# THE PHOTOELECTRON SPECTRA OF SEVERAL METHYLGERMANIUM AND PERFLUOROMETHYLGERMANIUM IODIDES

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#### ABSTRACT

He(I) photoelectron spectra are reported for the series of compounds  $(CH_3)_3GeI$ ,  $(CH_3)_2GeII$ ,  $CH_3GeH_2I$  and  $(CH_3)_2GeI_2$ , as well as for  $(CF_3)_3GeI$ ,  $(CF_3)_2GeI_2$  and  $CF_3GeI_3$ . He(II) photoelectron spectra are also reported for all of the perfluoromethyl compounds. Assignments are proposed on the basis of semi-empirical CNDO/2 calculations, band shapes and changes of relative intensities between the He(I) and He(II) spectra. Comparisons are drawn with the related bromides and chlorides.

### INTRODUCTION

We have previously reported the He(I) and He(II) excited photoelectron spectra of various methylgermanium and perfluoromethylgermanium halides including the series  $(CH_3)_3GeX$  [1],  $(CH_3)_2GeX_2$  [2],  $CH_3GeX_3$  [3] (X=F, Cl, H),  $(CH_3)_{4-n}GeBr_n$  [4], and  $(CF_3)_{4-n}GeX_n$  (X=Cl, Br) [5]. This study extends the work to a selection of methylgermanium and perfluoromethylgermanium iodides. Relatively few studies on iodides have been reported recently. Three of interest have involved variable energy and angle resolved photoelectron spectroscopy of  $CF_3I$  [6,7], HI and  $CH_3I$  [8].

### EXPERIMENTAL

The spectra were recorded either on a McPherson ESCA-36 photoelectron spectrometer using, when possible, both He(I) and He(II) excitation or on a

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Perkin-Elmer PS18 which is equipped only for He(I) spectra. The peaks were calibrated against the argon lines at 15.76 and 15.94 eV. Data of good quality were obtained in both the He(I) and He(II) modes for  $CF_3GeI_3$ ,  $(CF_3)_2GeI_2$ and  $(CF_3)_3GeI$  and in the He(I) mode for  $(CH_3)_3GeI$ ,  $(CH_3)_2GeHI$  and  $CH_3GeH_2I$ . The He(II) mode for the latter three compounds was not of much help because of a high signal-to-noise ratio. The He(I) spectrum of  $(CH_3)_2GeI_2$ was also of marginal quality while the spectra of  $CH_3GeHI_2$  and  $CH_3GeI_3$  were of such poor quality, possibly because of the decreasing volatility of the iodides, that it was decided not to include them in this work. In general, but particularly

with the McPherson spectrometer, longer runs designed to accumulate better data resulted in a deterioration in the response of the detector and considerable loss of resolution. In the interests of economy and of other users we had to restrict the length of the runs.

CNDO/2 calculations were performed on those species that contained only one iodine atom by utilizing the program GEOMO-FORTRAN IV developed by Rinaldi [9]. In accord with previous work [1-5], a non-standard basis that did not include *d*-orbitals was used for germanium and iodine. For germanium, a Slater exponent of 1.69510 was used for both s and p orbitals with a beta integral of 12.88930 eV. The core integrals (eV) of s (12.20990) and p (4.04510) produced satisfactory results in a trial run on GeH<sub>4</sub>. For iodine, a Slater exponent of 2.39330 was used for both s and p orbitals with a beta integral of 17.96000 eV. The core integrals (eV) of s (17.70400) and p (6.42380) orbitals produced satisfactory results in a trial run on HI. Our experience with the related compounds [1-5] suggested that if the CNDO/2 computed eigenvalues were adjusted by recognition of the parentages of the orbitals (arbitrarily reduced by 29% for C, H and Ge and by 16% for I and H') then a closer correspondence with the value and order of the experimental ionization energies could be anticipated. The coordinates of the atoms were calculated using bond lengths previously reported in the literature for related compounds [10-12]. All tetrahedral angles were assumed because we have already noted [1] that the use of exact values of angles, where known, results in insignificant changes in eigenvalues and eigenvectors. This is also true for the use of the optimization routine, so that this was not utilized, leading to a considerable saving of computer time.

