studied. (It should be noted that [Cu^{2+}(aq)] cannot be increased due to reaction 9 and the pH lowered due to reaction 7.) When the pulse intensity was increased to yield a total radical concentration of 300 μM, the rate of decomposition of Cu-H^+(aq) increased, probably due to the fact that reaction 3 is an equilibrium process with $K_{-3} \approx 10^3$ s^{-1} and reaction 12 is diffusion controlled. A contribution of reaction 13 under these conditions cannot be ruled out.

The rate of reaction 14 is considerably greater than that of the corresponding reaction for Cl_3CuH^{2-}. For the latter the rate law has the form $d[Cl_3CuH^{2-}]/dt = 5.5 \times 10^2 \times [Cl_3CuH^{2-}][H_3O^+]$, and the intercept of a plot of the rate vs. [H_3O^+] at low acidities has a value of <10 s^{-1}.[8] This result suggests that the rate-determining step in the heterolytic Cu-H^+ bond cleavage involves a nucleophilic attack on the copper atom. The maximum of the spectrum of Cl_3CuH^{2-}[8] seems to be slightly red shifted relative to that of Cu-H^+(aq).

The spectrum of Cu-H^+(aq) is blue shifted relative to those of all other Cu^{II}-R(aq) compounds reported.[4-7] A similar blue shift for $Cr(H_2O)_5H^{2+}$ was attributed to a larger optical electronegativity of hydride than that of most alkyls.[19] The proposal that the mechanism of decomposition of Cu-H^+(aq) is mainly heterolytic is in agreement with that reported for $CuCH_3^+$,[6] $CuCH_2CH_2OH^+$, and $CuCH_2C(CH)_3(H)OH^+$;[4] in none of these is the free radical that should be formed in a homolytic process resonance stabilized.[4] On the other hand, $CuCH_2OH^+$ and $CuCH(CH_3)OH^+$ decompose homolytically.[4] It has been suggested that $Cu^{II}CO_2$ decomposes heterolytically in acid media,[7] the homolytic route being electrostatically unfavorable. However, the reaction $Cu^{II}CO_2 + Cu^{2+} \rightarrow 2Cu^+ + CO_2$ reported in neutral solutions[7] probably involves a homolytic cleavage of $Cu^{II}CO_2$.

Acknowledgment. We are indebted to R. M. Clarke for preparing the high-pressure samples.

Registry No. Cu^+, 17493-86-6; Cu^{2+}, 15158-11-9; H, 12385-13-6.

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(19) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 1974.

Contribution from the Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada,
and Anorganische Chemie, FB 9, Universität Gesamthochschule, 5600 Wuppertal 1, West Germany

ESCA and UV Photoelectron Spectra of Methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Ge(CH_3)_n$ (n = 1-3), and Tetrakis(trifluoromethyl)germane, $(CF_3)_4Ge$

JOHN E. DRAKE,*[1a] REINT EUJEN,[1b] and KRYSTYNA GORZELSKA[1a]

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Core-level binding energies have been recorded for germanium 3d and 3p, carbon 1s, and fluorine 1s levels for the series of methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Ge(CH_3)_n$ (n = 1-3), and for tetrakis(trifluoromethyl)germane, $(CF_3)_4Ge$. The UV-excited photoelectron spectra were also recorded in the range 9-26 eV with use of both He I and He II radiation. Comparisons are drawn to results on related molecules.

Introduction

We have reported the results of our research on the photoelectron spectroscopy of halogen and hydrogen derivatives of (trifluoromethyl)germanes.[2-4] In these studies, the spectra of the (trifluoromethyl)germanium derivatives were compared and contrasted with those of their methyl analogues.[5-7] Therefore, it is appropriate to extend this work to an examination of the mixed methyl-trifluoromethyl series $(CF_3)Ge(CH_3)_3$, $(CF_3)_2Ge(CH_3)_2$, and $(CF_3)_3Ge(CH_3)$, as well as $(CF_3)_4Ge$, in both the X-ray-excited (ESCA) and the UV-excited (He I and He II) regions.

