incorrectly to lie above the  $A\ {}^1\Pi$  state, but for the states that lie considerably higher than the  $A\ {}^1\Pi$  state, the agreement between INDO/S and experiment is almost quantitative. Experimentally, the best known state of SiO is the  $A\ {}^1\Pi$  state, A large difference between the observed and INDO/S transition energies ( $15\,000\text{ cm}^{-1}$ ) is also met with the corresponding transition in CO ( $15\,800\text{ cm}^{-1}$ ), CS and SiS (see Tables II and V). Fig. 1 shows clearly that the observed trend of decreasing  ${}^1\Pi \leftarrow {}^1\Sigma^+$  transition energies in the series CO–SiO–CS–SiS is perfectly reproduced.

The results for the diatomic radicals, SiH, SiN, SiO<sup>+</sup>, SiF and SiCl, are collected in Table III. In SiH the three states arising from the  $4\sigma^25\sigma^2\pi^2$  configuration,  $A\ {}^2\Delta$ ,  ${}^2\Sigma^-$ ,  $B\ {}^2\Sigma^+$ , are very similar to the corresponding states of CH (Table V). Table III shows that the INDO/S calculations are in agreement with both the experimental values and the *ab initio* calculations. Compared to experiments, the predicted  $D\ {}^2\Delta$  and  $E\ {}^2\Sigma^+$  states are too high by  $15\,000\text{ cm}^{-1}$ . For the predicted  ${}^2\Pi$  states there is no experimental evidence. They should lie between the  $B\ {}^2\Sigma^+$  and  $D\ {}^2\Delta$  states and they should be both mainly due to the  $5\sigma \rightarrow 6\sigma$  transition. In agreement with experiment, INDO/S predicts for the two isoelectronic species SiN and SiO<sup>+</sup> the

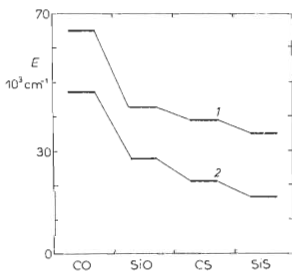


FIG. 1

Transition energies in CO, SiO, CS, SiS.  
1 experiment, 2 calculation

TABLE III  
 Doublet transition energies (in  $10^3 \text{ cm}^{-1}$ ) for SiH, SiN, SiO<sup>+</sup>, and SiF

Radical	State	Main configuration <sup>a</sup>	Calcd. ( <i>f</i> · 10 <sup>3</sup> ) INDO/S	Observed <sup>b</sup>	<i>ab initio</i>	
SiH	<i>X</i> <sup>2</sup> Π	4σ <sup>2</sup> 5σ <sup>2</sup> 2π	0	0	0	
	<i>C</i> <sup>2</sup> Σ <sup>+</sup>	4σ <sup>2</sup> 5σ <sup>2</sup> 6σ	21·8 (1)	30·8 <sup>g</sup>		
	<i>A</i> <sup>2</sup> Δ	4σ <sup>2</sup> 5σ2π <sup>2</sup>	23·6 (12)	24·2 <sup>g</sup>	25·0 <sup>c</sup>	
	<sup>2</sup> Σ <sup>-</sup>	4σ <sup>2</sup> 5σ2π <sup>2</sup>	26·2 (17)		26·8 <sup>c</sup>	
	<i>B</i> <sup>2</sup> Σ <sup>+</sup>	4σ <sup>2</sup> 5σ2π <sup>2</sup>	28·0 (14)	30·8 <sup>g</sup>	31·9 <sup>g</sup>	
	<sup>2</sup> Π	4σ <sup>2</sup> 5σ2π6σ	34·2 (1)			
	<sup>2</sup> Π	4σ <sup>2</sup> 5σ2π6σ	54·1 (295)			
	<i>D</i> <sup>2</sup> Δ	4σ5σ <sup>2</sup> 2π <sup>2</sup>	64·9 (71)	48·5 <sup>g</sup>		
	<i>E</i> <sup>2</sup> Σ <sup>+</sup>	4σ5σ <sup>2</sup> 2π <sup>2</sup>	69·4 (78)	52·4 <sup>g</sup>		
	<sup>2</sup> Σ <sup>-</sup>	4σ5σ <sup>2</sup> 2π <sup>2</sup>	80·6 (338)			
	SiN	<i>X</i> <sup>2</sup> Σ <sup>+</sup>	6σ <sup>2</sup> 2π <sup>4</sup> 7σ	0	0	
		<sup>2</sup> Π	6σ <sup>2</sup> 2π <sup>3</sup> 7σ <sup>2</sup>	0·1		
<i>B</i> <sup>2</sup> Σ <sup>+</sup>		6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	15·6	24·2		
<sup>2</sup> Σ <sup>-</sup>		6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	17·1			
<sup>2</sup> Δ		6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	19·0			
<sup>2</sup> Δ		6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	20·9			
<sup>2</sup> Π		6σ <sup>2</sup> 2π <sup>4</sup> 3π	22·4			
<sup>2</sup> Σ <sup>-</sup>		6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	22·8			
<sup>2</sup> Σ <sup>+</sup>		6σ2π <sup>4</sup> 7σ <sup>2</sup>	34·8			
<sup>2</sup> Π		6σ <sup>2</sup> 2π <sup>3</sup> 7σ8σ	39·3			
<sup>2</sup> Σ <sup>+</sup>		6σ <sup>2</sup> 2π <sup>4</sup> 8σ	40·4	50·3		
<sup>2</sup> Π	6σ2π <sup>4</sup> 7σ3π	52·5				
SiO <sup>+</sup>	<i>X</i> <sup>2</sup> Σ <sup>+</sup>	6σ <sup>2</sup> 2π <sup>4</sup> 7σ	0	0		
	<i>A</i> <sup>2</sup> Π	6σ <sup>2</sup> 2π <sup>3</sup> 7σ <sup>2</sup>	3·6 (0·4)	—	(4·7) <sup>d</sup>	
	<i>B</i> <sup>2</sup> Σ <sup>+</sup>	6σ2π <sup>4</sup> 7σ <sup>2</sup>	20·9 (56·1)	30·5	(25·7) <sup>d</sup>	
	<sup>2</sup> Π	6σ <sup>2</sup> 2π <sup>4</sup> 3π	35·6 (7·8)			
	<sup>2</sup> Σ <sup>-</sup>	6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	38·5			
	<sup>2</sup> Δ	6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	40·7			
	<sup>2</sup> Σ <sup>+</sup>	6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	43·1 (5·7)			
	<sup>2</sup> Δ	6σ <sup>2</sup> 2π <sup>3</sup> 7σ3π	44·5			
	SiF	<i>X</i> <sup>2</sup> Π <sub>f</sub>	2π <sup>4</sup> 7σ <sup>2</sup> 3π	0	0	
<i>A</i> <sup>2</sup> Σ <sup>+</sup>		2π <sup>4</sup> 7σ <sup>2</sup> 8σ	32·4 (0·0)	22·8		
<i>C</i> <sup>2</sup> Δ		2π <sup>4</sup> 7σ3π <sup>2</sup>	35·1 (38)	39·5		
<i>B</i> <sup>2</sup> Σ <sup>+</sup>		2π <sup>4</sup> 7σ3π <sup>2</sup>	39·8	34·6 <sup>e</sup>		
<i>D</i> <sup>2</sup> Σ <sup>-</sup>		2π <sup>4</sup> 7σ3π <sup>2</sup>	45·7	47·5 <sup>e</sup>		
<sup>2</sup> Π		2π <sup>3</sup> 7σ <sup>2</sup> 3π <sup>2</sup>	57·0			
<sup>2</sup> Φ		2π <sup>3</sup> 7σ <sup>2</sup> 3π <sup>2</sup>	59·3			
<sup>2</sup> Π		2π <sup>3</sup> 7σ <sup>2</sup> 3π <sup>2</sup>	62·4			
<sup>2</sup> Π		2π <sup>3</sup> 7σ <sup>2</sup> 3π <sup>2</sup>	64·3			