The perfluoromethylated germanium iodides were prepared as described previously [13]. The methylgermanium iodides  $(CH_3)_2GeI_2$ ,  $(CH_3)_3GeI$ ,  $CH_3GeHI_2$  and  $CH_3GeH_2I$  were prepared by the exchange reaction of hydrogen iodide and the corresponding bromo derivatives based on details described in an earlier publication [14]. The hydrido(bromo)methyl germanes are not commercially available and were prepared by the controlled bromination of methylgermane using boron tribromide [15]. Methylgermane and dimethylgermane were obtained from  $CH_3GeBr_3$  and  $(CH_3)_2GeBr_2$  by lithium aluminum hydride reduction in dry n-butyl ether. The reaction of dimethylgermane with hydrogen iodide was used to prepare  $(CH_3)_2$ GeHI [16]. Vibrational and <sup>1</sup>H or <sup>19</sup>F NMR spectroscopy confirmed that the purity of the compounds was better than 98% in terms of hydrogen- or fluorine-containing materials [13,15,16].

# **RESULTS AND DISCUSSION**

The experimental vertical ionization energies and the predicted eigenvalues of the orbitals as calculated by the adjusted CNDO/2 method are presented in Table 1 for  $(CH_3)_3$ GeI,  $(CH_3)_2$ GeHI and  $CH_3$ GeH<sub>2</sub>I, along with the designated symmetries and principal contributions to the molecular orbitals. In Table 2, the experimental values are summarized, along with those of  $(CH_3)_2$ GeI<sub>2</sub> and GeH<sub>3</sub>I [17] for comparison, and the approximate descriptions of the principal functions of the corresponding orbitals are included. The core-level values [18,19] are also included in this table for comparative purposes.

The He(I) spectrum of  $(CH_3)_3$ GeI shows the iodine lone pair clearly split into two distinct peaks as a result of spin-orbit coupling. The separation of 0.4 eV is close to that noted for  $(CH_3)_3$ GeBr and somewhat less than the values of 0.62 and 0.52 eV in CH<sub>3</sub>I [20] and *exo-* or *endo-*2-norboryl iodides, respectively [21]. The second set of peaks corresponds to ionizations from the germanium p orbitals involved in bonding; the Ge-I bonding orbital,  $5a_1$ , being slightly less stable than the Ge-C bonding orbital, 4e, as indicated by the CNDO/2 calculations and by the assignments in  $(CH_3)_3$ GeBr [4]. The next cluster corresponds to the CH<sub>3</sub>-bonding orbitals and is in the typical region of the spectrum. The envelope contains features that are as expected for an  $a_2$  $e-a_1-e$  sequence and so is assigned accordingly. Finally, the feature at 16.1 eV corresponds to the orbital with germanium *s*-orbital contributions. The CNDO/ 2 calculations suggest considerable mixing between the  $3a_1$  and  $4a_1$  orbitals which may contribute to this feature showing up more clearly in the iodides than in other halides [1-4].

The He(I) spectrum of  $(CH_3)_2$ GeHI is displayed in Fig. 1. The iodine lonepair region is again clear with a separation of 0.45 eV for the two peaks corresponding to 8a' and 5a". The germanium *p*-orbital bonding region shows three distinct peaks assignable as 7a', mainly Ge–I bonding, 4a", Ge–C bonding, and 6a', mainly Ge–H bonding. As with  $(CH_3)_3$ GeI, four peaks appear and are assigned within the CH<sub>3</sub>-bonding envelope. Finally, the weaker but distinct feature associated with the germanium *s* orbital appears at approximately 16.8 eV.