Experimental Section

Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer with aluminum Kα X radiation (1486.6 eV) for photoelectron excitation. Samples were introduced in the vapor phase. Argon was bled in to form up to 20% of the total sample and served as an internal standard (argon $3p_{3/2}$ level at 248.68 eV[8]). The general operating details, mode of accumulation, treatment of data, and specific difficulties associated with the recording of spectra of (trifluoromethyl)germanium compounds were as described previously.[2,5] The average full-width at half-maximum of the 1s peaks of C and F were 1.45 and 1.5 eV, respectively. The germanium 3d peaks were broader because of the slight splitting of the $3d_{5/2}$ and $3d_{3/2}$ levels and because the F 2s levels also occur in this region. However, as described in an earlier paper,[2] the Ge 3d orbitals have relatively much larger cross sections than the F 2s so that the average position of the peak can be assumed to be the position of the Ge 3d level. The fact that the trends in the Ge 3p levels parallel those in the 3d lends support to this statement. The half-widths are only slightly larger than those that were observed with use of Mg K X radiation

Table I. Core-Level Binding Energies (eV) for the $(CF_3)_{4-n}Ge(CH_3)_n$ Series

compd	Ge 3d[a]	Ge 3p	C 1s (H)	C 1s (F)	F 1s
$Ge(CH_3)_4$	36.10		289.80		
$(CF_3)Ge(CH_3)_3$	36.90	129.45	290.40	297.20	694.0
$(CF_3)_2Ge(CH_3)_2$	37.55	130.35	291.00	297.70	694.35
$(CF_3)_3Ge(CH_3)$	38.35	131.15	291.45	298.00	694.65
$(CF_3)_4Ge$	39.20			298.60	695.10

[a] Relative to Ne 2s at 48.47 eV.[8]

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(1) (a) University of Windsor. (b) Universität Gesamthochschule Wuppertal.

(2) Drake, J. E.; Eujen, R.; Gorzelska, K. *Inorg. Chem.* **1982**, *21*, 558.

(3) Drake, J. E.; Eujen, R.; Gorzelska, K.; Helbing, R. *J. Electron Spectrosc. Relat. Phenom.*, in press.

(4) Drake, J. E.; Eujen, R.; Gorzelska, K. *J. Electron Spectrosc. Relat. Phenom.*, in press.

(5) Drake, J. E.; Riddle, C.; Coatsworth, L. *Can. J. Chem.* **1975**, *53*, 3602. Drake, J. E.; Riddle, C.; Henderson, H. E.; Glavincevski, B. M. *Ibid.* **1976**, *54*, 3876.

(6) Drake, J. E.; Gorzelska, K. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *21*, 365.

(7) Drake, J. E.; Glavincevski, B. M.; Gorzelska, K. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *17*, 73; **1979**, *16*, 331; *Can. J. Chem.* **1979**, *57*, 2278.

(8) Johansson, G.; Hedman, J.; Berneltsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 295.

0020-1669/82/1321-1784$01.25/0

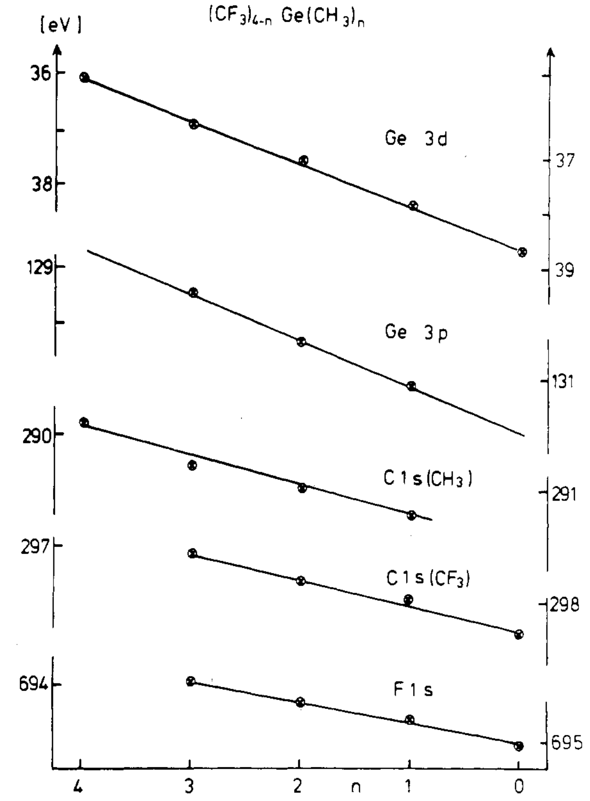

Figure 1. Correlation of core-level binding energies for the series $(CF_3)_{4-n}Ge(CH_3)_n$.