TABLE III  
 (Continued)

Radical	State	Main configuration <sup>a</sup>	Calcd. ( $f \cdot 10^3$ ) INDO/S	Observed <sup>b</sup>	<i>ab initio</i>
SiCl	$X^2\Pi$	$3\pi^4 9\sigma^2 4\pi^1$	0	0	
	$A^2\Sigma^+$	$3\pi^4 9\sigma^2 10\sigma$	13.5	23.0 <sup>f</sup>	
	$C^2\Delta$	$3\pi^4 9\sigma 4\pi^2$	28.2	41.2 <sup>f</sup>	
	$B^2\Sigma^-$	$3\pi^4 9\sigma 4\pi^2$	29.9	34.1 <sup>f</sup>	
	$^2\Sigma^+$	$3\pi^4 9\sigma 4\pi^2$	32.4		
	$^2\Pi$	$3\pi^4 9\sigma 4\pi 10\sigma$	33.1		
	$^2\Pi$	$3\pi^3 9\sigma^2 4\pi^2$	35.3		
	$^2\Sigma$	$3\pi^3 9\sigma^2 4\pi 10\sigma$	36.8		
	$^2\Delta$	$3\pi^3 9\sigma^2 4\pi 10\sigma$	37.1		
	$^2\Pi$	$3\pi^3 9\sigma^2 4\pi^2$	38.4		
	$^2\Phi$	$3\pi^3 9\sigma^2 4\pi^2$	38.8		
	$^2\Sigma$	$3\pi^2 9\sigma^2 4\pi 10\sigma$	39.2		
	$^2\Delta$	$3\pi^3 9\sigma^2 4\pi 10\sigma$	39.7		
	$^2\Sigma$	$3\pi^3 9\sigma^2 4\pi 10\sigma$	40.0		
	$^2\Pi$	$3\pi^3 9\sigma^2 4\pi^2$	42.7		

<sup>a</sup> Inner shells accounted for; <sup>b</sup>  $T_0$  from ref.<sup>1</sup>; <sup>c</sup> ref.<sup>32</sup>, basis set (Si 6s,3p; H 1s); <sup>d</sup> Values estimated from the photoelectron spectrum of SiO, ref.<sup>33</sup>; <sup>e</sup> Probably Rydberg states; <sup>f</sup>  $T_e$  values from ref.<sup>24</sup>; <sup>g</sup>  $T_0$  values from ref.<sup>34</sup>.

