contributions in turn contains a part due to the L_1–L_2 magnetic mixing and a part due to the L–B magnetic mixing. If $n \neq 4N + 2$, the former part is expected to predominate.[12] The signs of the μ^- contributions to B terms are then equal to the sign of μ^- for L_2 and B_2 and opposite to it for L_1 and B_1. In our case, μ^- is positive, and since a positive B term corresponds to a negative MCD peak, the expected MCD signs due to μ^- contributions alone are +, –, +, – in the order of increasing energy.

The μ^+ contributions to the four B terms are more sensitive to the nature of the perturbation that produced the molecule of interest from the parent perimeter. This perturbation splits the originally degenerate pair of highest occupied molecular orbitals by an amount that we refer to as ΔHOMO. Similarly, it splits the original pair of lowest unoccupied molecular orbitals by an amount ΔLUMO (Figure 2). If ΔHOMO = ΔLUMO, the μ^+ contributions to B terms vanish. If ΔHOMO > ΔLUMO, their signs are +, –, +, – in the order of increasing energy, and if ΔHOMO < ΔLUMO, they are –, +, –, +.

The spectra of $S_4N_3^+$ (Figure 1) are in perfect qualitative agreement with expectations for a perturbed ten-π-electron seven-center perimeter, except that the order of the nearly degenerate transitions L_1 and L_2 seems to be interchanged, since L_1 has lower absorption intensity than L_2. This could be confirmed by a determination of polarization directions, which are presently unknown. According to the simple perimeter model, the stronger transition should be polarized along the S–S bond and the weaker transition perpendicular to it. In order to account for this possible interchange, additional configurations would have to be considered in the perimeter model.

In view of the expected positive sign and sizable magnitude of the magnetic moment μ^-, it is tempting to assign the observed B term sequence (–, +, –, +) entirely to the μ^- contribution. Although this appears to account for the bulk of the observed effect and agrees with our PPP calculations, which suggest that ΔHOMO and ΔLUMO are of similar size, a simple check suggests that the μ^+ contribution is probably not totally negligible and that ΔHOMO actually is smaller than ΔLUMO,[15] so that the μ^- and μ^+ contributions reinforce

each other. If the magnitude of the transition magnetic moment μ between two nearly degenerate states is estimated by treating their contribution to MCD as an A term and using the relation $\mu = -2A/D$, where D is the dipole strength, the values 1.0 and 0.46 μ_B are obtained for the L pair and B pair, respectively. Although these are only crude estimates, the value for the L pair is sufficiently in excess of the expected value of about 0.6 μ_B that one strongly suspects that a contribution of the μ^+ type is also present. This suspicion is reinforced by the results of ab initio calculations on the $S_4N_3^+$ cation,[16] which lead to the order ΔHOMO < ΔLUMO.

Whatever the detailed origin of the numerical magnitudes of the observed B terms, it is clear that the observed absorption and MCD spectra are in perfect agreement with the notion that a delocalized ten-π-electron system is present in $S_4N_3^+$. This is not in contradiction to the absence of any spectacular shortening of the S–S bond (2.06 Å) in the equilibrium ground-state geometry. The fact that the bond order calculated for this bond in the ground state is quite low (about 0.3 in our calculations) does not mean that there is no interaction between the 3p-type orbitals on the two adjacent sulfur atoms, only that it is not particularly stabilizing in the ground state, so that there is little driving force for making this bond shorter in this state of the cation.

(15) More accurately: the $2 \to -1$ configuration is lower in energy than the $1 \to -2$ configuration, where the occupied MOs are labeled 1, 2, ... in the order of decreasing energy and the vacant MOs are labeled –1, –2, ... in the order of increasing energy. If the π-electron system in question does not deviate too strongly from the parent perimeter, this condition is equivalent to the condition ΔHOMO < ΔLUMO.[12]

(16) W. G. Laidlaw, personal communication.

ESCA Investigation of Perfluoromethylated Germanium Halides

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

Core-level binding energies have been recorded for all atoms in the series of compounds $(CF_3)_{4-n}GeX_n$, where n = 0–3 and X = F, Cl, Br, and I. The binding energy shifts are compared with those observed in the corresponding methyl series and are discussed in terms of estimated atomic charges derived from CNDO/2 and electronegativity-equalization procedures. The inclusion of potential and relaxation terms is also investigated.