on halomethylgermanes.[5] The aluminum anode was used to avoid the Auger lines that occur in the region of the Ge 3p levels with the magnesium excitation.[9] The He I and He II excited spectra were also calibrated against argon (15.76 and 15.94 eV). Data collection was normally at intervals of 0.02 eV for He I or 0.04 eV for He II for 2 s. The number of scans varied and depended considerably on the quality of accumulating data. Increased times did not necessarily lead to better resolution because the compounds obviously had an adverse effect on the detector. Spectra normally took from 1 (He I) to 4 h (He II). CNDO/2 calculations[10] were carried out as described previously,[2-4,6,7] but in general the peaks are too broad to make individual rather than regional assignments. Partial charges on germanium were obtained from EESOP calculations,[5] which are based on the Hinze–Jaffé concept,[11] with use of the following values for electronegativity: $\chi_{Ge} = 8.07 + 6.82\delta_{Ge}$; $\chi_{CF_3} = 9.6 + 5.32\delta_{CF_3}$;[2] $\chi_{CH_3} = 7.98 + 13.27\delta_{CH_3}$.[2,5]

Tetrakis(trifluoromethyl)germane was prepared as described previously.[12] The mixed $(CF_3)_{4-n}Ge(CH_3)_n$ compounds were prepared, via the iodides, by treatment with dimethylcadmium[12] and separated by trap-to-trap distillation and GC using a SE30 column. The purity of the samples was established by IR, Raman, and ^1H and ^{19}F NMR spectroscopy to be better than 98% in terms of hydrogen- or fluorine-containing materials.

Results and Discussion

The experimentally determined core-level binding energies of the $(CF_3)_{4-n}Ge(CH_3)_n$, $n = 0$–4, series are shown in Table I and displayed in Figure 1. Obviously, there is a stepwise increase in the binding energies of all levels as CF_3 groups replace CH_3 groups across the series. The "rate of change" is greatest for the germanium core levels, which is as expected if the overriding factor is the increased electron-withdrawing capacity of CF_3 relative to CH_3. As more CF_3 groups are substituted, the electron density around germanium is reduced, its effective nuclear charge is increased, and thus the attracting force on the 3d and 3p electrons becomes larger. This inductive effect also leads to a reduction in the electron density around the remaining carbon atoms so that their C (1s) levels increase but to a slightly lesser extent. The marked difference in the electronegativities of fluorine and hydrogen is reflected by the difference of more than 6 eV in the carbon 1s binding energies between $C(F_3)$ and $C(H_3)$ atoms (Figure 2). The figure also shows the expected changes in relative intensities as CF_3 groups replace CH_3 and demonstrates that both levels shift together by similar amounts. The electron-withdrawing power of the CF_3 group is transmitted through the whole molecule as is shown by the similar stepwise increase in the fluorine 1s levels (Figure 1).

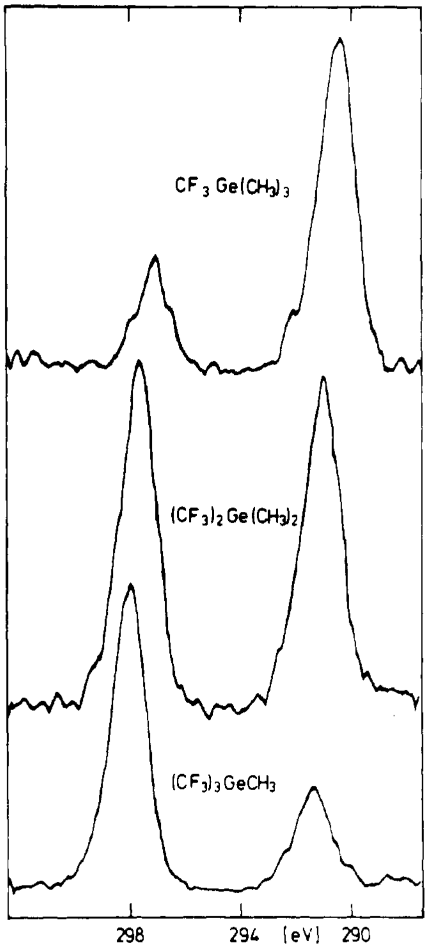

Figure 2. C (1s) binding energies for the series $(CF_3)_{4-n}Ge(CH_3)_n$.

The values of the force constants, $f(Ge–CH_3)$, increase as CF_3 groups replace CH_3 groups in the series $(CF_3)_{4-n}Ge(CH_3)_n$ to about the same degree as when Cl atoms replace CH_3 groups in the series $Cl_{4-n}Ge(CH_3)_n$.[13] This suggests that as a group the CF_3 moiety behaves as though its electronegativity is very similar to that of a chlorine atom. If the carbon 1s levels of the CH_3 group are compared in the two series, it can be seen that those of the CF_3 series are marginally higher than their Cl counterparts,[5] suggesting if anything a slightly higher electronegativity for the CF_3 group. On the other hand, when the germanium 3d levels are compared, the chlorides and even bromides give consistently higher values (e.g., $X_3Ge(CH_3)$ = 39.11 (Cl), 38.71 (Br),[5] and 38.4 (CF_3)), suggesting a somewhat lower electronegativity. The CNDO/2 calculated

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(9) Jolly, W. L.; Perry, W. B. *Chem. Phys. Lett.* **1973**, *20*, 617.

