# Photoelectron Spectra of Some Group 4 Pseudohalides and Related Compounds

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## Received 28th May, 1971

The photoelectron spectra of the pseudohalides RQ (R = H, CH<sub>3</sub>, SiH<sub>3</sub>, GeH<sub>3</sub>, Me<sub>3</sub>Si; Q = NCO, NCS, N<sub>3</sub>) have been recorded. The spectra provide a basis for semi-quantitative discussions of structure and bonding in these compounds, and are consistent with the occurrence of  $(\pi \rightarrow d)\pi$ -bonding in the silicon and germanium compounds.

There are interesting structural variations in the series of pseudohalides MH<sub>3</sub>Q  $(M = C, Si, Ge; Q = NCO, NCS, N_3)$ . All the methyl compounds are bent at N<sup>1</sup>: so are silyl azide<sup>2</sup> and germyl azide.<sup>3</sup> Microwave spectra show that the skeletons of silvl isocyanate <sup>4</sup> and silvl isothiocyanate <sup>5</sup> are linear; the interpretation of electron diffraction results <sup>6</sup> for these molecules is complicated by "shrinkage" due to low-frequency bending vibrations. The ground-state structures of germyl isocyanate  $^{7}$  and isothiocyanate  $^{8}$  are not known with certainty; electron diffraction measurements<sup>9</sup> are again difficult to interpret due to shrinkage effects, but it seems likely that if the skeletons are bent at N, the angles are rather larger than in the methyl compounds. Shrinkage also affects results for trimethylsilyl isocyanate and isothiocyanate, where electron diffraction results interpreted without allowance for shrinkage <sup>10</sup> show apparent angles at N considerably less than 180°. The widening of the angles at N when  $CH_3$  is replaced by  $SiH_3$  may be connected with interaction between electrons at N and empty 3d orbitals at Si; in order to obtain information about the electronic structures of all these molecules we have recorded their photoelectron (P.E.) spectra.

P.E. spectroscopy has been used to determine the ionization potentials of molecules.<sup>11</sup> When the molecules are small, the observed bands can be assigned to ionization from specific molecular energy levels; it is usual to accept Koopmans' theorem <sup>12</sup> and to equate the observed ionization potential (I.P.) with (minus the appropriate orbital energy). For larger molecules, it is only the first I.P. that can be readily associated with ionization from a particular molecular orbital (of course the highest occupied level); careful comparison of the P.E. spectra of a series of related molecules, however, can reveal changes in the positions of bands that may lead to additional assignments to particular energy levels. This is the approach that we have used in the study reported here. We have recorded the spectra of the acids HQ, and our assignments for these, based on a comparison with the spectra of the linear triatomic species CO<sub>2</sub>, COS and N<sub>2</sub>O,<sup>13</sup> follow those of Eland.<sup>14</sup> With the assignments for the acids HQ, it is possible to make plausible assignments in the spectra of MH<sub>3</sub>Q by comparison.

#### EXPERIMENTAL

#### INSTRUMENTS

P.E. spectra between 6 and 21.2 eV were recorded using a Perkin-Elmer PS16 photoelectron spectrometer. HeI (584 Å) radiation was used for excitation; the instrument employs a 127° sector electrostatic analyser to sweep the spectrum of emitted electron energies. The resolution achievable was between 20 meV and 40 meV depending on the exit slit setting. Samples, many of which were air-sensitive and potentially corrosive and explosive, were admitted through a stainless steel needle valve from a vacuum system fitted with Quickfit Rotaflow taps; the sample inlet pressure was adjusted to give optimum signal from a suitable peak in the spectrum. U.-v. spectra were recorded using a Unicam SP 800 spectrometer.

#### PREPARATIONS

HN<sub>3</sub>, HNCO and HNCS were prepared by heating their sodium or potassium salts with stearic acid <sup>15</sup>; the deuterated analogues were obtained using deuterated stearic acid prepared by melting stearic acid with an excess of D<sub>2</sub>O. HNCO was also produced by pyrolysis of (HNCO)<sub>3</sub> under a pressure of N<sub>2</sub>,<sup>16</sup> condensing the product and purifying it by fractional condensation. The purity of HN<sub>3</sub> and of HNCO was confirmed by i.-r. spectroscopy; their P.E. spectra contained no bands attributable to other species. The identity of the product from KNCS and stearic acid was established using mass spectroscopy; the strongest peak appeared at  $m/e = 59(^{1}H^{14}N^{12}C^{32}S^+; 100\%)$  with fragment peaks at  $m/e = 58(^{14}N^{12}C^{32}S^+; 10\%)$ ,  $m/e = 32(^{32}S^+; 20\%)$  and  $m/e = 27(^{1}H^{14}N^{12}C^+; 10\%)$ . The exact mass at m/e = 59 was 58.982 70 (theoretical 58.982 97). The P.E. spectrum was consistent with the identification of the species as HNCS; we were unable to obtain sufficient pressure in a 10 cm gas cell to record an i.-r. spectrum.