Introduction

Bonding in trifluoromethyl derivatives of group 4 elements, especially in relation to analogous methyl compounds, has become a subject of both experimental and theoretical investigations. The preparation of several (trifluoromethyl)-germanes[2] makes it possible to undertake a systematic study of their properties. An electron diffraction study of $(CF_3)_4Ge$[3]

confirms the conclusion, based on the vibrational spectra[4] of the complete series $(CF_3)_{4-n}GeX_n$, n = 1–4, X = F, Cl, Br, I, that the Ge–C bond is weakened relative to that in the methyl analogues, and that the CF_3 group, in terms of second-order effects, behaves in a manner similar to the chlorine atom.

We report an ESCA investigation of the complete series of perfluoromethyl(halo)germanes. Earlier work on the methylhalogermanes[5,6] has shown that, in the gas phase, the

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

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Table I. Core-Level Binding Energies (eV)[a] for (Trifluoromethyl)germanium Halides

compd	Ge 3d	Ge 3p	C 1s	F 1s	χ^b
$(CF_3)_4Ge$	39.2		298.60	695.10	
$(CF_3)_3GeF$	39.6		298.65	695.15	693.00
$(CF_3)_3GeCl$	39.4	132.0	298.45	695.00	207.00
$(CF_3)_3GeBr$	39.2	131.5	298.40	694.95	76.90
$(CF_3)_3GeI$	38.9	131.0	298.25	694.80	627.75
$(CF_3)_2GeF_2$	40.2		298.80	695.30	693.40
$(CF_3)_2GeCl_2$	39.6	131.8	298.40	694.85	206.80
$(CF_3)_2GeBr_2$	39.2	131.5	298.25	694.75	76.70
$(CF_3)_2GeI_2$	38.7	131.0	297.90	694.60	627.40
$(CF_3)GeF_3$	40.9		299.00	695.50	693.70
$(CF_3)GeCl_3$	39.75	132.0	298.40	694.80	206.80
$(CF_3)GeBr_3$	39.3	131.7	298.15	694.65	76.50
$(CF_3)GeI_3$	38.55		297.60	694.40	627.20
GeF_4[c]	42.05	133.75			694.55
$GeCl_4$[c]	40.07	132.12			206.70
$GeBr_4$[c]	39.42	131.35			76.40
GeI_4[c]	38.52	130.45			626.30

[a] Values corrected relative to Ar $2p_{3/2}$ = 248.63 eV except for Ge 3d, Ge 3p, and Br 3d reported relative to Ne 2s = 48.47 eV. Uncertainties are ±0.10 eV except for Ge 3p (±0.2), F(Ge) 1s (±0.4). [b] F is attached to germanium, Cl $2p_{3/2}$, Br $3d_{5/2}$, I $3d_{5/2}$. [c] Bakke, A. A.; Chen, M. W.; Jolly, W. L. "A Table of Core Electron Binding Energies For Gaseous Atoms and Compounds", Department of Chemistry, University of California, Berkley, CA, May 1980.

chemical shifts are relatively large and can be related to changes in the electronegativity of the halogens. In this work we examine the altered behaviour of the ESCA chemical shifts when trifluoromethyl groups are substituted for methyl groups.

Experimental Section

Core-electron binding energies (Table I) were determined on a McPherson ESCA-36 photoelectron spectrometer using mainly magnesium Kα X irradiation (1253.6 eV) for photoelectron excitation. On a few runs, aluminum Kα X irradiation (1486.6 eV) was used. Samples were introduced in the vapor phase at pressures close to 5 × 10^{-5} torr. Argon gas was bled in to form up to 20% of the total sample and served as an internal standard because all binding energies for each compound are referred to the argon $2p_{3/2}$ level at 248.63 eV.[7] Those of the germanium 3d and bromine $3d_{5/2}$ level are reported relative to the neon 2s level at 48.47 eV.[7] The general operating details, mode of accumulation and treatment of data, were as described previously.[5] In general, however, fewer repeat scans were recorded because considerable problems had been met with data collection on a similar machine and we were concerned with minimizing the possibility of harmful effects on the source, detector, and analyser. The average full-width at half-maximum (fwhm) of the C 1s level is 1.05 and of the F 1s level is 1.62 and 1.25 respectively for the fluorines attached to carbon and germanium. The particularly broad fluorine band was also noted for CF_4.[8]

For Cl $2p_{3/2}$, I $3d_{5/2}$, and I $4d_{5/2}$, where the separation from the lesser component is significant, the average fwhm was 1.30, 1.20, and 1.29 respectively. The Br $3d_{5/2}$ level is not well separated from the Br $3d_{3/2}$ level, but the average fwhm was only 1.40. The identification of the Ge 3d and F 2s levels presented a significant problem in deconvolution. The relative intensity ratio of F 1s to F 2s peaks in CF_3SCl was used to calculate the relative contribution of the F 2s peaks (see Discussion). Additionally, for a few compounds, Ge $3p_{3/2}$ data was collected which required the use of an Al Kα excitation in order to avoid strong Auger lines in that region with Mg Kα radiation.[9] The results are listed in Table I.