The He(I) spectrum of  $CH_3GeH_2I$  is also displayed in Fig. 1 and the expansion clearly shows the separation of the iodine lone pairs (3a'' and 7a') as well as the three distinct peaks corresponding essentially to Ge–I (6a'), Ge–C (2a'') and Ge–H (5a') bonding orbitals. Figure 1, in addition to the data in Tables 1 and 2, clearly demonstrate that as hydrogen atoms replace the methyl groups,

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CND0/2 Calculated orbital symmetry, adjusted eigenvalue, experimental vertical ionization energies and parentages for (CH<sub>3</sub>)<sub>3</sub>GeI, (CH<sub>3</sub>)<sub>2</sub>GeH'I

	121120													
(CH <sub>3</sub> ) <sub>3</sub> (	JeI				$(CH_3)_2G$	eH'I				CH <sub>3</sub> GeH	21 2			
Orbital	CNDO/2 (eV)	Exp. (eV)	Parentage <sup>a</sup>		Orbital	CNDO/2 (eV)	Exp. (eV)	Parentage <sup>a</sup>		Orbital	CNDO/2 (eV)	Exp. (eV)	Parentage <sup>a</sup>	
5e	9.32	9.10		0.90	5a" 82'	9.38 0.52	9.30 0.75		0.90	7a' 3a"	9.47 0.55	9.45	dI c1	0.91
$5a_1$	10.25	10.50	Gep L	0.19	7a'	10.58	9.79 10.90	Gep L	0.20	оа 6а′	10.99	11.30	Gep L	0.23
4 <i>e</i>	10.70	10.90	င်ာ ဗီဗီ	0.19	4α"	11.02	11.35	Co eb	$0.22 \\ 0.52$	5a'	11.84	11.80	cp 66	0.30
			Hs	0.16	6a'	11.51	11.80	$H_{s}$ Gep	$0.16 \\ 0.21$	2a"	12.18	12.30	Hs Gep	$0.11 \\ 0.24$
								$\mathbf{C}^{\mathbf{H}'s}_{\mathbf{C}}$	$0.25 \\ 0.26 \\ 0.26 \\ 0.26$				$_{Cp}^{\mathrm{H'}_{s}}$	0.41
1a2	13.40	13.40	$_{\rm H_e}^{ m Cp}$	0.48	3a″	13.79	13.60	Hs Cp Hs	0.16				Hs	0.16
3e	13.77	13.90	ср Н	0.46	2a"	13.97	14.00	на Ср	0.47					
$4a_1$	14.79	14.40	C H C	0.31 0.15	5а′	14.91	14.60	d H C	0.29	4a'	14.60	14.20	$_{ m Hs}^{ m Cp}$	0.34 0.31 0.31
			Ls Is	0.29				Is I	0.29	1α″	15.44	15.20	$_{\rm Hs}^{\rm Cp}$	0.35
2e	15.06	14.60	$_{ m Hs}^{ m Cp}$	$0.48 \\ 0.45$	4a'	14.96	14.80	$_{ m Hs}^{ m Cp}$	$0.48 \\ 0.40$				Gep H's	0.16
$3a_1$	15.50	16.10	${ m G}_{ m Cp}^{ m Ges}$	0.07 0.45 0.32	3a'	16.67	16.80	Ges Cp Hs	0.09 0.18 0.30 0.24	3a'	16.68	17.10	Ges Gep Cp	0.19 0.13 0.23 0.19
								H's	0.17				$H_{s}$	0.15

<sup>a</sup>Parentages normally only listed if greater than 0.10.

$(CH_3)_2GeI_2^a$	(CH <sub>3</sub> ) <sub>3</sub> GeI	(CH <sub>3</sub> ) <sub>2</sub> GeHI	CH <sub>3</sub> GeH <sub>2</sub> I	GeH₃I	Description
9.2	9.10	9.30	9.45	9.59	
9.4					I lone pairs
9.7	9.50	9.75	9.95	10.14	-
10.2					
11.0	10.50	10.90	11.30	11.71	Ge-I
11.4	10.90	11.35	11.80	-	Ge-C
-	-	11.80	12.30	12.6	Ge-H
13.5	13.40	13.60	_	_	
*	13.90	14.00	14.30	-	$CH_3$
Ļ	14.40	14.60	-	-	
15.0	14.60	14.80	15.20	-	
n.o.	16.10	16.80	17.10	_	Ge(s)
Core levels (eV)	) <sup>b</sup>				
	36.9	37.2	37.5	37.8	Ge(3d)
	290.2	290.3	290.5	-	C(1s)
	625.6	625.7	626.1	626.4	$I(3d_{5/2})$