(10) Rinaldi, D. GEOMO, Université de Nancy; QCPE 290 available through Quantum Chemistry Program Exchange, Indiana University, Program No. 290.

(11) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540; *J. Phys. Chem.* **1963**, *67*, 1501.

(12) Lagow, R. J.; Eujen, R.; Gerchman, L. L.; Morrison, J. A. *J. Am. Chem. Soc.* **1978**, 100, 1722. Gerchman, L. L.; Eujen, R.; Lagow, R. J. *J. Fluorine Chem.* **1977**, *10*, 333.

(13) Eujen, R.; Bürger, H. *Spectrochim. Acta, Part A* **1979**, *35A*, 1135.

Table II. Experimental Ionization Energies (eV) of the Methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Ge(CH_3)_n$, $n = 0–4$

	$Ge(CH_3)_4$[a]	$(CF_3)Ge(CH_3)_3$		$(CF_3)_2Ge(CH_3)_2$		$(CF_3)_3Ge(CH_3)$		$(CF_3)_4Ge$	
	He I	He II	He I	He II	He I	He II	He I	He II	He I
Ge(p)–C	ca. 10.2	10.7	10.6	11.3	11.2	12.1	12.2	12.9	12.9
		11.1	11.0	11.7	11.5	12.6	12.6		
				12.2	12.0				
CH_3	ca. 13.0		13.05	13.3					
		13.3	13.25		13.5				
			13.42						
		13.5	13.57						
		13.8	13.85	14.0		14.4	14.5		
			14.05						
			14.28						
		14.4	14.40	14.5					
	ca. 15.0		14.55		14.8				
F (p)		14.6	14.6	14.9	14.9	15.2	15.1	15.6	15.8
					15.1		15.2	16.0	16.0
					15.3	15.7	15.6		16.3
		15.2	15.1	15.5	15.6	15.9	15.8	16.4	16.5
					15.8	16.2	16.3		
		16.1	16.1	16.5	16.5	17.0	17.0	17.4	17.4
Ge (s)	15.8	(17.2)		(17.5)				18.5	18.5
CF_3		18.9		19.6		20.1		20.2	
				20.0		20.4		20.7	
		19.3		20.4		20.7			
C (s)		22.7		23.2		23.8		24.1	

[a] See ref 14.

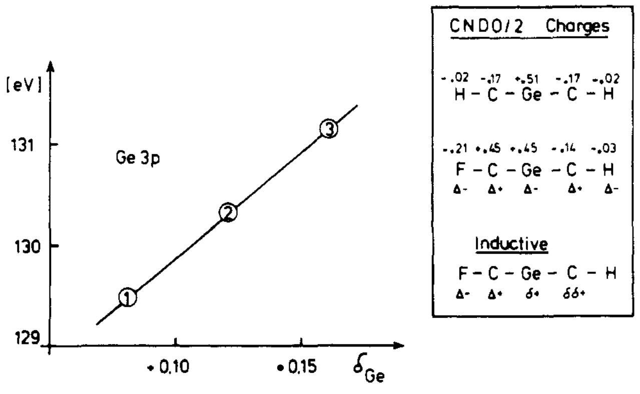

Figure 3. Ge (3p) binding energies vs. calculated partial charge on germanium.

charges on carbon (e.g., $CF_3Ge(CH_3)_3$ 0.443+ (CF_3), 0.158– (CH_3); $(CF_3)_2Ge(CH_3)_2$ 0.454+ (CF_3), 0.145– (CH_3)) certainly reflect the large difference in binding energies as well as the increase in the binding energies of both types of carbon on substitution of a CF_3 group. By contrast, the partial charge on germanium is more positive in $CF_3Ge(CH_3)_3$ (0.511+) than in $(CF_3)_2Ge(CH_3)_2$ (0.453+) contrary to the increase in observed binding energies and to chemical experience. The CNDO/2 method sets up an alternating charge sequence (see insert in Figure 3) that overrides inductive effects. Thus a less positive charge is calculated for the germanium atom when fluorine atoms replace hydrogen atoms. A simple inductive model in fact gives a better correlation with experimental data, and the EESOP[5] calculated charges correlated with Ge (3p) binding energies as expected (Figure 3). A blend of the alternating charge and simple inductive effects would account for the apparent anomalies in relative values of binding energies in CF_3- as opposed to Cl-substituted methylgermanes. In the case of CF_3 substitution, as can be seen from the insert in Figure 3, the two effects suggest an enhancement of positive charge on carbon (CH_3) and a relative reduction on germanium. By contrast the two effects will be in phase at germanium but out of phase at carbon in the case of chlorine substitution ($Cl^{\Delta-}–Ge^{\Delta+}–C^{\delta-}$ and $Cl^{\Delta-}–Ge^{\Delta+}–C^{\delta+}$).