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Table II. Atomic Partial Charge (δ) Calculated by CNDO/2

compd	δ(Ge)	δ(C)	δ(F(δ(H)))	δ(X)[a]
$(CF_3)_3GeF$	+0.724	+0.443	−0.194	−0.311
$(CF_3)_2GeF_2$	+1.004	+0.411	−0.192	−0.336
CF_3GeF_3	+1.298	+0.384	−0.190	−0.371
GeF_4	+1.594			−0.399
$(CF_3)_3GeCl$	+0.476	+0.470	−0.198	−0.102
$(CF_3)_2GeCl_2$	+0.541	+0.457	−0.201	−0.124
CF_3GeCl_3	+0.617	+0.452	−0.204	−0.152
$GeCl_4$	+0.650			−0.163
$(CF_3)_3GeBr$	+0.435	+0.469	−0.200	−0.035
$(CF_3)_2GeBr_2$	+0.450	+0.459	−0.206	−0.065
$(CF_3)GeBr_3$	+0.521	+0.443	−0.213	−0.109
$GeBr_4$	+0.550			−0.138
$(CH_3)_3GeF$	+0.679	−0.186	+0.029	−0.384
$(CH_3)_2GeF_2$	+1.013	−0.222	+0.036	−0.393
CH_3GeF_3	+1.285	−0.255	+0.056	−0.399
$(CH_3)_3GeCl$	+0.468	−0.156	+0.025	−0.228
$(CH_3)_2GeCl_2$	+0.601	−0.168	+0.027	−0.212
CH_3GeCl_3	+0.648	−0.168	+0.037	−0.197
$(CH_3)_3GeBr$	+0.451	−0.154	+0.021	−0.176
$(CH_3)_2GeBr_2$	+0.542	−0.165	+0.019	−0.164
CH_3GeBr_3	+0.656	−0.172	+0.027	−0.156

[a] δ(F) (attached to germanium), δ(Cl), and δ(Br).

Table III. Experimental (ΔE_C) and Calculated $(kq_C + V + l)^a$ Binding Energy Shifts for C 1s Referred to CH_4 (290.7 eV) as 0

compd	q_C	kq_C	V	$kq_C + V + l^a$	ΔE_C
$(CF_3)_3GeF$	0.443	9.70	−2.80	7.95	7.95
$(CF_3)_2GeF_2$	0.411	9.00	−2.13	7.93	8.10
CF_3GeF_3	0.384	8.41	−1.47	7.99	8.30
$(CF_3)_3GeCl$	0.470	10.29	−3.56	7.78	7.75
$(CF_3)_2GeCl_2$	0.457	10.00	−3.67	7.39	7.70
CF_3GeCl_3	0.452	9.89	−3.78	7.17	7.70
$(CF_3)_3GeBr$	0.469	10.27	−3.67	7.65	7.78
$(CF_3)_2GeBr_2$	0.459	10.05	−3.45	7.67	7.55
CF_3GeBr_3	0.443	9.70	−3.79	7.46	7.45

[a] k = 21.9 and l = 1.05.

Table IV. Experimental (ΔE_F) and Calculated $(kq_F + V + l)^a$ Binding Energy Shifts for F 1s Referred to HCF_3 (694.40 eV) as 0

compd	q_F	kq_F	V	$kq_F + V + l^a$	ΔE_F
$(CF_3)_3GeF$	−0.194	−5.35	4.19	1.00	+0.75
$(CF_3)_2GeF_2$	−0.192	−5.30	4.05	0.91	1.00
CF_3GeF_3	−0.189	−5.22	4.19	1.13	1.35
$(CF_3)_3GeCl$	−0.198	−5.46	4.14	0.84	0.60
$(CF_3)_2GeCl_2$	−0.201	−5.55	3.86	0.47	0.45
CF_3GeCl_3	−0.204	−5.63	3.76	0.27	0.40
$(CF_3)_3GeBr$	−0.200	−5.52	4.03	0.66	0.55
$(CF_3)_2GeBr_2$	−0.206	−5.69	3.70	0.17	0.35
CF_3GeBr_3	−0.213	−5.88	3.59	−0.13	0.25
$(CF_3)_3GeF$	−0.311	−8.58	5.39	−1.03	−1.40
$(CF_3)_2GeF_2$	−0.336	−9.27	5.85	−1.26	−1.00
CF_3GeF_3	−0.371	−10.24	6.53	−1.55	−0.70

[a] k = 27.6; l = 2.16.