The samples of CH<sub>3</sub>NCO and CH<sub>3</sub>NCS were obtained commercially; their i.-r., u.-v. and P.E. spectra showed no impurities.  $CH_3N_3$ ,<sup>17</sup> SiH<sub>3</sub>NCO,<sup>4</sup> SiH<sub>3</sub>NCS,<sup>5</sup> SiH<sub>3</sub>N<sub>3</sub>,<sup>2</sup> GeH<sub>3</sub>NCO,<sup>7</sup> GeH<sub>3</sub>NCS,<sup>8</sup> GeH<sub>3</sub>N<sub>3</sub>,<sup>3</sup> Me<sub>3</sub>SiNCO,<sup>18</sup> Me<sub>3</sub>SiNCS <sup>19</sup> and Me<sub>3</sub>SiN<sub>3</sub> <sup>20</sup> were prepared by established methods and purified by vacuum fractionation. Purities were checked by i.-r. spectroscopy.

#### RESULTS

The bands observed in the P.E. spectra of the fifteen compounds RQ (R = H, CH<sub>3</sub>, SiH<sub>3</sub>, GeH<sub>3</sub>, Me<sub>3</sub>Si; Q = N<sub>3</sub>, NCO, NCS) are given in table 1. Spectra of HQ are given by Eland <sup>14</sup>; our spectra of CH<sub>3</sub>Q, SiH<sub>3</sub>Q and GeH<sub>3</sub>Q are reproduced

compound			vertical I.P.† an	id band type *		_
	band no. 1	1 <i>a</i>	2	3	4	5
HNCO	11.62N	12.30P	15.8P	17.50P	19.24P	
HNCS	9.94	10.3P	13.31P	15.12	6.7.9	
HN <sub>3</sub>	10.72N	12.24P	15.37N	16.8		
CH₃NCO	10.67N	11.20	14.7	16.1P	16.7	18.0
CH <sub>3</sub> NCS	9.37		12.6	14.6	15.6P	17.5
CH <sub>3</sub> N <sub>3</sub>	9.81N	11.32	14.4	14.2	16.6	17.9
SiH₃NCO	11.10P		13.1P	15.7P	17.1	
SiH₃NCS	9.54		12.5	13.9P	14.7	15.9
SiH <sub>3</sub> N <sub>3</sub>	10.33	11.00	13.0	15.0	16.2	
GeH₃NCO	10.76		12.8	15.3	16.9	
GeH <sub>3</sub> NCS	9.14		12.3	13.4	14.1	15.5
GeH <sub>3</sub> N <sub>3</sub>	10.01	10.77	12.8	14.7	16.2	—
Me <sub>3</sub> SiNCO	10.3		11.5)	broad band w	ith sharp on	set at
Me <sub>3</sub> SiNCS	9.3		11.0	at 12.5 eV	extending to	about
Me <sub>3</sub> SiN <sub>3</sub>	9.7	10.3	11.2)	16 eV.	0	

#### TABLE 1

\* for band types N and P see text.  $\dagger$  I.P. in eV ( $\pm 0.02$  eV or  $\pm 0.1$  eV depending on number of figures listed).



FIG. 1.-Photo-electron spectra of MH<sub>3</sub>NCO.



FIG. 2. — Photo-electron spectra of  $MH_3NCS$ . Dashed peaks vary in relative intensity and are assigned to impurity. For SiH<sub>3</sub>NCS, section of spectrum 16-19 eV was recorded at higher detector sensitivity.

in fig. 1-3. Some bands can clearly be identified as largely "non-bonding" in character—the strongest feature corresponds to the adiabatic transition in which no change of vibrational quanta occurs. These are denoted by N in table 1. Other



FIG. 3.—Photo-electron spectra of  $MH_3N_3$ . Section of curve for  $CH_3N_3$  13-19 eV recorded at higher detector sensitivity.

bands show the broad outline expected for excitation of bonding (or anti-bonding) electrons, and in some cases a progression in one vibration frequency appears. "Bonding" bands with a progression are denoted by P.

#### DISCUSSION

## MOLECULAR ORBITALS

We confine our discussion to the m.o. principally derived from the valence shell orbitals of the atoms involved, as excitation at 21.2 eV is unable to provide information about inner shell electrons, whose ionization potentials are expected to be of the order of 100 eV or more. In COS the molecular  $\sigma$ -orbitals are derived from 2s and  $2p_z$  of oxygen, 2s and  $2p_z$  of carbon, 3s and  $3p_z$  of sulphur; the pattern of occupied molecular orbitals may be described (in order of decreasing stability) as  $1\sigma$ ,  $2\sigma$ ,  $3\sigma$ ,  $4\sigma$ ,  $1\pi$  and  $2\pi$ . It is possible that 3d-orbitals of sulphur may be significantly involved in  $\sigma$  and  $\pi$  levels, but the non-quantitative treatment used here does not require them. A similar set of m.o. may be derived for CO<sub>2</sub> and N<sub>2</sub>O. We use such a set of energy levels as a basis for our treatment of the pseudohalogen groups

in our compounds; the complication is that bent pseudohalides belong to the point group  $C_s$  rather than the  $C_{\infty v}$  of COS. The  $\sigma$  levels then become a', while the  $\pi$ levels split into a' and a'' components. We denote the levels as, e.g.,  $4\sigma(a')$  in a bent molecule, and where necessary distinguish the components derived from the  $n\pi$  level as  $n\pi(a')$  and  $n\pi(a'')$ . The relative energies of the  $\sigma$  and  $\pi$  sets need not remain fixed in a series of compounds, and we believe that in the azides, as in N<sub>2</sub>O,<sup>12</sup> the  $1\pi$  level is lower in energy than the  $4\sigma$  level.