Experimental values (eV) of vertical ionization energies and core level binding energies of several iodiogermanes

<sup>a</sup>See text. 9.2  $(4b_1)$ ; 9.4  $(6a_1)$ ; 9.7  $(4b_2)$ ; 10.2  $(2a_2)$ ; 11.0  $(3b_2, 5a_1)$ ; 11.4  $(3b_1)$ . <sup>b</sup>See refs. 12 and 19.

all of the orbitals become stabilized regardless of their parentage and regardless of whether they are in valence or core levels. The iodine lone-pair orbitals range from an average of 9.3 to 9.9 eV along the series  $(CH_3)_3GeI-(CH_3)_2GeHI CH_3GeH_2I-GeH_3I$ . A similar range is displayed by the iodine  $3d_{5/2}$  core level (625.6 to 626.4 eV) suggesting that changes in effective nuclear charge are reflected to a similar degree by both the non-bonding valence orbitals and the core levels of iodine. However, there is a larger change in the increasing stability of the Ge-I bonding orbitals, 10.5 to 11.7 eV, suggesting a gradual increase in the stability of the Ge-I bond. Alternatively, the trend may be described by the difference between the energies of the lone-pair iodine orbitals and those involved in Ge–I bonding. For the sequence  $(CH_3)_3$ GeI,  $(CH_3)_2$ GeHI, CH<sub>3</sub>GeH<sub>2</sub>I and H<sub>3</sub>GeI the differences are 1.20, 1.38, 1.60 and 1.85 eV, respectively. The same conclusion can be reached by noting the increase in the values of the Ge–I force constants which are 1.13, 1.17, 1.34 and 1.83 mdyn  $Å^{-1}$  for (CH<sub>3</sub>)<sub>3</sub>GeI [22], (CH<sub>3</sub>)<sub>2</sub>GeHI [16], CH<sub>3</sub>GeH<sub>2</sub>I [23] and H<sub>3</sub>GeI [24], respectively. The carbon 1s core level only increases slightly in stability from  $(CH_3)_3$ GeI to  $CH_3GeH_2I$  indicating only a slight increase in the partial positive charge on carbon, but the predominantly Ge-C bonding orbitals increase more markedly in stability from 10.9 to 11.8 eV. The force constants for the



Fig. 1. The He(I) photoelectron spectra of (CH<sub>3</sub>)<sub>2</sub>GeHI and CH<sub>3</sub>GeH<sub>2</sub>I.

Ge–C stretching vibration increase from 2.87 to 2.95 mdyn Å<sup>-1</sup> from  $(CH_3)_3$ GeI [22] to  $CH_3$ GeH<sub>2</sub>I [23].

The He(I) and He(II) spectra of  $CF_3GeI_3$ ,  $(CF_3)_2GeI_2$  and  $(CF_3)_3GeI$  are assigned in Table 3 and representative examples are displayed in Figs. 2–4. The assignments are made with considerable certainty by comparison with the series  $(CF_3)_nGeX_{4-n}$ , X=Cl, Br, and with the changes in peak intensities between the He(I) and He(II) spectra. This is well illustrated in the spectrum of  $(CF_3)_3GeI$  where the iodine lone-pair orbitals, which show up clearly in the He(I) spectrum, virtually disappear in the He(II) spectrum. The loss in intensity is further demonstrated by the fact that peaks in this region, and even at lower apparent ionization energy, can be readily assigned as satellite spectra arising from the excitation of the fluorine lone-pair orbitals by the He(II) 48.37 and even 51.0 eV radiations. These allow for fairly specific assignments in the cases of  $(CF_3)_3GeI$  and  $CF_3GeI_3$  but the spectra are not of sufficient quality in the He(II) spectrum of  $(CF_3)_2GeI_2$  to allow for the same precision in assignment.

The spin-orbit splitting of the iodine 5p lone pairs in  $(CF_3)_3GeI$  (14e) is greater than that observed in  $(CH_3)_3GeI$ , just as is found for  $CF_3I$ , 0.78 eV [25], compared with  $CH_3I$ , 0.62 eV [20]. The iodine lone-pair regions are similarly distinctive in the He(I) spectra of  $(CF_3)_2GeI_2$  and  $CF_3GeI_3$  where the predicted four peaks can be clearly seen and assigned.