Materials. The (trifluoromethyl)iodogermanes were prepared from GeI_4 and $(CF_3)_2Hg$ as described previously. Conversion to the other halides was achieved by reaction with AgX (X = F, Cl, Br). All samples were purified by trap to trap condensation or by distillation using a spinning-band column. The purity of all samples was established by IR, Raman, and NMR spectroscopy to be better than 98%. Only $(CF_3)_3GeF$ was slightly contaminated with $[(CF_3)_3Ge]_2O$.

Calculations. CNDO/2 calculations were carried out both for trifluoromethyl- and methylgermanes using the program GEOMO-FORTRAN IV developed by Rinaldi.[10] The program did not have the facilities for running iodides. The coordinates of the atoms were

(10) Rinaldi, D. GEOMO, Universite de Nancy; QCPE 290 available through Quantum Chemistry Program Exchange, University of Indiana.
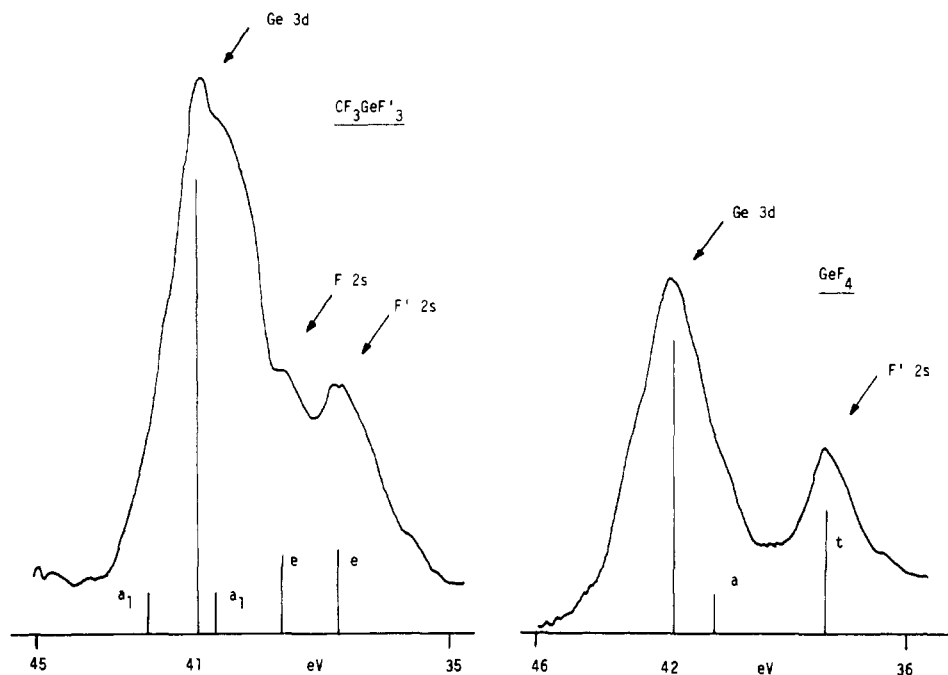
Figure 1. Germanium 3d and fluorine 2s levels in CF₃GeF′₃ and GeF′₄.

Table V. Experimental (ΔE_{Ge}) and Calculated $(kq_{Ge} + V + l)^a$ Binding Energy Shifts of Ge 3d Referred to Me₄Ge (36.10 eV) as 0

compd	q_{Ge}	kq_{Ge}	V	$\dfrac{kq_{Ge} + V + l^a}{}$	ΔE_{Ge}
(CF₃)₃GeF	0.729	8.38	−2.01	5.00	3.50
(CF₃)₂GeF₂	1.004	11.55	−5.61	4.58	4.10
CF₃GeF₃	1.287	14.80	−9.50	3.93	4.80
(CF₃)₃GeCl	0.476	5.47	+0.33	3.77	3.30
(CF₃)₂GeCl₂	0.541	6.22	−1.31	3.54	3.50
CF₃GeCl₃	0.617	7.10	−2.94	2.79	3.65
(CF₃)₃GeBr	0.435	5.00	+0.65	2.98	3.10
(CF₃)₂GeBr₂	0.450	5.18	−0.54	3.27	3.15
CF₃GeBr₃	0.521	5.99	−2.15	2.47	3.20