The above basis suffices for the acids HQ: for the MH<sub>3</sub> derivatives we must include the MH levels. These are well separated (as in the parents  $MH_4$ )<sup>21</sup> into sets derived from the (*np*) orbitals of M, which we denote by Mp, and from the (*ns*) orbitals of M, which we denote by Ms. In a bent molecule, Ms is of symmetry class a', while Mp has two components Mp(a') and Mp(a''). In a linear species Ms becomes  $\sigma$ , Mp becomes  $\pi$ .

Of these orbitals, some are expected to lie below -21.2 eV, and will not give rise to bands in our spectra. In general  $1\sigma$ ,  $2\sigma$  and Ms (M=C) are likely to be of low energy. In addition, when M is Si or Ge, Ms may be expected to give rise to very weak bands in the region between 15 and 19 eV as in the spectra of  $MH_4$ .<sup>21</sup> The discussion that follows concentrates on the levels  $3\sigma$ ,  $4\sigma$ ,  $1\pi$ ,  $2\pi$  and Mp. Mixing between "pseudohalide" and "MH<sub>3</sub>" orbitals of the same symmetry will occur and it will not always be possible to assign a band to one of these levels rather than another.

### ASSIGNMENT OF BANDS TO MOLECULAR ENERGY LEVELS

We take as our starting point the vertical ionization potentials <sup>13</sup> for CO<sub>2</sub>, COS and N<sub>2</sub>O (table 2). The highest energy level for each is  $2\pi$ , with a gap of over 3 eV before the next level. The spectra of the acids HNCO, HNCS and HN<sub>3</sub> each contain a *pair* of bands (1 and 1*a*) of I.P. between 10 and 12 eV, which are separated in each case from the next band by about 3 eV. We assign these to the two components  $2\pi(a')$  and  $2\pi(a'')$  in a bent ion that are derived from the  $2\pi$  level of a linear triatomic.

#### TABLE 2

level	vertical I.P. CO <sub>2</sub>	of corresponding COS	band (eV) N <sub>2</sub> O
2π	13.79	11.19	12.89
1π	17.32	15.53	18.24
$4\sigma$	18.08	16.04	16.39
$3\sigma$	19.40	17 <b>.9</b> 6	20.11

The difference in vertical I.P. between the a' and the a'' components is larger (1.5 eV) for HN<sub>3</sub> than for HNCO (0.7 eV) and HNCS (0.4 eV). This is consistent both with a narrower angle in HN<sub>3</sub><sup>+</sup> than in HNCO<sup>+</sup> (as in the neutral molecules <sup>22</sup>), and with greater concentration of the  $2\pi a''$  component on the N atom bound to H in HN<sub>3</sub><sup>+</sup> than in HNCO<sup>+</sup> or HNCS<sup>+</sup>. The shape of the component at lower I.P. is of the non-bonding type in each case, while that of the component at higher I.P. is of bonding type. We accordingly assign the second component as  $2\pi(a'')$ , which cannot be involved in NH bonding, and the first component as  $2\pi(a'')$ , which cannot be involved in that bond.

In the spectra of the MH<sub>3</sub> derivatives, we find either one or two bands, designated 1 and 1*a*, in the region 9-12 eV; we assign these to the " $2\pi$ " level or to its two components. The spectra of all the azides we have studied show two resolved components; all the molecules concerned are bent at N, and the splitting of the

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	GeH <sub>3</sub> N <sub>3</sub>	10.01	10.77	16.2	14.7	1	12.8	
	GeH <sub>3</sub> NCS	9.14		13.4	14.1	$15.5^{*}$	12.3	
	GeH <sub>3</sub> NCO		10.76	15.3	16.9	1	12.8	
VELS (eV)	SiH <sub>3</sub> N <sub>3</sub>	10.33	11.00	16.2	15.0	ł	13.0	text).
ENERGY LE	SiH <sub>3</sub> NCS	9.54		13.9	14.7	15.9*	12.5	om M <sub>S</sub> (see
MOLECULAR	SiH <sub>3</sub> NCO	11.10		15.7	17.1		13.1	tribution fro
TIALS FOR	CH <sub>3</sub> N <sub>3</sub>	9.81	11.32	16.6	15.2	17.9	14.4	antial con
ON POTEN	<b>CH</b> <sub>3</sub> NCS	9.37	1	12.6	14.6	17.5	15.6	udes subst
-IONIZATI	CH <sub>3</sub> NCO	10.67	11.20	14.7	16.1	18.0	16.7	bably inclu
TABLE 3	HN <sub>3</sub>	10.72	12.24	16.8	15.47		I	* pro
	HNCS	9.94	10.3	13.31	15.12	1	1	
	HNCO	11.62	12.30	15.8	17.50	19.24	1	
	energy level	$2\pi(a'')$	$2\pi(a)$	$1\pi$	4σ	30	$M_{p}$	

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photoelectron bands at lowest I.P. indicates that the ions are all bent at N too. There are two bands in the spectrum of methyl isocyanate, but only one in the spectra of silyl or germyl isocyanates.