The experimental vertical ionization energies of the valence levels for the series $(CF_3)_{4-n}Ge(CH_3)_n$ are displayed in Table II along with an approximate description of the nature of the orbitals. The methyl group bonding orbitals typically give rise to very broad ionization bands such as those in $Ge(CH_3)_4$, where the Ge(p)–C bonding orbital ionizations from the $3t_2$ state extend from ca. 9.5 to 11 eV while the CH_3 bonding region itself spans from ca. 12.5 to nearly 15 eV.[14] Thus the analysis will be of a fairly general nature. The clearest picture will of course be obtained for the cubic $(CF_3)_4Ge$.

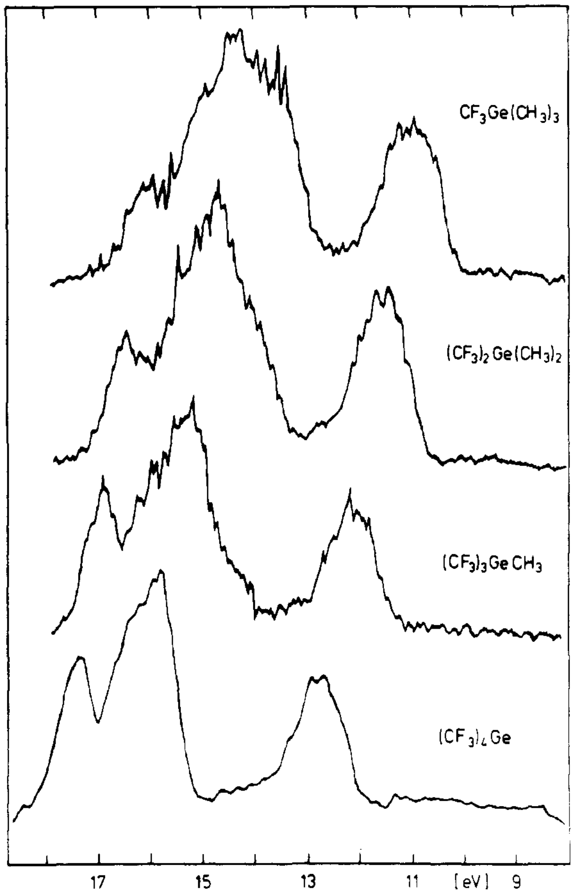

Figure 4. He I photoelectron spectra of the series $(CF_3)_{4-n}Ge(CH_3)_n$.