TABLE IV

Comparison of calculated and observed energies for the lowest allowed transition in  $C_3$ , SiCC and SiCSi (in  $10^3 \text{ cm}^{-1}$ )

Molecule	Geometry	State	Main configuration	INDO/S	Observed
CCC	$D_{\infty h}$ (exp.)	$X^1\Sigma_g^+$	$(4\sigma_g^+)^2 1\pi_u^4 (3\sigma_u^+)^2$	0	0
		$A^1\Pi_u$	$(4\sigma_g^+)^2 1\pi_u^4 (3\sigma_u^+)^1 1\pi_g^1$	18.4	24.7 <sup>a</sup>
SiCC	$C_{\infty v}^d$	$X^1\Sigma^+$	$8\sigma^2 2\pi^4 9\sigma^2$	0	0
		$A^1\Pi$	$8\sigma^2 2\pi^4 9\sigma^1 3\pi^1$	11.3	20.1 <sup>a</sup>
SiCSi	$D_{\infty h}^d$	$X^1\Sigma_g^+$	$(6\sigma_g^+)^2 (5\sigma_u^+)^2 2\pi_u^4$	0	0
		$A^1\Pi_u$	$(6\sigma_g^+)^2 (5\sigma_u^+)^1 2\pi_u^4 2\pi_g^1$	12.8	18.9 <sup>b</sup> 19.3 and 19.9, resp. <sup>c</sup>

<sup>a</sup>  $T_0$  value from ref.<sup>25</sup>; <sup>b</sup> In Ar matrix, refs<sup>1,40</sup>; <sup>c</sup> In Ne matrix, refs<sup>1,40</sup>; <sup>d</sup> Geometry optimization employing 4-31G *ab initio* SCF method.

TABLE V

Comparison of excitation energies (in  $10^3 \text{ cm}^{-1}$ ) between silicon and the corresponding carbon compounds

General formula	Transition	Experiment			Calculation (INDO/S)		
		Si <sup>a</sup>	C	difference	Si	C	difference
AH <sup>+</sup>	$^1\Pi \leftarrow ^1\Sigma^+$	25.0	23.6 <sup>b</sup>	1.4	24.1	24.6	- 0.5
AH	$^2\Delta \leftarrow ^2\Pi$	24.2	23.2 <sup>b</sup>	1.0	23.6	25.3 <sup>d</sup>	- 1.7
	$^2\Sigma^+ \leftarrow ^2\Pi$	30.8	31.8 <sup>b</sup>	- 1.0	28.0	34.3 <sup>d</sup>	- 6.3
AH <sub>2</sub>	$^1B_1 \leftarrow ^1A_1$	15.5	7.1 <sup>e</sup>	8.4	23.3	16.7	6.6
AN	$^2\Sigma^+ \leftarrow ^2\Sigma^+$	24.2	25.8 <sup>b</sup>	- 1.6	15.6	31.4	-15.8
AO <sup>+</sup>	$^2\Pi \leftarrow ^2\Sigma^+$	(4.7) <sup>g</sup>	20.4 <sup>b</sup>	(-15.7)	3.6	29.5	-25.9
	$^2\Sigma^+ \leftarrow ^2\Sigma^+$	30.5	45.6 <sup>b</sup>	-15.1	20.9	43.9	-23.0
AF	$^2\Sigma^+ \leftarrow ^2\Pi$	22.8	53.6 <sup>c</sup>	-30.8	32.4	51.7 <sup>d</sup>	-19.3
AO	$^1\Pi \leftarrow ^1\Sigma^+$	42.6	64.7 <sup>b</sup>	-22.1	27.9	49.3	-21.4
AS	$^1\Pi \leftarrow ^1\Sigma^+$	34.9	38.8 <sup>b</sup>	- 4.0	16.5	21.0	- 4.5
AF <sub>2</sub>	$^1B_1 \leftarrow ^1A_1$	44.1	37.7 <sup>e</sup>	6.4	31.1	30.4	0.7
ACl <sub>2</sub>	$^1B_1 \leftarrow ^1A_1$	30.0	30.3 <sup>h</sup>	- 0.3	23.4	19.3	4.1
ACC	$^1\Pi \leftarrow ^1\Sigma^+$	20.1	24.7 <sup>e</sup>	- 4.6	11.3	18.4	- 7.1
ACA	$^1\Pi_u \leftarrow ^1\Sigma_g^+$	18.9	24.7 <sup>e</sup>	- 5.8	12.8	18.4	- 5.6

<sup>a</sup> Experimental values (preferably  $T_0$ ) taken from ref.<sup>1</sup> if not otherwise noted; <sup>b</sup>  $T_0$  from ref.<sup>24</sup><sup>c</sup> For references see the cited paper<sup>13</sup>; <sup>d</sup> ref.<sup>13</sup>; <sup>e</sup> ref.<sup>25</sup>; <sup>f</sup> For references see the cited paper<sup>35</sup>;<sup>g</sup> PES for SiO, ref.<sup>33</sup>; <sup>h</sup> ref.<sup>27</sup>.

TABLE VI

Comparison of excitation energies (in  $10^3 \text{ cm}^{-1}$ ) between silicon and aluminum compounds

Orbital transition	Silicon				Aluminium <sup>a</sup>			
	species	observed	INDO/S	difference	species	observed	INDO/S	difference
$2b_1 \leftarrow 5a_1$	SiH <sub>2</sub>	15.5	23.3	-7.8	AlH <sub>2</sub>	<15.2	20.5	<-5.3
$2\pi \leftarrow 5\sigma$	SiH <sup>+</sup>	25.0	24.1	0.9	AlH	23.8	25.6	-1.8
$7\sigma \leftarrow 2\pi$	SiO <sup>+</sup>	(4.7)	3.6	1.1	AlO	5.4	0.1	5.5
$3\pi \leftarrow 7\sigma$	SiF	39.5	35.1	4.4	AlF	43.9	39.5	4.4
$4\pi \leftarrow 9\sigma$	SiCl	41.2	28.2	13.0	AlCl	38.2	32.2	6.0