It seems that CH<sub>3</sub>NCO<sup>+</sup>, like CH<sub>3</sub>NCO is bent at N; SiH<sub>3</sub>NCO<sup>+</sup> and GeH<sub>3</sub>NCO<sup>+</sup> may be linear or nearly so, but we do not know the limiting skeletal angle that would allow us to resolve the a' and a'' components of this level. In the spectra of all three isothiocyanates only one band is observed in this region, but it is broad and could easily include a weaker component separated by 0.4 eV (as in HNCS) or less from the main peak.

In the spectra of the trimethylsilyl derivatives we expect,<sup>23</sup> and find, a band near 11 eV associated with the Me<sub>3</sub>Si group, but at lower I.P. we find two bands in the spectra of the azide, and one in those of the isocyanate and the isothiocyanate. These bands in the azide and isocyanate are shifted to lower I.P. by about 0.8 eV as compared with the analogous bands in the SiH<sub>3</sub> derivatives, presumably by interaction with the Me<sub>3</sub>Si levels near 11 eV. The  $2\pi$  band in Me<sub>3</sub>SiNCS is only 0.2 eV to lower I.P. than in SiH<sub>3</sub>NCS, presumably because of the greater energy separation from the Me<sub>3</sub>Si level near 11 eV.



FIG. 4.-Energy levels of CO<sub>2</sub> and RNCO.

For the bands at higher I.P., we find 3 bands in the spectrum of HNCO, which we can assign to  $3\sigma$ ,  $4\sigma$ , and  $1\pi$ . Of these three, the band at highest I.P. is almost certainly due to  $3\sigma$ , and calculation,<sup>24</sup> as well as comparison with CO<sub>2</sub>, suggests that the order of I.P. in HNCO should be  $2\pi < 1\pi < 4\sigma < 3\sigma$ . The bands 2, 3 and 4 are thus assigned respectively to  $1\pi$ ,  $4\sigma$  and  $3\sigma$ . The absence of observed splitting of  $1\pi$  into  $1\pi(a')$  and  $1\pi(a'')$  is noted; it may be that the breadth of the band, due to the excitation of a bonding electron, obscures the second component at higher I.P.

In HNCS, only 2 bands appear in this region; we assign them by analogy with HNCO and COS to  $1\pi$  (at lower I.P.) and  $4\sigma$  (at higher I.P.). In HN<sub>3</sub>, by analogy with N<sub>2</sub>O we might expect the order of  $1\pi$  and  $4\sigma$  to be reversed; band 2 is indeed of non-bonding type, which is consistent with its assignment to  $4\sigma$ , while band 3, assigned to  $1\pi$ , again shows no discernible splitting.





In the MH<sub>3</sub> derivatives we expect a band due to ionization from Mp to fall in the same region as  $4\sigma$  and  $1\pi$  and between 12 eV and 17.4 eV we indeed find 3 bands in each of the nine spectra. All the silyl and germyl compounds give a band around 13 eV that we may assign as Mp by analogy with MH<sub>4</sub><sup>21</sup> and MH<sub>3</sub>X<sup>25</sup> (X = Cl, Br, I). Assuming that the  $1\pi$  and  $4\sigma$  retain the relative order found in the acids HQ, we may assign bands 3 and 4 in these compounds. In the CH<sub>3</sub> compounds, band 3 is narrow in each case as compared with bands 2 and 4 and may be assigned to  $4\sigma$ ; assignment of Mp and  $1\pi$  then depends on whether  $1\pi$  is expected at higher I.P. (azide) or lower I.P. (isocyanate and isothiocyanate) than  $4\sigma$ . This "assignment" cannot take account of the mixing that occurs among all a' levels and among all a" levels. Nevertheless, the spectra can be interpreted on this simple basis. No splitting of bands due to Mp or to  $1\pi$  in the spectra of the methyl compounds is observed, despite splittings in the  $2\pi$  bands of CH<sub>3</sub>N<sub>3</sub> and CH<sub>3</sub>NCO (see above).

In the CH<sub>3</sub> compounds and in SiH<sub>3</sub>NCS and GeH<sub>3</sub>NCS an additional band appears (band 5). We assign this to  $3\sigma$ , since in the silvl and germyl compounds Ms is expected in this region and may well contribute to the observed band. It is difficult to explain the sharp fall in I.P. between CH<sub>3</sub>NCS and SiH<sub>3</sub>NCS unless involvement of Si 3s is taken into account.