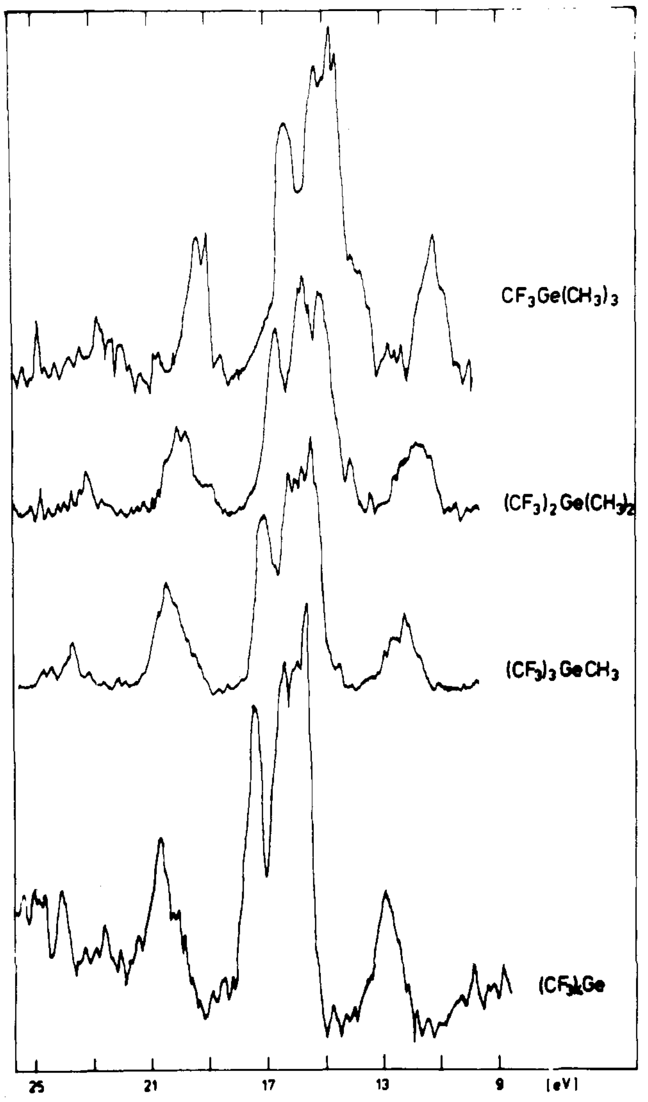

Figure 5. He II photoelectron spectra of the series $(CF_3)_{4-n}Ge(CH_3)_n$.

The He I and He II spectra of $(CF_3)_4Ge$ are shown in Figures 4 and 5, respectively. The first ionization potential, which corresponds to the germanium p orbitals interacting with those of carbon, Ge(p)–C, can be seen centered at 12.9 eV. This is ca. 2.7 eV more stable than the counterpart in $Ge(CH_3)_4$,[14] which is slightly less than the difference in the energies of the germanium 3d levels (3.1 eV) and appreciably less than the stabilization of the carbon 1s levels (8.8 eV). The shape and width of the band are similar to the first ionization bands in $M(CH_3)_4$, M = C, Si, Ge, compounds where Jahn–Teller distortion was invoked.[14] The next feature in the spectrum corresponds to the fluorine p-orbital lone pairs, F 2p, which show a remarkable similarity in appearance and position to those in CF_3H. One report on CF_3H assigns the a_2, e, and e set of lone pairs to 15.5, 16.2, and 17.24 eV with relative intensities of 3, 5, and 3.5, respectively.[15] This could well describe the assignment of the bands in $(CF_3)_4Ge$ with only a minor shift of position. Thus the four CF_3 groups have little influence on one another so that the spectrum looks like a superimposition of four individual CF_3 groups. The effective electronegativity of a $(CF_3)_3Ge$ group in this context is somewhat similar to that of a hydrogen atom. The resemblance to the spectrum of CF_3H is maintained in the CF_3 bonding region, which is centered at 20.6 eV in $(CF_3)_4Ge$. The peaks beyond 23 eV, particularly the clearly defined one at 24.0 eV, presumably correspond to the carbon 2s orbitals involved in bonding. In CF_3H, the corresponding carbon $2s^{-1}$ ionization was placed at 24.44 eV.[15] The weak feature at ca. 18.5 eV could correspond to the orbital in which the germanium s orbital is an important contributor. Its intensity is usually low, particularly in the He I spectrum, but it can be identified with some certainty in the He II spectrum, as in GeH_4, where it was placed at 18.3–18.9 eV.[16,17] However, the increase in the relative intensity of the fluorine lone pairs and their close proximity to this band make it difficult to assign it with certainty in derivatives of (trifluoromethyl)germanes.[3,4]

The He I and He II spectra of $(CF_3)Ge(CH_3)$, $(CF_3)_2Ge(CH_3)_2$, and $(CF_3)Ge(CH_3)_3$ are displayed in Figures 4 and 5, which demonstrate that many of the principal features have similar appearances and that there is a steady decrease in the energies of all groups of ionizations along the series. The first ionization band is of about the same width in all compounds, and their positions are between those of $(CF_4)_4Ge$ (mainly Ge–C(F) overlap) and $Ge(CH_3)_4$ (Ge–C(H) overlap). In $(CF_3)Ge(CH_3)_3$, the CNDO/2 calculations suggest that the a_1 band, though of mixed parentage, has mainly Ge–C(F) bonding character along with some C–F antibonding contributions. This results in its being slightly less stable than the e component, which must be mainly Ge–C(H) bonding in character. The band is very broad, presumably as a result of extensive vibrational structure and Jahn–Teller distortion of the e component, so that specific assignments can only be tentative, but there is the appearance of a shoulder on the less energetic side of the peak. In $(CF_3)_3Ge(CH_3)$ the parentage of the a_1 and e levels is reversed and a distinct shoulder, corresponding to the Ge–C(H) bonding orbital, a_1, is on the higher energy side of the band. Three components are expected for this region for $(CF_3)_2Ge(CH_3)_2$, which are assumed to be spread out across a similarly broad envelope. As has been noted, the Ge core levels are stabilized significantly and the C 1s levels to a great extent by the replacement of a fluorine atom for hydrogen. On the basis of the increased effective nuclear charge on carbon one might expect a degree of stabilization of all its bonding orbitals relative to those of the methyl carbons. The fact that both Ge–C(F) and Ge–C(H) bonding levels are close together in these mixed species suggests a relative destabilization of the Ge–C(F) bonding orbitals that could in part arise from the antibonding C–F contributions and less effective overlap with the contracted carbon p-orbitals. The Ge–C bond is indeed longer in $(CF_3)_4Ge$ than in $Ge(CH_3)_4$,[18] and the value of the Ge–C force constant is smaller.[19]