<sup>a</sup> INDO/S results taken from ref.<sup>16</sup>, for experimental references see the cited paper<sup>16</sup>.

ground state to be  ${}^2\Sigma^+$ . The  ${}^2\Pi$  state is calculated to be slightly above the ground state. Although it was not observed directly in the spectra of SiN or SiO<sup>+</sup>, evidence for the existence of such a state can be derived from the photoelectron spectrum<sup>33</sup> of SiO. The difference in ionization potentials of SiO corresponds to the excitation energies of the ionized species (Table III, values in parenthesis). The agreement with the calculated value ( $3\,600\text{ cm}^{-1}$ ) is fair. The energy of the  $B\ {}^2\Sigma^+$  state, however, is considerably underestimated. The underestimation is almost uniform, being  $8\,600\text{ cm}^{-1}$  for SiN and  $9\,600\text{ cm}^{-1}$  for SiO<sup>+</sup>. In contrast, the excitation energies of the analog carbon radicals are fairly reproduced or even overestimated (Table V). With SiF the calculation overestimates the first transition by  $10\,400\text{ cm}^{-1}$ . However a large decrease of this transition energy when compared to CF is qualitatively reproduced (Table V). The symmetry and electron configuration of the  $X\ {}^2\Pi$ ,  $A\ {}^2\Sigma^+$  and  $C\ {}^2\Delta$  states are in agreement with the conclusions from experiment. The agreement for the  $C\ {}^2\Delta$  transition is rather good. The  ${}^2\Sigma^+$  and  ${}^2\Sigma^-$  states arising from the  $2\pi^47\sigma3\pi^2$  configuration might be assigned to the states ( $B$  and  $D$ ) observed at  $34\,600$  and  $47\,500\text{ cm}^{-1}$ . It should be noted, however, that the latter seem to have Rydberg character as suggested by its vibrational frequencies<sup>1</sup>. The same also holds for the  ${}^2\Pi$  states ( $C'$  and  $D'$ ) found at  $42\,000$  and  $46\,700\text{ cm}^{-1}$  and the  $G$  state at  $52\,000\text{ cm}^{-1}$ . One may expect that the higher valence  ${}^2\Pi$  states due to the

TABLE VII  
Calculated transition energies (in  $10^3\text{ cm}^{-1}$ ) for HNSi

State	Main configuration	INDO/S ( $f \cdot 10^3$ )	<i>ab initio</i> <sup>a</sup>
${}^1\Sigma^+$	$7\sigma^22\pi^4$	0	0
${}^3\Sigma^+$	$7\sigma^22\pi^33\pi$	9.0	~35
${}^3\Delta$	$7\sigma^22\pi^33\pi$	12.7	} ~40–45
${}^3\Sigma^-$	$7\sigma^22\pi^33\pi$	16.0	
${}^1\Sigma^-$	$7\sigma^22\pi^33\pi$	16.0 (0)	
${}^1\Delta$	$7\sigma^22\pi^33\pi$	19.2 (0)	
${}^3\Pi$	$7\sigma^22\pi^43\pi$	28.8	} ~60
${}^3\Pi$	$7\sigma^22\pi^38\sigma$	34.9	
${}^1\Pi$	$7\sigma2\pi^43\pi$	40.3 (80)	
${}^1\Pi$	$7\sigma^23\pi^38\sigma$	43.6 (54)	
${}^1\Sigma^+$	$7\sigma2\pi^48\sigma$	48.3 (166)	
${}^3\Sigma^+$	$7\sigma2\pi^48\sigma$	50.3	

<sup>a</sup> Approximate data inferred from ref.<sup>2,3</sup>.

TABLE VIII  
Transition energies (in  $10^3 \text{ cm}^{-1}$ ) for  $\text{SiO}_2$  and  $\text{CO}_2$

State	O=C=O			O=Si=O			
	main configuration <sup>a</sup>	observed <sup>b</sup>	observed <sup>c</sup>	<i>ab initio</i> <sup>d</sup>	INDO/S <sup>e</sup>	INDO/S	main configuration <sup>a</sup>
$1\Sigma^+$	$1\pi_u^4 3\sigma_u^2 1\pi_g^4$	0	0	0	0	0	$2\pi_u^4 4\sigma_u^2 1\pi_g^4$
$1\Sigma^-$	$1\pi_u^4 3\sigma_u^2 1\pi_g^3 2\pi_u^1$	52.7	60.5	76.0	48.3	42.8	$2\pi_u^4 4\sigma_u^2 1\pi_g^3 3\pi_u^1$
$1A_u$	$1\pi_u^4 3\sigma_u^2 1\pi_g^3 2\pi_u^1$	67.8	69.0	76.1	51.1	45.0	$2\pi_u^4 4\sigma_u^2 1\pi_g^3 3\pi_u^1$
$1\Pi_g$	$1\pi_u^4 3\sigma_u 1\pi_g^4 2\pi_u^1$	75.0	75.0	73.4	75.7	49.8	$2\pi_u^4 4\sigma_u 1\pi_g^4 3\pi_u^1$
$1\Sigma^+$	$1\pi_u^4 3\sigma_u^2 1\pi_g^3 2\pi_u^1$	89.4	90.3	90.3 <sup>g</sup>	88.8 (1.28) <sup>f</sup>	55.7 (0.17) <sup>f</sup>	$2\pi_u^4 4\sigma_u 1\pi_g^4 6\sigma_g^1$
$1\Sigma^-$	$1\pi_u^3 3\sigma_u^2 1\pi_g^4 2\pi_u^1$				90.8	77.1	$2\pi_u^3 4\sigma_u 1\pi_g^4 3\pi_u^1$
$1A_g$	$1\pi_u^3 3\sigma_u^2 1\pi_g^4 2\pi_u^1$				94.7	79.5	$2\pi_u^3 4\sigma_u 1\pi_g^4 3\pi_u^1$
$1\Pi_g$	$1\pi_u^4 3\sigma_u 1\pi_g^3 5\sigma_g$				102.6	52.8	$2\pi_u^4 4\sigma_u 1\pi_g^3 6\sigma_g^1$
$1\Pi_u$	$4\sigma_g 1\pi_u^4 3\sigma_u 1\pi_g^4 2\pi_u^1$		(93.6)	92.3 <sup>g</sup>	104.6	86.1 (0.12) <sup>f</sup>	$5\sigma_g 2\pi_u^4 4\sigma_u 1\pi_g^4 3\pi_u^1$