The final "assignment" of bands to the expected energy levels is given in table 3 and the trends in the derivatives of each pseudohalogen shown in fig. 4-6.

### VIBRATIONAL STRUCTURE

In general, the spectra of the acids show vibrational fine-structure (due to excita tion to vibrationally excited states of the ion) on almost every band; the methyl compounds show fine-structure only on the  $2\pi$  (a'') band, and the silyl compounds show no consistent pattern. The germyl and trimethylsilyl compounds give no fine structure at all; this may be attributed to the greater number of vibrations in the larger ions that may be excited.



FIG. 6.—Energy levels of N<sub>2</sub>O and RN<sub>3</sub>.

For the bands in order of increasing I.P., we find typical non-bonding vibration structure on  $2\pi(a'')$  in HNCO, HN<sub>3</sub>, CH<sub>3</sub>NCO and CH<sub>3</sub>N<sub>3</sub>, comparable with the structure on the  $2\pi$  bands in CO<sub>2</sub> and N<sub>2</sub>O.<sup>13</sup> The frequencies excited are shown in table 4. The two lower frequencies may reasonably be assigned respectively to  $v_s$  and  $v_{as}$ , where  $v_s$  is the symmetric and  $v_{as}$  the antisymmetric pseudohalogen stretching vibration, or the corresponding vibration for the triatomic. Deuteration of HNCO and HN<sub>3</sub> did not affect the highest frequency component, which therefore could not be assigned exclusively to vNH. In HNCO it may reasonably be assigned to  $(v_s + v_{as})$ but in HN<sub>3</sub> and DN<sub>3</sub> the agreement between the frequencies for this component and the sum of the frequencies assigned to  $v_s$ . and  $v_{as}$  is very poor. However, the infra-red spectra of gaseous HN<sub>3</sub> and DN<sub>3</sub> are unexpectedly complicated near 3300 cm<sup>-1</sup>, so various combinations could be involved. The corresponding bands in HNCS and CH<sub>3</sub>NCS are comparatively broad, probably because of spin-orbit coupling at S, and no fine-structure was resolved.

The bands assigned as  $2\pi(a')$  in HNCO, HNCS and HN<sub>3</sub> all show a typical "bonding" contour, with a progression in a frequency of about 600 cm<sup>-1</sup> (table 4).

It seems probably that this is the NH deformation mode of the ion in each case: after deuteration the fine structure could no longer be detected.

Progressions appear on the bands assigned to  $1\pi$  in HNCO, HNCS, SiH<sub>3</sub>NCO and SiH<sub>3</sub>NCS. As with the progressions on the corresponding bands in CO<sub>2</sub> and COS<sup>13</sup> it seems reasonable to assign these to the symmetric pseudohalogen stretch, reduced because of the removal of a  $\pi$  bonding electron. No such simple progressions were observed for CH<sub>3</sub>NCO and CH<sub>3</sub>NCS : we suggest that considerable mixing between  $1\pi$  and Mp is responsible both for this and for the irregularities in  $1\pi$  band positions for the CH<sub>3</sub> compounds.

TABLE 4V	IBRATIONAL STRU	CTURE (AL	L INTERVAI	.s in cm <sup>−1</sup> ,	$\pm 50 \text{ cm}^{-1}$ )	
band	compound		vibrational	frequencies		
$2\pi(a'')$	HNCO	1080	19	80	3200	
	DNCO	1130	20	70	3230	
	CH <sub>3</sub> NCO	1150	21	80	3260	
	assigned to	vs	v	15	$v_{s} + v_{as}$	
	$HN_3$	840	17	80	3000	
	$CD_3$	870	18	90	3060	
	CH <sub>3</sub> N <sub>3</sub>	<b>9</b> 10	18	20		
	assigned to	vs	v	15		
$2\pi(a')$	HNCO	progr	ession in 6	$10 \text{ cm}^{-1}$		
	HNCS	progression in 600 cm <sup>-1</sup>				
	$HN_3$	progr	ession in 5	70 cm <sup>-1</sup>		
$1\pi$	HNCO	D progression in 1120 cm <sup>-1</sup>				
	HNCS progression in 850 cm <sup>-1</sup>					
	SiH <sub>3</sub> NCO progression in 790 cm <sup><math>-1</math></sup>					
	SiH <sub>3</sub> NCS	progr	ression in 4	$90 \text{ cm}^{-1}$		
4σ	HNCO	progr	ession in 4	$60 \text{ cm}^{-1}$		
	CH <sub>3</sub> NCO	progr	ession in 7	$00 \text{ cm}^{-1}$		
	$HN_3$	560	900	2340	2800	
	$DN_3$	480	1000	2280	2800	
	assigned to	δ	$v_s$	$v_{as}$	$v_{as} + \delta$	
3σ	HNCO	progr	ession in 1	000 cm <sup>-1</sup>		
	SiH <sub>3</sub> NCS	2 pea	ks, separat	ion 740 cn	n-1	
	SiD <sub>3</sub> NCS	2 pea	ks, separat	ion 600 cn	n <sup>-1</sup>	