The germanium *p*-orbital bonding regions lie between the iodine and fluo-

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$CF_3GeI_3$		$(CF_3)_2GeI_2$		(CF <sub>3</sub> ) <sub>2</sub> Ge	I	Approximate description of orbital		
Orbital	Exp. (eV)	Orbital	Exp. (eV)	Orbital	Exp. (eV)	oi ordital		
7a <sub>1</sub>	10.10	9b <sub>1</sub>	10.20			······································		
8e	10.30	$11a_1$	10.45	14e	10.55	I(p) lone pairs		
$2a_2$	10.65	$8b_2$	10.75		11.05			
7e	11.00	$6a_2$	11.15					
$6a_1$	12.40	$8b_1$	12.30	13e	12.45	Ge–C bonding		
		$10a_1$	12.60			_		
6e	12.70	$7b_2$	12.90	$10a_{1}$	12.80	Ge–I bonding		
		7b <sub>1</sub>	15.25	12e	15.45			
		$5a_2$	15.45	$5a_2$	15.60 <sup>a</sup>	F(p) lone pairs		
5e	15.30ª	$6b_2$	15.60	11e	16.05ª			
$1a_2$	15.90 <sup>a</sup>	$9a_1$	15.80	$4a_2$	16.15			
		$4a_2$	16.15	10e	16.35ª			
		$5b_{2}$	16.40	$9a_1$	16.55			
$5a_1$	16.50ª	$8a_1$	16.80	$8a_1$	16.80 <sup>a</sup>	Ge(s) bonding		
		$6b_1$	17.00	9e	17.00 <sup>a</sup>			
4e	17.05 <sup>a</sup>	$3a_2$	17.25	$3a_2$	17.25ª	$\mathbf{F}(p)$ lone pairs		
		$4b_2$	17.30	8e	17.30			
		$7a_1$	17.45	$7a_1$	17.45			
3e	19.80ª	$5b_1$	19.9	7e	19.85	CF <sub>3</sub> bonding		
		$2a_2$	1 î	$2a_2$	Î			
$4a_1$	20.20ª	$6a_1$		6e				
		$3b_2$		$6a_1$	1			
		$4b_1$	V	5e	¥			
		$5a_1$	21.6	$5a_1$	22.0			

Orbital symmetries, He(I) and He(II) vertical ionization energies and approximate description of parentages for  $CF_3GeI_3$ ,  $(CF_3)_2GeI_2$  and  $(CF_3)_3GeI$ 

\*Assignment aided by Satellite Spectra.

rine lone pairs. In  $(CF_3)_3$ GeI, the change in peak contour between the He(I) and He(II) spectra allows the orbital with predominant Ge–I character,  $10a_1$ , to be assigned to the more stable component, that with decreased relative intensity in the He(II) spectrum. In CF<sub>3</sub>GeI<sub>3</sub>, the decreased relative intensity is again seen for the more stable component requiring its assignment to 6e, the orbital with predominantly Ge–I character. The predicted three peaks in the germanium *p*-orbital bonding region can be seen clearly in the He(I) spectrum of  $(CF_3)_2$ GeI<sub>2</sub>. The most stable orbital shows a large decrease in intensity in the He(II) spectrum and so is assigned as that which is essentially Ge–I bonding in character. The least stable orbital becomes the most intense in the He(II)



Fig. 2. The He(I) photoelectron spectrum of CF<sub>3</sub>GeI<sub>3</sub>.