<sup>a</sup> Inner shells accounted for; <sup>b</sup> ref. 37; <sup>c</sup> ref. 38; <sup>d</sup> Vertical energy levels from ref. 39; <sup>e</sup> CNDO/S results are given in ref. 36; <sup>f</sup> Oscillator strength calculated; <sup>g</sup> Rydberg character.

$2\pi^3 7\sigma^2 3\pi^2$  configuration mix with Rydberg  $^2\Pi$ -states. With SiCl the three lowest excited doublet states given by calculations correspond to the observed transitions. The transition energies are underestimated (by 4 200 to 13 000  $\text{cm}^{-1}$ ) and the predicted order of the  $C^2A$  and  $B^2\Sigma^-$  states is reversed.

Table IV presents a comparison for the lowest transitions in the linear molecules CCC, SiCC and SiCSi. The transition with  $T_0 = 20\,100\text{ cm}^{-1}$  assigned to SiC<sub>2</sub> was observed in the spectra of N-type stars and under laboratory conditions, in the vapour of silicon carbide. A second transition with  $T_0 = 18\,900\text{ cm}^{-1}$  (trapped in argon) and  $T_0 = 19\,300$  or  $19\,900\text{ cm}^{-1}$  (assignment ambiguous, trapped in neon) was attributed to Si<sub>2</sub>C (ref.<sup>40</sup>). A decrease in the transition energy when passing from C<sub>3</sub> to Si<sub>2</sub>C (about 6 000  $\text{cm}^{-1}$ ) is correctly reproduced by the calculation. The transition energy in SiC<sub>2</sub> is predicted to be lower than in Si<sub>2</sub>C, whereas the interpretation of experiments tends to favour the reversed order<sup>40</sup>. Anyhow the difference in transition energies between Si<sub>2</sub>C and SiC<sub>2</sub> is small, both experimentally and theoretically.

Tables V and VI present a comparison of silicon compounds with carbon and aluminum analogs. The aim of these tables is to show that our parameter set for Si performs equally well as parameter sets suggested previously for other elements, including the recent extension to aluminum. The entries of Table V have already been mentioned in the preceding discussion with the exception of SiH<sup>+</sup> and CH<sup>+</sup>. The calculated transition energies conform to the experimental finding that there is almost no difference between the two systems. The content of Table V may be summarized in the mean square difference between the observed and calculated transition energies for silicon and carbon compounds,  $\langle \Delta v \rangle = [1/n \sum_i (v_i^{\text{obs}} - v_i^{\text{calc}})^2]^{1/2}$ . The two respective values are very close in absolute value, the difference being only 8 per cent in favour of carbon compounds.

When comparing with aluminum compounds we face the problem that aluminum has one valence electron less than silicon. Therefore we either compare transitions between the same states of isoelectronic pairs (SiH<sup>+</sup>-AlH, SiO<sup>+</sup>-AlO) or we compare singlet states with doublet states in the pairs SiH<sub>2</sub>-AlH<sub>2</sub>, AlF-SiF, AlCl-SiCl, in which the same critical orbitals are involved in the excitation. Table VI shows the same trends in errors of calculations for silicon and aluminum species, though with the former the errors in absolute value are somewhat larger than with the latter.

Concluding this paragraph we present results for HNSi and SiO<sub>2</sub>. Excited states of the HNSi molecule (Table VII) have not been observed so far. Our prediction for the first transition differs largely (by 20 000  $\text{cm}^{-1}$  too low) from the prediction given by *ab initio* calculations<sup>23</sup>. This is not due to the Si parameters as the same failure was also found with the HCN molecule. For the latter molecule CNDO/S gives transition energies which are for the  $^1A$  and  $^1\Pi$  states too low by 20 000 and 10 000  $\text{cm}^{-1}$ , respectively<sup>36</sup>.

To make the INDO/S prediction for  $\text{SiO}_2$  more reliable, we performed the INDO/S calculation for  $\text{CO}_2$  as a reference system (Table VIII). The INDO/S calculation reproduces the spectrum of  $\text{CO}_2$  remarkably well. Two systems of weak absorptions may be assigned to forbidden  ${}^1A_u \leftarrow {}^1\Sigma_g^+$  and  ${}^1\Pi_g \leftarrow {}^1\Sigma_g^+$  transitions, whereas the strong absorption may be assigned to the allowed  ${}^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$  ( $f = 1.28$ ) and  ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$  transitions. The corresponding states in  $\text{SiO}_2$  are generally lower in energy. The lowest one, corresponding to a forbidden transition, is predicted to lie at  $42\,800\text{ cm}^{-1}$ . The allowed  ${}^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$  transition should be much weaker than it is in  $\text{CO}_2$  and it should be shifted considerably to lower wavenumbers (by about  $30\,000\text{ cm}^{-1}$ ). The second allowed transition is also to be expected at lower energies, the predicted shift being about  $20\,000\text{ cm}^{-1}$ .