Only HN<sub>3</sub>, HNCO and CH<sub>3</sub>NCO showed fine structure on the band assigned to  $4\sigma$ . HNCO gives a progression in 460 cm<sup>-1</sup>, which is probably a deformation at N or C: this implies that here  $4\sigma$  may be mixing appreciably with  $2\pi(a')$ , which has the same symmetry. In CH<sub>3</sub>NCO, the  $4\sigma$  band is overlapped by the band assigned as Mp, but a few peaks possibly belonging to a progression can be distinguished. In HN<sub>3</sub> as in N<sub>2</sub>O,<sup>13</sup> the  $4\sigma$  level gives a *non-bonding* band, and several vibrational levels can be distinguished in the spectra of both the normal and the deuterated compound. The frequencies found are readily assigned in terms of the fundamental vibrations of the ground state molecules.

The  $3\sigma$  band in HNCO shows a progression in  $1020 \text{ cm}^{-1}$ ; this is probably the symmetric NCO stretch. In SiH<sub>3</sub>NCS, the  $3\sigma$  band has 2 peaks of equal intensity, whose separation is reduced on deuteration, followed by a much broader component;

the splitting is therefore assigned to excitation of the SiH<sub>3</sub> rocking mode, rather than to spin-orbit coupling.

The Mp band in  $SiH_3NCO$  shows a complicated structure that may be assigned as 2 overlapping progressions in  $1100 \text{ cm}^{-1}$ . We suggest that the vibration involved is the symmetric  $SiH_3$  deformation, while the doubling is ascribed to the expected Jahn-Teller splitting. A similar band is found in the P.E. spectrum of silvl acetylene.<sup>23</sup> The separation of the two (0-0) transitions is 630 cm<sup>-1</sup>. Unfortunately, deuteration reduces the vibration frequency so that the two progressions can no longer be distinguished; the resulting structure is still irregular and is no doubt composed of two similar progressions. It is possible that the fine-structure mentioned above as occurring on the band in the spectrum of CH<sub>3</sub>NCO that we have assigned as  $4\sigma$ can be explained in the same way; it would then be necessary to interchange the assignments of  $4\sigma$  and Mp for CH<sub>3</sub>NCO. As the skeleton of CH<sub>3</sub>NCO<sup>+</sup> is not linear, however, the doubling would be ascribed not to Jahn-Teller distortion but to the a' and a'' components of Mp.

#### U.-V. SPECIRA

Interpretation of the u.-v. spectra of the pseudohalide molecules has been hampered by the impossibility of separating effects due to changes in the occupied and the unoccupied levels involved. With our "observed" values for the energies of the occupied levels, we may deduce the positions of the unoccupied levels involved in the observed electronic transitions.

Bands observed in the non-vacuum u.-v., corresponding to transition energies up to about 52 000 cm<sup>-1</sup> (6.5 eV) are due to transitions from the top occupied  $\pi$ level (or its two components) to the lowest unoccupied levels (probably an antibonding  $\pi^*$  level or its components in most cases, but possibly also MH anti-bonding levels or higher atomic levels such as 3d orbitals of Si or S). In table 5 we list the

			TABLE 5		
compound	1 2π(a")	occupied energy lev $2\pi$	els (eV) $2\pi(a')$	transition energies (eV)	unoccupied levels (eV)
CO <sub>2</sub>		-13.79		8.4 <i>a</i>	- 5.4
HNCO	-11.6		-12.3	>6.5	above $-5.1$
CH <sub>3</sub> NCO	-10.7		-11.2	5.6	-5.1
SiH <sub>3</sub> NCO		-11.10		6.4	-4.7
GeH <sub>3</sub> NCO		-10.8		>6.5	above $-4.3$
Me <sub>3</sub> SiNCO		-10.3		>6.5	above $-3.8$
COS		-11.2		6.2 <i>a</i>	-5.0
HNCS	- 9.9		-10.3	5.0, 6.3	-4.9, -4.0
CH₃NCS		-9.4		5.1, 6.2	-4.3, -3.2
SiH <sub>3</sub> NCS		-9.5		5.0	-4.5
GeH <sub>3</sub> NCS		-9.1		5.0, 5.9	-4.1, -3.2
Me <sub>3</sub> SiNCS		-9.3		5.1, 6.4	-4.2, -2.9
$N_2O$		-12.9		6.8 <i>a</i>	-6.1
HN <sub>3</sub>	10.7		-12.2	4.7, 6.2	-6.0, -6.0
CH <sub>3</sub> N <sub>3</sub>	9.9		-11.3	4.3, 5.7	-5.5, -5.6
SiH <sub>3</sub> N <sub>3</sub>	-10.3		-11.0	5.9	-5.1
GeH <sub>3</sub> N <sub>3</sub>	-10.0		-10.8	4.9, 6.0	-5.1, -4.8
Me <sub>3</sub> SiN <sub>3</sub>	-9.6		-10.2	4.9, 5.8	-4.7, -4.4

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energies of the  $2\pi$  level or its components, the observed transition energies (measured at maximum absorption to give "vertical" values) and the deduced energies of the upper levels of the transitions. Where two components of  $2\pi$  and two transitions are observed we have assumed that the two transitions occur one from each level, the lower energy transition connecting the highest occupied level with the lowest unoccupied level. The deduced unoccupied levels are shown as such in the energy level correlation diagrams (fig. 4-6). The results are still incomplete, as some of the relevant u.-v. bands clearly lie beyond the region investigated, and we do not believe that detailed analysis is profitable as yet.