Fig. 3. The He(II) photoelectron spectrum of CF<sub>3</sub>GeI<sub>3</sub>.

spectrum and so is assigned as being primarily Ge–C bonding. It is notable that the ionization energies of the iodine lone pairs, Ge–C bonding and Ge–I bonding orbitals are very similar for all three iodides and there is, at best, a very slight indication of an increase in stability as  $CF_3$  groups replace iodine atoms. It should, however, be noted that the difference between the average energy of the iodine lone pairs and the Ge–I bonding orbital is larger in  $(CF_3)_3$ GeI (2.00 eV) than in  $(CH_3)_3$ GeI (1.20 eV) by an amount proportionally comparable to



Fig. 4. The He(I) and He(II) photoelectron spectra of  $(CF_3)_3$ GeI.

the values of the Ge–I stretching force constants, 1.83 mdyn Å<sup>-1</sup> for  $(CF_3)_3$ GeI [26] and 1.21 mdyn Å<sup>-1</sup> for  $(CH_3)_3$ GeI [22]. Both, presumably, are indicative of a stronger Ge–I bond in the perfluoromethylderivatives. In general, the substitution of a CF<sub>3</sub> group for CH<sub>3</sub> has a much larger effect on the stability of the bonding orbitals than does substitution of a halogen atom.

The fluorine lone-pair regions are typical of  $CF_3$ -containing compounds. In the spectrum of  $CF_3GeI_3$ , the two main envelopes,  $5e/1a_2$  and 4e, can readily be assigned specific vertical ionization energies on the basis of a match with the 48.37 eV satellite spectra. As is typical, the  $e/a_2$  cluster is considerably more intense and shows extensive vibrational fine structure. The same basic features can be seen at similar energies in the spectra of  $(CF_3)_2GeI_2$  and  $(CF_3)_3GeI$ . The bands appear as expected for the superimposition of the spectra arising from the two and three  $CF_3$  groups respectively, as was noted for the series  $(CF_3)_nGeX_{4-n}$ , X = CI, Br [5]. The quality of the spectrum does not allow for specific assignments for  $(CF_3)_2GeI_2$  but in  $(CF_3)_3GeI$  the assignments can be made on the basis of agreement with the satellite spectrum.

In the spectra of all three compounds, there is a peak between the two fluorine lone-pair envelopes whose relative intensity changes in a different fashion from those of the lone pairs. This peak is associated with the orbital in which bonding involves a contribution from the germanium 4s-orbital.

As with other CF<sub>3</sub>-containing compounds, the CF<sub>3</sub>-bonding orbitals are seen at around 20 eV in the spectra of CF<sub>3</sub>GeI<sub>3</sub>,  $(CF_3)_2GeI_2$  and  $(CF_3)_3GeI$ . There

is also a distinct feature in the 23.6 eV region which presumably corresponds to orbitals that involve contributions from the carbon 2s and iodine 5s orbitals. This is in a region where Koopmans' theorem may be no longer an acceptable approximation, but that the peaks arise predominantly because of the presence of  $CF_3$  groups seems clear because similar features are seen at approximately 23 eV in the spectra of  $CF_3Br$ ,  $CF_3I$  [25] and  $CF_3Cl$  [20].

The parentages and energy levels of halogen lone pairs and germanium pbonding orbitals, are presented in Table 4 for  $(CH_3)_3GeBr$ ,  $(CH_3)_3GeI$ ,  $(CF_3)_3GeI$  and  $(CF_3)_3GeBr$ . It is apparent that replacing the less electronegative iodine atom by a bromine atom results in a similar relative increase in ionization energies for both the methyl and perfluoromethyl derivatives. The similarities in the parentages of these orbitals for  $(CH_3)GeBr$  and  $(CH_3)_3GeI$ indicate that substitution of the halogen causes no substantial changes in the overall nature of the bonding. In contrast, the correlations between the levels in  $(CH_3)_3GeI$  and  $(CF_3)_3GeI$  show clearly the effect on stability of the considerably more electron-withdrawing  $CF_3$  groups compared with  $CH_3$  groups. The "cross-over" of the relative energy levels of the bonding orbitals is consistent with what was observed for the related bromides and chlorides [5]. There is also a marked difference in the parentages of the 4e and 13e orbitals in  $(CH_3)_3GeI$  and  $(CF_3)_3GeI$ , respectively. The contributions from the carbon porbitals to these bonding orbitals are much less in the trifluoromethyl. This

# TABLE 4

Vertical ionization energies and CNDO/2 calculated parentages for the lone-pair orbitals of iodine and bromine and the bonding *p*-orbitals of germanium in  $(CH_3)_3GeBr$ ,  $(CH_3)_3GeI$ ,  $(CF_3)_3GeI$  and  $(CF_3)_3GeBr$ 