### *The Effect of Silyl Substitution and the Introduction of Silicon into Conjugated Systems*

This paragraph does not aim at a complete account of the topics of silyl substitution and silicon participation in conjugated systems but its purpose is rather to show a potential usefulness of INDO/S calculations in this field. The results are presented in Tables IX–XII. Phenylsilane was selected as a model system for studying the influence of silyl groups on  $\pi$ -electron systems, whereas silaethylene and silabenzene represent systems containing silicon in the  $\pi$ -electron system. An extreme case is disilylene, which is a conjugated system formed only from silicon atoms. As possible isomers of silaethylene and disilylene, methyl- and silylsilylene as well as silylmethylene have recently been considered<sup>8,22</sup>. The results for the latter are given in Table XII. Presented in Table XII are also results for the unsubstituted silylene and methylene for the sake of comparison.

In phenylsilane only a slight shift to more positive values was found for the energies of both occupied and vacant orbitals with respect to benzene. There is also a slight increase in the gap between the  $\pi$  orbitals (Table X). This results in a rather small red shift of the first  $\pi\pi^*$  transition (Table IX). The experimental results,  $37\,900\text{ cm}^{-1}$  for benzene and  $36\,900\text{ cm}^{-1}$  for phenylsilane<sup>41</sup>, are in agreement with our prediction. Also a small experimentally observed shift of the first ionization potential of benzene on silyl substitutions is reproduced ( $+0.38\text{ eV}$  for  $\text{Si}(\text{CH}_3)_3$ , see Table X)<sup>42</sup>. In the charge transfer spectra of TCNE complexes with benzenes no effect of silyl substitution was observed<sup>43</sup>. Moreover, the photoelectron spectrum of vinylsilane<sup>44</sup> exhibits almost no shift for the first band with respect to ethylene. This findings indicate an almost constant energy of the uppermost  $\pi$  orbital of benzene and ethylene on silyl substitution.

The  $B_{2u} \leftarrow A_{1u}$  transition in benzene is predicted to undergo a blue shift of  $3\,500\text{ cm}^{-1}$  on silyl substitution. It should be noted that there is a low-lying vacant orbital above  $-2\text{ eV}$  localized mainly on the substituent (*vide infra*). Electron promotion

TABLE IX

INDO/S results for  $\pi\pi^*$  transition energies in phenylsilane, benzene and silabenzene in comparison to experimental data

Phenylsilane			Benzene			Silabenzene				
$\Delta E^a$ calc.	$f$ calc.	$\Delta E^b$ obs.	state	$\Delta E$ calc.	$f$ calc.	$\Delta E^c$ obs.	state	$\Delta E^{e,f}$ calc.	$f$ calc.	$\Delta E^d$ obs.
37.6	0.00	36.9	$B_{1u}$	38.0	0.0	39.5	$^1A_1$	22.2	0.11	31.25
							$^1B_2$	30.7	0.0	36.8
48.3	0.32		$B_{2u}$	44.8	0.0	50.5	$^1B_2$	44.0	0.40	47.2
52.4	0.86		$E_{1u}$	52.5	0.59	56.0	$^1A_1$	50.4	0.71	
54.9	0.71									

<sup>a</sup>  $A\sigma\sigma^*$  transition connected with the silylsubstituent is found at  $30\,500\text{ cm}^{-1}$  ( $f = 0.13$ ); <sup>b</sup> ref.<sup>41</sup>, comparable value for benzene  $37\,900\text{ cm}^{-1}$ ; <sup>c</sup> Experimental values taken from band maxima, ref.<sup>50</sup>; <sup>d</sup> Argon matrix at 10 K, ref.<sup>45</sup>; <sup>e</sup> CNDO/CI calculation of H. Bock and B. Roth (unpublished) predicts transition energies of 34 400, 38 400, 51 400 and 52 500  $\text{cm}^{-1}$ , ref.<sup>46</sup>; <sup>f</sup> Further transitions are obtained at 8 700 ( $B_1, \pi\sigma^*$ ), 25 500 ( $B_2, \sigma\sigma^*$ ), 43 200 ( $A, \sigma\sigma^*$ ), 48 700 ( $B_1, \pi\sigma^*$ ) which are connected with the low-lying orbital belonging to Si.

TABLE X

Orbital energies ( $\epsilon$ ) obtained by INDO/S calculations in phenylsilane, benzene and silabenzene in comparison to experimental ionization potentials ( $I$ , in eV)

Orbitals	Phenylsilane		Benzene			Silabenzene		
	MO	$\epsilon$ , calc.	MO	$\epsilon$ , calc.	$I$ , obs. <sup>b</sup>	MO	$\epsilon$ , calc.	$I$ , obs. <sup>c</sup>
Vacant orbitals	$a'', \pi^*$	0.28	$b_{1g}, \pi^*$	2.50		$a_2, \pi^*$	0.56	
	$a'', \pi^*$	0.26	$e_{2u}, \pi^*$	0.17		$b_1, \pi^*$	-0.95	
	$a'$	-2.14				$a_1$	-2.04	
Occupied orbitals	$a'', \pi$	-8.83 <sup>a</sup>	$e_{1g}, \pi$	-9.15	9.24	$b_1, \pi$	-7.02	8.0
	$a'$	-9.06				$a_2, \pi$	-9.08	9.3
	$a'$	-9.08	$e_{2g}$	-11.80	11.49	$b_2$	-9.29	
	$a'$	-10.48				$a_1$	-10.35	
	$a'', \pi$	-11.55	$a_{1u}, \pi$	-13.53	12.1	$b_1, \pi$	-12.31	11.3
		$e_{1u}$	-15.10	13.8				