#### EFFECT OF M ON I.P.

We may consider the interaction of an occupied m.o. principally involving the  $MH_3$  group with an occupied m.o. principally involving the pseudohalide group in two parts. First, electron repulsion will cause an increase in the energies of both m.o., which will depend purely on the spatial relationship of the groups, increasing as the bond angle at N decreases and as the MN bond length decreases. Secondly, overlap of the two orbital wavefunctions will cause mixing, and the energies of the two resultant orbitals will be more separated than those of the "pure"  $MH_3$  and pseudohalide orbitals. The extent of this effect will vary both with the spatial relationship of the groups (including changes in orbital overlap) and with the energy gap between the "pure" orbitals.

<b>FABLE 6.</b> —SEPARATION	OF	ENERGY	LEVELS	(eV)	IN	MH <sub>3</sub>	Q
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Q	levels	M = C	Si	Ge
NCO	$2\pi(a'')$ —Mp $2\pi(a')$ —Mp $1\pi$ —Mp $4\sigma$ —Mp	$\left. \begin{array}{c} -6.0 \\ -5.5 \end{array} \right\}$ -2.0 -0.6	-2.0 +2.6 +4.0	-2.0 -2.5 +4.1
NCS	2π—Mp 1π—Mp 4σ—Mp	-6.2 -3.0 -1.0	-3.0 +1.4 +2.1	-3.2 +1.1 +1.8
N <sub>3</sub>	2π(a")—Mp 2π(a')—Mp 4σ—Mp 1π—Mp	-4.6 -3.1 +0.8 +2.2	-2.7 -2.0 +2.0 +3.2	-2.8 -2.0 +1.9 +3.4

Thus, for the effects of changing M from C to Si on the interaction of Mp with the various pseudohalide levels, it seems likely that the first effect will decrease as the bond angle at N and the MN bond length increase. It is more difficult to predict how the extent of mixing will be affected; overlap integrals are likely to decrease, whereas the energy gaps between MH orbitals and the higher  $\pi$  levels depend on the particular systems concerned. We may obtain some idea of the likely extent of mixing by considering the observed spectra, both in themselves and as series.

Thus, from table 3, the *resultant* energy separations of Mp from various pseudohalide orbitals are as shown in table 6. Orbital mixing is impossible between Mp and  $a\sigma$  orbital in a molecule with a linear skeleton, but the energy separations are included for completeness. In any case, better overlap may well be expected with  $\pi$  type orbitals, especially their a' components, in bent molecules.

The general conclusions drawn from table 6 is that on the basis of energy, orbital mixing is most important between Mp and  $4\sigma$  in CH<sub>3</sub> compounds, between Mp and  $2\pi$  in SiH<sub>3</sub>NCO and GeH<sub>3</sub>NCO, between Mp and  $1\pi$  in SiH<sub>3</sub>NCS and GeH<sub>3</sub>NCS and between Mp and  $both 2\pi(a')$  and  $4\sigma$  in SiH<sub>3</sub>N<sub>3</sub> and GeH<sub>3</sub>N<sub>3</sub>. The main effects on the I.P. we may expect are (a)  $2\pi$  in SiH<sub>3</sub>NCO and GeH<sub>3</sub>NCO will be raised in energy by interaction with Mp; (b)  $1\pi$  and  $4\sigma$  in CH<sub>3</sub>NCO will be raised in energy; (c)  $1\pi$  in SiH<sub>3</sub>NCS and GeH<sub>3</sub>NCS will be *lowered* in energy; (d)  $4\sigma$  in CH<sub>3</sub>NCS will be raised in energy; (f)  $1\pi$  in CH<sub>3</sub>N<sub>3</sub> will be lowered in energy. These effects may well explain some of the irregularities shown by the I.P. of the pseudohalide levels as M varies (see fig. 4-6).

A second form of interaction may occur between occupied orbitals of  $MH_3$ and empty pseudohalide orbitals (hyperconjugation). This will tend to (a) increase the bond angle at N; (b) lower the Mp level energy; (c) be less important for Si or Ge than for C because of the shorter M—N bond length for C, which should lead to better overlap; (d) be more effective in NCO and NCS compounds than in azides because of the smaller bond angle at N in azides. We can detect no trends in the I.P. consistent with such a process.