Orbital	IE (eV)	(CH <sub>3</sub> ) <sub>3</sub> Ge	Brª	IE (eV)	(CH <sub>3</sub> )	3GeI	Orbital	IE (eV)	(CF <sub>3</sub> )	₃GeI	IE (eV)	(CF <sub>3</sub> ) <sub>3</sub> (	GeBr <sup>ь</sup>
5e	9.91	Brp 0 Cp 0	).78 ).13	9.3°	Ip Cp	0.90 0.06	14e	10.8°	Ip Cp Fp	0.79 0.11 0.07	11.70	Brp Cp Fp	0.51 0.15 0.25
5a <sub>1</sub>	11.02	Gep         0           Brp         0           Cp         0           Hs         0	).17 ).53 ).15 ).11	10.5	Gep Ip Cp Hs	0.19 0.53 0.13 0.10	10 <i>a</i> <sub>1</sub>	12.80	Gep Ip Cp Fp	0.25 0.38 0.09 0.20	13.35	Gep Brp Cp Fp	0.22 0.33 0.07 0.36
4e	11.46	Gep         0           Cp         0           Hs         0           Brp         0	).17 ).44 ).15 ).19	10.9	Gep Cp Hs Ip	0.19 0.51 0.15 0.09	13e	12.45	Gep Cp Fp Ip	0.20 0.18 0.40 0.20	13.00	GeP Cp Fp Brp	0.13 0.09 0.31 0.47

"Taken from ref. 4.

<sup>b</sup>Taken from ref. 5.

<sup>c</sup>Average values.

reduced participation of the carbon orbitals in bonding to germanium is also consistent with earlier observations that the Ge–C bond is apparently weaker in trifluoromethylgermane derivatives compared with methylgermane derivatives [10,26].

The spectrum of  $(CH_3)_2 GeI_2$  (see Table 2) can be discussed by comparison with those of  $(CH_3)_2GeBr_2$  and  $(CF_3)_2GeI_2$ . In  $(CH_3)_2GeBr_2$ , the predominantly Ge–CH<sub>3</sub> bonding orbitals were assigned at 12.40 to  $3b_1$ , mainly Ge(p)– C, and at 16.75 eV to  $3a_1$ , mainly Ge(s)-C. The spectrum of  $(CH_3)_2$ GeI<sub>2</sub> is of much poorer quality and no clear features corresponding to the weak peak associated with  $3a_1$  are visible so this has to be left unassigned. However, a peak at 11.4 eV can reasonably be assigned to  $3b_1$ , the most stable orbital in the region involving the germanium p orbitals. This is consistent with an assignment of the main Ge(p)-halogen (p) bonding orbital,  $3b_2$ , to 11.0 eV in  $(CH_3)_2$ GeI<sub>2</sub> comparable with 11.90 eV in  $(CH_3)_2$ GeBr<sub>2</sub>. In the spectrum of the latter, the  $5a_1$  orbital could be assigned separately at 12.11 eV but in  $(CH_3)_2GeI_2$ the features are less well defined so  $5a_1$  is assumed to be overlapping with  $3b_2$ . The  $CH_3$ -bonding in  $(CH_3)_2GeI_2$  is essentially one broad envelope ranging from approximately 13.5 to 15.0 eV. However, the lone-pair region is relatively well resolved, so that the four iodine lone pairs are well separated at 9.2, 9.4, 9.7 and 10.2 eV and can be assigned to  $4b_1$ ,  $6a_1$ ,  $4b_2$  and  $2a_2$  by direct comparison with those at 10.14, 10.36, 10.58 and 10.80 eV in  $(CH_3)_2GeBr_2$  where they are approximately 1 eV more stable. Similarly, the greater electron-withdrawing power of  $CF_3$  groups relative to  $CH_3$  groups results in the lone pairs in  $(CF_3)_2$ GeI<sub>2</sub> being similarly more stable, with the corresponding four peaks appearing in the range 10.2-11.15 eV (Table 3).