<sup>a</sup> Experimental value for  $C_6H_5Si(CH_3)_3$  8.72 eV, comparable value for benzene 9.20 eV, ref.<sup>42</sup>; <sup>b</sup> ref.<sup>47</sup>; <sup>c</sup> ref.<sup>46</sup>.

to this orbital gives rise to a low-lying state (below  $\pi\pi^*$  states, at 30 500  $\text{cm}^{-1}$  in phenylsilane) for which no experimental evidence exists. Recently attempts met success to observe silabenzene. As it was expected for a donor substituent, the highest  $\pi$  orbital is lifted by about 1 eV and the  $\pi\pi^*$  transitions are shifted bathochromically, the shift being especially large for the lowest transition (from 39 500 in benzene to 31 250  $\text{cm}^{-1}$ ). These trends are reproduced by the calculations, although the shifts are overestimated by about 1 eV and 9 000  $\text{cm}^{-1}$ , respectively. The calculated transition energies at 22 200 and 44 000  $\text{cm}^{-1}$  can be assigned to the observed bands at 31 250 ( $A_1, \pi\pi^*$ ) and 47 200  $\text{cm}^{-1}$  ( $B_2, \pi\pi^*$ ), whereas the origin of the band at 36 800  $\text{cm}^{-1}$  is not quite clear because of the zero oscillator strength of the  $\pi\pi^*$  transition calculated at 30 700  $\text{cm}^{-1}$ .

It may be concluded that our parametrization gives a qualitatively correct account of the participation of silicon in conjugated systems but it reduces the conjugation with neighbouring atoms too much. This becomes even more evident for disilylene. Whereas in silaethylene the occupied  $\pi$  orbital is lifted to  $-7.4$  eV and the transition energy is lowered to 24 100  $\text{cm}^{-1}$ , with disilylene our parameter set fails to produce a conjugated  $\pi$ -electron system at all. As a consequence of a too strong upwards

TABLE XI  
INDO/S results for orbital energies and  $\pi\pi^*$  transition energies in vinylsilane, silaethylene and disilylene

Energies	Type	Vinylsilane	Silaethylene	Disilylene <sup>a</sup>	
				$\beta_0 = -6$ eV	$\beta_0 = -4$ eV <sup>a</sup>
Orbital energies in eV	vacant	$-0.86\pi^*$	$-0.67\pi^*$	$-1.49\pi^*$	$-1.42\pi^*$
		$-2.19$ (SiH <sub>3</sub> )	$-2.03$ (SiH <sub>2</sub> )	$-2.84$ (SiH <sub>2</sub> )	$-2.42\pi^*$
	occupied	$-9.44\pi$	$-7.42\pi$	$-6.05\pi$	$-7.25$
		$-9.83$	$-10.79$	$-9.39$	$-9.10$
		$-10.59$	$-11.11$	$-11.03$	$-10.68$
					$-11.80$
$\pi\pi^*$ transition energies in 1 000 $\text{cm}^{-1}$	singlet	57.1	24.1	15.8	(11.26; 17.47) <sup>a</sup>
	triplet	16.3	1.3	0.25	

<sup>a</sup> Using the parameter set proposed in this study ( $\beta_0 = -4$  eV) no occupied  $\pi$  orbitals are obtained for disilylene. The electronic structure resembles two loosely bound SiH<sub>2</sub> species. See text for details.



TABLE XII

Comparison of orbital energies, transition energies and dipole moments of methyl- and silylsubstituted silylenes and methylenes (INDO/S results)

Quantity	Type	SiH <sub>2</sub>		HSiCH <sub>3</sub>	HSiSiH <sub>3</sub>	HCSiH <sub>3</sub>	HCH	
		exp.	calc.				calc.	exp.
Orbital energies in eV	vacant		-1.94 b <sub>1</sub>	-1.89 a''	-2.31 a''	-0.25 a''	-0.55 b <sub>1</sub>	
	occupied		-8.76 a <sub>1</sub>	-8.38 a'	-2.43 a'	-2.04 a'	-10.94 a <sub>1</sub>	
			-10.24 b <sub>2</sub>	-9.70 a'	-7.04 a'	-9.48 a'	-10.79 a'	-15.77 b <sub>2</sub>
Transition energies 1000 cm <sup>-1</sup>	singlets		23.3 <sup>1</sup> B <sub>1</sub>	20.9 <sup>1</sup> A''	9.4 <sup>1</sup> A''	9.0 <sup>1</sup> A''	16.7 <sup>1</sup> B <sub>1</sub>	7.1 <sup>c</sup> (T <sub>0</sub> )
	triplets		29.0 <sup>1</sup> A <sub>2</sub>	26.9 <sup>1</sup> A''	25.1 <sup>1</sup> A''	36.7 <sup>1</sup> A''	58.8 <sup>1</sup> A <sub>2</sub>	69.5 <sup>c</sup>
			12.9 <sup>3</sup> B <sub>1</sub>	11.8 <sup>3</sup> A''	18.7 <sup>1</sup> A'	18.7 <sup>1</sup> A'	24.7 <sup>1</sup> A'	0.05 <sup>3</sup> B <sub>1</sub>
Energy difference 1 000 cm <sup>-1</sup>	<sup>1</sup> B <sub>1</sub> - <sup>3</sup> B <sub>1</sub>	12.0 <sup>b</sup>	10.4	9.1	2.5	11.3	16.7	14.0 <sup>b</sup>
Dipole moment 10 <sup>-30</sup> Cm		0.33 <sup>b</sup>	2.07	1.77	9.27	6.40	7.27	5.70 <sup>b</sup>