The third form of interaction is that between empty orbitals of the MH<sub>3</sub> group and the occupied pseudohalide orbitals. The available empty orbitals are : (a) antibonding  $Mp^*$  orbitals in each case ; (b) orbitals of the next shell for each M atom ( $Mp^1$  and  $Ms^1$ ); (c) Si 3d or Ge 4d orbitals with no valence-shell counterpart for C.

The effects of  $\sigma$ - donation in this direction would be difficult to detect, so we confine discussion to  $\pi$ -donation from the pseudohalide  $2\pi$  or  $1\pi$  levels to  $Mp^*$ ,  $Mp^1$  or Md orbitals of  $\pi$  symmetry relative to the M—N bond. It seems clear that the extent of such donation of class (a) and (b) above will depend on the overlap of the relevant orbitals, and this may well be *less* for M=Si or Ge than for M=C simply because of the longer M—N bonds for heavier M. This will apply equally to donation to  $Mp^*$  or  $Mp^1$ , so any effect of this nature that is greater for M=Si than for M=C is more likely to be due to donation to Md. The observed effect will simply be to lower the orbital energy of the pseudohalide  $\pi$  level and to render it "M—N bonding".

Q	level	M = C	Si	Ge
NCO	$2\pi$	10.93*	11.10	10.76
	$1\pi$	14.70	15.70	15.28
NCS	$2\pi$	9.37	9.54	9.14
	1π	12.58	13.90	13.40
N <sub>3</sub>	$2\pi$	10.57*	10.67*	10.39*
	$1\pi$	16.60	16.22	16.16

TABLE 7.—VERTICAL I.P. OF  $\pi$  LEVELS IN MH<sub>3</sub>O

\* mean of two components.

The I.P. of  $2\pi$  and  $1\pi$  levels are collected in table 7; the mean of the values for  $2\pi(a'')$  and  $2\pi(a')$  are taken where two bands are observed. The I.P. for a  $\pi$  level adjacent to silicon is greater than for the same  $\pi$  level adjacent to carbon, except for  $1\pi$  of the azide. We recall that we have predicted that  $Mp - \pi$  interaction will shift  $1\pi$  to higher I.P. in CH<sub>3</sub>N<sub>3</sub> and in SiH<sub>3</sub>NCS, and will lower the I.P. for  $2\pi$  in SiH<sub>3</sub>NCO and SiH<sub>3</sub>N<sub>3</sub>, so the overall pattern that emerges is striking.

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It has often been suggested that the wide angles at nitrogen in SiH<sub>3</sub>NCO and SiH<sub>3</sub>NCS are associated with  $(\pi \rightarrow d)$   $\pi$ -bonding from the pseudohalide group to silicon. Our results seem consistent with this; the changes in ionization potential of the  $2\pi(a'')$  electron from CH<sub>3</sub>NCO or CH<sub>3</sub>NCS to the corresponding silv compounds, coupled with the change in shape of the associated P.E. band from the "non-bonding" type in the methyl compounds to the "bonding" type in the silyl derivatives, imply that the silvl group acts as a  $\pi$  electron acceptor. The shapes of the bands in the germyl compounds suggest that the germyl group also acts as a  $\pi$ -acceptor. On the other hand, these arguments depend on the assumption that Koopmans' theorem applies equally to methyl, silyl and germyl compounds; this assumption has yet to be tested.

Table 1 shows that the first I.P. for the Me<sub>3</sub>Si derivatives are lower than those for the CH<sub>3</sub> compounds. We need not postulate absence of  $(\pi \rightarrow d)\pi$  bonding in trimethylsilyl compounds; interaction with the Me<sub>3</sub>Si level near 11 eV could raise the  $2\pi$  level in each case. The difference in first I.P. between corresponding Me<sub>3</sub>Si and CH<sub>3</sub> compounds is least in the isothiocyanates, where the separation of  $2\pi$  from the 11 eV level is greatest. Direct comparison of data for Me<sub>3</sub>Si and CH<sub>3</sub> compounds is thus frustrated by differing degrees of electronic interactions and also by obscuring of the lower levels  $1\pi$  and  $4\sigma$  by Me<sub>3</sub>Si bands in the region 12.5-16 eV. This illustrates the danger of comparing I.P. of Me<sub>3</sub>Si compounds with their methyl analogues; even comparison with t-butyl species is of doubtful validity, except to illustrate differences in interactions between C-C and C-Si systems.

#### CONCLUSIONS

Detailed comparisons within the set of similar molecules and also with simple but related molecules can make possible satisfactory assignments of P.E. bands in moderately complex molecules without the aid of computed energy levels. In the compounds studied, interactions between energy levels must be taken into account to explain the details of band positions, and we have distinguished between occupied-The occupied orbital interactions and occupied-unoccupied orbital interactions. most clear-cut of these interactions is  $(\pi \rightarrow d)\pi$  bonding between  $\pi$  levels of the pseudohalide and empty 3d orbitals of appropriate symmetry on Si, for which we have presented evidence based on I.P. values as well as band splittings and shapes. The evidence for similar interaction involving the germanium 4d orbitals is purely qualitative but is almost equally convincing.

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