In the He II spectra, particularly that of $(CF_3)_3Ge(CH_3)$, the fluorine lone pairs dominate the region from about 13 to 17 eV, whereas in the He I spectra, particularly that of $(CF_3)Ge(CH_3)_3$, the typically broad multistructured bands associated with CH_3 bonding[14] become apparent. Only in the He I spectrum of $(CF_3)Ge(CH_3)_3$ is it possible to detect a regular array of fine structure in the CH_3 bonding band, but it is still very complex and no clear correspondence to particular vibrational sequences can be detected. The principal spikes in the spectra are recorded in the table, but these cannot be assigned to any specific ionization. As with all CF_3 compounds, the F lone-pair region is broad because of extensive vibrational fine structure,[15,20] which further complicates the

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(14) Jonas, A. E.; Schweitzer, G. K.; Grimm, F. A.; Carlson, T. A. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 29.

(15) Brundle, C. R.; Robin, M. B.; Basch, H. *J. Chem. Phys.* **1970**, *53*, 2796.

(16) Pullen, B. P.; Carlson, T. A.; Moddeman, W. E.; Schweitzer, G. K.; Bull, W. E.; Grimm, F. A. *J. Chem. Phys.* **1970**, *53*, 768.

(17) Cradock, S. *Chem. Phys. Lett.* **1970**, *53*, 2196.

(18) Oberhammer, H.; Eujen, R. *J. Mol. Struct.* **1979**, *51*, 216.

(19) Eujen, R.; Bürger, H. *Spectrochim. Acta, Part A* **1979**, *35A*, 542.

(20) Cvitas, T.; Güsten, H.; Klasine, L. *J. Chem. Phys.* **1977**, *67*, 2687. Cvitas, T.; Güsten, H.; Klasins, L.; Novadj, I.; Vancik, H. *Z. Naturforsch., A* **1978**, *33A*, 1528.

overlapping region. Here again the main spikes are recorded, but, in general, specific assignments are not possible. The ionization of the most stable lone pairs of fluorine in $(CF_3)Ge(CH_3)_3$, or sets of orbitals for the other two species, stands out clearly in all spectra, emphasizing that again in this region there is essentially a superimposition of ionizations for each CF_3 group. The shift of 0.7 from 16.9 eV in $(CF_3)_3Ge(CH_3)$ to 16.2 eV in $(CF_3)Ge(CH_3)_3$ is very similar to that observed between the fluorine 1s orbitals (694.65 and 694.0 eV, respectively). This demonstrates that where there is no appreciable change in the makeup of an orbital, the valence levels show the same trends to the same degree as the core levels. The principal features of the remaining lone pairs of fluorine can be seen in the He II spectra to correspond to those in $(CF_3)_4Ge$ or other (trifluoromethyl)germanes[3,4] apart from a slight progressive shift. The counterparts to these features can be detected in the He I spectra, allowing the remainder of the envelope to be assigned in a general fashion to the CH_3 bonding orbitals.

The CF_3 bonding orbitals show approximately the same tendency toward stabilization from $(CF_3)Ge(CH_3)_3$ to $(CF_3)_3Ge(CH_3)$ as do the fluorine lone pairs, and the intensity of the peak around 19 eV is in the same proportion to the fluorine lone pairs, so no particularly unusual features appear. For $(CF_3)Ge(CH_3)_3$ the band splits into the expected e and a components, and an assignment of the rather sharp band at 18.8 eV is in accord with the spectra of CF_3 halides.[19] In $(CF_3)_2Ge(CH_3)_2$ and $(CF_3)_3Ge(CH_3)$ the band structure gets more complex but hardly broadens so that there is again essentially a superimposition of the spectrum of one bonding CF_3 group.

The evidence for the Ge (4s) ionization is not good. It is assumed to occur between 15.8 (as in $Ge(CH_3)_4$) and 18.5 eV (as in $(CF_3)_4Ge$), and high-energy shoulders on the most stable F (2p) lone pair are assumed to arise from this ionization, placing it at 17.0 eV for $(CF_3)Ge(CH_3)_3$ and 17.5 eV for $(CF_3)_2Ge(CH_3)_2$.