<sup>a</sup> Ref. <sup>1</sup>; <sup>b</sup> *ab initio* calculation, ref. <sup>28</sup>; <sup>c</sup> ref. <sup>25</sup>; <sup>d</sup> Experimental value, cited in ref. <sup>28</sup>.

shift of the  $\pi$  orbital there is no occupied  $\pi$ -orbital. The electronic structure resembles those of two weakly interacting silylenes which is indicated by the energies given in Table XI ( $\text{SiH}_2$  in Table XII) and the charge distribution. It is known from both *ab initio* calculations<sup>22</sup> and experiment<sup>48</sup> that the Si=Si bond in disilylene has a double bond character<sup>22</sup> with a rotational barrier<sup>48</sup>. If our parametrization is modified in direction of a stronger resonance with silicon ( $\beta_{\text{Si}}^0 = -4 \rightarrow \beta_{\text{Si}}^0 = -6 \text{ eV}$ ) the occupied  $\pi$  orbital is found at  $-6.0 \text{ eV}$  (*ab initio*:  $-6.7 \text{ eV}$ <sup>22</sup>) and the excitation energy becomes  $16\,100 \text{ cm}^{-1}$ . The bond order for the Si=Si bond (1.87) is only slightly smaller than it is in silaethylene (1.94). We believe, however, that the results for disilylene are actually in favour of our parametrization. Namely, according to *ab initio* calculations mentioned above the proper ground state of the  $\text{Si}_2\text{H}_4$  system is singlet silylsilylene<sup>22</sup>. Assuming this system, the INDO treatment gave a good account of the observed facts. The energies of the occupied orbitals are seen in Table XII to be in fair agreement with the *ab initio* results<sup>22</sup> ( $-7.8$  and  $-10.4 \text{ eV}$ ). Even such a subtle problem as determination of the nature of the ground state was correctly accounted for. *Ab initio* calculations predicted the  $^3A'$  triplet state of this system to lie  $3\,900 \text{ cm}^{-1}$  above the singlet ground state<sup>22</sup>. INDO/S gives for this energy difference  $6\,900 \text{ cm}^{-1}$ .

Table XII also comprises results for silylmethylene and methylsilylene which are isomers of silaethylene. According to the prediction of *ab initio* calculations<sup>8</sup> methylsilylene is more stable than silaethylene. To begin with discussing Table XII we would like to point out the capability of the present INDO/S method of giving a good account of the difference in the electronic structure between silylene and methylene (transition energy,  $^1B_1 - ^3B_1$  energy difference, dipole moment). Even the trend in the energy difference between the lowest triplet state and the lowest singlet state is correctly predicted. On the basis of our calculations we predict methyl- and silylsilylene to have singlet ground states and silylmethylene to have a triplet ground state. Exactly this has been given by *ab initio* calculations<sup>8,22</sup>. If we use the trends in our calculated values for the extrapolation of experimental excitation energies of silylene and methylene to  $\text{HSiSiH}_3$  and  $\text{HCSiH}_3$ , we may expect very low excitation energies in the infrared region for  $\text{HSiSiH}_3$  and  $\text{HCSiH}_3$  and a transition near  $13\,000 \text{ cm}^{-1}$  for  $\text{HSiCH}_3$ . The latter value is of some significance for the discussion of the experiments by Drahnak, Michl and West<sup>49</sup> who assigned an excited state observed at  $18\,700 \text{ cm}^{-1}$  ( $T_0$  value) to  $\text{Si}(\text{CH}_3)_2$ . According to our calculations we would expect a transition energy in  $\text{Si}(\text{CH}_3)_2$  to be lower than in  $\text{HSiCH}_3$ , i.e. below  $13\,000 \text{ cm}^{-1}$ .

As with phenylsilane, a low-lying vacant orbital, which is due to the silyl substitution, is also found with silylsilylene and silylmethylene. This orbital is involved in  $^1A'$  and  $^3A'$  transitions (at  $18\,700$  and  $24\,700$  and  $2\,600$  and  $10\,300 \text{ cm}^{-1}$ , respectively).

Concluding this paragraph, we believe that INDO/S with parameters for silicon provides a reasonable explanation for the known experimental facts and we hope that it will be of some help in identifying new silicon-organic species.

*Note added in proof:* After the completion of our manuscript the results of *ab initio* calculations on SiS excited states became available (J. M. Robbe, H. Lefebvre-Brion, R. A. Gottscho: *J. Mol. Spectr.* 85, 215 (1981)). The calculated excitation energies are the following (in  $10^3 \text{ cm}^{-1}$ , experimental values in parenthesis):  $X^1\Sigma^+$  0.0 (0.0),  $C^1\Sigma^-$  29.4 (29.1),  $D^1\Delta$  29.7 (28.9),  $A^1\Pi$  38.1 (35.0),  $E^1\Sigma^+$  48.0 (41.9).

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Translated by the author (P. Č.).