Extending the observations on the differences in energy levels between iodine lone-pair and Ge–I bonding orbitals, it can be noted in conclusion that for  $(CF_3)_2GeI_2$  the difference is 2.26 eV, whereas for  $(CH_3)_2GeI_2$  it is 1.40 eV, comparable with the values of 2.0 and 1.20 eV observed for the perfluoromethyl and methyl monoiodides.

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#### REFERENCES

- J.E. Drake, B.M. Glavinčevski and K. Gorzelska, J. Electron Spectrosc. Relat. Phenom., 16 (1979) 331.
- 2 J.E. Drake, B.M. Glavinčevski and K. Gorzelska, Can. J. Chem., 57 (1979) 2278.
- 3 J.E. Drake, B.M. Glavinčevski and K. Gorzelska, J. Electron Spectrosc. Relat. Phenom., 17 (1979) 73.

- 4 J.E. Drake and K. Gorzelska, J. Electron Spectrosc. Relat. Phenom., 21 (1981) 365.
- 5 J.E. Drake, K. Gorzelska, G.S. White and R. Eujen, J. Electron Spectrosc. Relat. Phenom., 26 (1982) 1.
- 6 G.M. Bancroft, B.W. Yates, K.H. Tan and L.L. Coatsworth, J. Chem. Soc. Chem. Commun., (1984) 1613.
- 7 B.W. Yates, K.H. Tan, G.M. Bancroft and J.S. Tse, J. Chem. Phys., 85 (1986) 3840.
- 8 T.A. Carlson, A. Fahlman, M.O. Krause, P.R. Keller, J.W. Taylor, T. Whitley and F.A. Grimm, J. Chem. Phys., 80 (1984) 3521.
- 9 D. Rinaldi, Université de Nancy, GEOMO, QCPE 290 was obtained through the Quantum Chemistry Program Exchange, University of Indiana.
- 10 H. Oberhammer and R. Eujen, J. Mol. Struct., 51 (1979) 221.
- 11 J.E. Drake, R.T. Hemmings, L. Hencher, F. Mustoe and Q. Shen, J. Chem. Soc. Dalton Trans., (1976) 811; Can. J. Chem., 55 (1977) 1104.
- 12 R.K. Chadha, J.E. Drake and M.K.H. Neo, J. Cryst. and Spect. Res., 15 (1985) 39.
- 13 R.J. Lagow, R. Eujen, L.L. Gerchmann and J.A. Morrison, J. Am. Chem. Soc., 100 (1978) 1722.
- 14 S. Craddock and E.A.V. Ebsworth, J. Chem. Soc. A, (1967) 12.
- 15 J.E. Drake, R.T. Hemmings and C. Riddle, J. Chem. Soc. A, (1970) 3359.
- 16 G.K. Barker, J.E. Drake and R.T. Hemmings, Can. J. Chem., 52 (1974) 2622.
- 17 S. Cradock and R.A. Whiteford, Trans. Faraday Soc., 67 (1971) 3425.
- 18 J.E. Drake, C. Riddle, H.E. Henderson and B. Glavinčevski, Can. J. Chem., 54 (1976) 3876.
- 19 J.E. Drake, C. Riddle, B. Glavinčevski, K. Gorzelska and H.E. Henderson, Inorg. Chem., 17 (1978) 2333.
- 20 T. Cvitas, H. Gusten and L. Klasinc, J. Chem. Phys., 67 (1977) 2687.
- 21 E. Honegger, E. Heilbronner, A. Dratva and C.A. Crob, Helv. Chim. Acta, 67 (1984) 1691.
- 22 J.W. Anderson, G.K. Barker, J.E. Drake and R.T. Hemmings, Can. J. Chem., 49 (1971) 2931.
- 23 G.K. Barker, J.E. Drake, R.T. Hemmings and B. Rapp, Spectrochim. Acta Part A, 28 (1972) 1113.
- 24 D.E. Freeman, K.H. Rhee and M.K. Wilson, J. Chem. Phys., 39 (1963) 2908.
- 25 T. Cvitas, H. Gusten, L. Klasinc, I. Novadj and H. Vancik, Z. Naturforsch. Teil A, 32 (1978) 1528.
- 26 R. Eujen and H. Burger, Spectrochim. Acta Part A, 35 (1979) 541, 549 and 1135.