The spectra above 21 eV are noisy, but the main feature, which is assumed to correspond to ionization from the C (2s) levels, does shift progressively from the highest energy in $(CF_3)_3Ge(CH_3)$ to the lowest in $(CF_3)Ge(CH_3)_3$. In this it is of course reflecting the general trends in both the valence and the core-level binding energies of these molecules.

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Registry No. $Ge(CH_3)_4$, 865-52-1; $(CF_3)Ge(CH_3)_3$, 21907-59-5; $(CF_3)_2Ge(CH_3)_2$, 66348-20-7; $(CF_3)_3Ge(CH_3)$, 66348-19-4; $(CF_3)_4Ge$, 55642-43-8.

---

(21) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmask, T.; Werne, L.; Manne, L. O.; Baer, Y. "ESCA Applied to Free Molecules"; American Elsevier: New York, 1969.

Contribution from the General Chemistry Institute,
Faculty of Pharmacy, University of Florence, Florence, Italy

ESR Spectra of Low-Symmetry High-Spin Cobalt(II) Complexes. 10.[1] Five-Coordinated Trigonal-Bipyramidal Complexes

C. BENELLI and D. GATTESCHI*

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The EPR spectra of the five-coordinated complexes $[CoX(Me_6tren)]Y$ (Me_6tren = tris[2-(dimethylamino)ethyl]amine; X = Cl, Br, I; Y = Cl, Br, I, BPh_4) and $[CoX(np_3)]Y$ (np_3 = tris[2-(diphenylphosphino)ethyl]amine; X = Cl, Br, I; Y = PF_6, BPh_4) have been recorded. The Me_6tren complexes were found to yield $g_\parallel \approx 2$ and $g_\perp \approx 4$, in agreement with a ground $\pm^1/_2$ Kramers doublet. No ^{59}Co hyperfine was resolved. The np_3 complexes were found to give a g value in the range 6-7, but no other signal could be detected in the range 0-1.40 T. Single-crystal analysis showed that the g = 6-7 value is found parallel to the cobalt-axial ligand direction. The angular dependence of the spectra confirmed that the other two g values must be smaller than 0.45 and therefore outside the range available to our spectrometer. These data have been interpreted as indicative of a ground $\pm^3/_2$ Kramers doublet. The spin Hamiltonian parameters of the two sets of complexes have been justified on an angular overlap model.

Pursuing our project for characterizing the EPR spectra of low-symmetry high-spin cobalt(II) complexes,[1-3] we wish to report here the EPR spectra of some five-coordinate complexes formed with tripod ligands, which, although distorted to some extent, can be in every case loosely described as trigonal bipyramidal. In particular we have studied $[CoX(Me_6tren)]Y$ (Me_6tren = tris[2-(dimethylamino)ethyl]amine; X = Cl, Br, I; Y = Cl, Br, I, BPh_4) and $[CoX(np_3)]Y$ (np_3 = tris[2-(diphenylphosphino)ethyl]amine; X = Cl, Br, I; Y = PF_6, BPh_4). For these complexes the crystal structures are available,[4-6] which have shown that the Me_6tren complexes can be more closely described as trigonal bipyramidal,[4] while for the np_3 complexes the distortion toward a tetrahedral structure is quite remarkable.[5-7] The electronic spectra of the above complexes

Table I. Spin Hamiltonian Parameters for Some Five-Coordinate Trigonal-Bipyramidal Cobalt(II) Complexes

complexes	g_1	g_2	g_3
$[CoCl(Me_6tren)]Cl$	2.29	4.25	
$[CoBr(Me_6tren)]Br$	2.27	4.30	
$[CoI(Me_6tren)]I$	2.10	4.30	
$[CoBr(Me_6tren)]BPh_4$	*a*	4.70	6.30
$[CoCl(np_3)]PF_6$	*b*	*b*	6.70
$[CoBr(np_3)]PF_6$	*b*	*b*	6.50
$[CoI(np_3)]BPh_4$	*b*	*b*	6.40

[a] A broad signal in the $g = 2$ region is present, but a precise g value cannot be obtained. [b] No other signals could be detected in the range 0-1.40 T. g_1 and g_2 may be estimated to be smaller than 0.45.

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(1) Part 9: Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D. *Nouv. J. Chim.* **1980**, *4*, 393.

(2) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1980**, *19*, 3839.

(3) Bencini, A.; Bertini, I.; Canti, G.; Gatteschi, D.; Luchinat, C. *J. Inorg. Biochem.* **1981**, *14*, 81.

(4) Di Vaira, M.; Orioli, P. L. *Inorg. Chem.* **1967**, *6*, 955.

(5) Di Vaira, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1575.

(6) Di Vaira, M.; Bianchi Orlandini, A. *Inorg. Chem.* **1973**, *12*, 1292.

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