^{a} $k = 11.5$, calculated from Slater integrals, and $l = -1.37$ from best fit.

calculated with bond lengths previously reported in the literature.[3,11-15]

The CNDO/2 calculated charges (Table II) were used to calculate the potential term, $V = \sum q/r$, which in turn was used to calculate the chemical shifts (Tables III–V) according to the expression $(kq + V = E)$.[16] The equivalent-cores procedure was utilized to obtain the relaxation term, E_R.[17] Charges were also calculated (Table VI) for all the (CF₃)₄₋ₙGeXₙ compounds, including the iodides, by the EESOP method.[5,6] The values used for electronegativity were as follows: $\chi_{Ge} = 8.07 + 6.82\delta_{Ge}$; $\chi_F = 12.18 + 17.36\delta_F$ (pure p); $\chi_{Cl} = 10.39 + 11.17\delta_{Cl}$ (10% s character); $\chi_{Br} = 9.88 + 9.13\delta_{Br}$ (15% s character); $\chi_I = 9.23 + 8.47\delta_I$ (15% s character); $\chi_{CF_3} = 9.6 + 5.32\delta_{CF_3}$.

Results and Discussion

The experimentally determined core-electron binding energies for the complete series of compounds (CF₃)₄₋ₙGeXₙ (n

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(12) Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1210.
(13) Drake, J. E.; Hemmings, R. T.; Hencher, J. L.; Mustoe, F. M.; Shen, Q. *J. Chem. Soc., Dalton Trans.* **1976**, 394.
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(16) Reference 8, p 119.
(17) Jolly, W. L. In "Electron Spectroscopy"; Brundle, C. R., Baker, A. D., Eds; Academic Press: New York, 1977; Vol. I.

= 1–4, X = F, Cl, Br, I) are displayed in Table I. Comparison of this data with that of the corresponding methyl compounds[5,6] shows the general feature that all of the comparable binding energies are higher in the perfluorinated species. This is, of course, most marked for the C 1s level which is typically in the region of 298 eV for CF₃ compounds and 290 eV for CH₃ compounds.

The Ge 3d levels are typically shifted by ca. 0.7 eV when a CH₃ group is replaced by a CF₃. The peaks are broadened and distorted because of overlap with peaks arising from excitation of the F 2s level. In order that an estimate of the relative contributions of the F 2s and Ge 3d peaks, especially in the highly fluorinated species, could be obtained, the spectrum of CF₃SCl was run under identical conditions as for CF₃GeBr₃ in the regions around 39 and 690 eV. This provided a benchmark for the intensities of the F 2s level relative to both F 1s and Ge 3d. The very weak F 2s levels are split into a₁ and e sets at approximately 42 and 39 eV. The intensity of the e peak from these F atoms is still considerably less than the Ge 3d intensity. It becomes clear from the half-width that, in (CF₃)₄Ge, the Ge 3d and F 2s levels must esstentially overlap and this is apparently the case in most of the spectra. Thus the principal effect of the F 2s levels is to further broaden a peak which is already broad because of the very slight splitting arising from the separation (<0.4 eV) of the germanium 3d₃/₂ and 3d₅/₂ levels. In the case of the fluorides, the 2s levels of the fluorine atoms attached to germanium are clearly seen at lower binding energy and can be compared to the situation in GeF₄ (see Figure 1). Because fluorine substitution has the largest effect on the increase in binding energy of the Ge 3d levels, the separation between the Ge 3d levels and the F 2s levels of the CF₃ groups is only clear for these fluorides. In the other series, they essentially overlap, although with the iodides, where the Ge 3d levels are least shifted, the 2s e level can be seen as a shoulder at ca. 40 eV. In order that the small changes in the Ge 3d level binding energies noted for the bromide and chlorine series could be verified as real, the Ge 3p levels were recorded with Al Kα radiation, and it can be seen from Table I that the trends are identical. The relative changes in the Ge 3d levels with increasing halide substitution can be compared with the corresponding methyl series in Figure 2. Obviously, the total variation is much less

Table VI. Partial Charges (δ) Calculated with the EESOP Method[a]

	δ(Ge)	δ(CF$_3$(CH$_3$))	δ(X)
(CF$_3$)GeF$_3$	0.287	0.083	−0.123
(CF$_3$)GeCl$_3$	0.221	−0.003	−0.072
(CF$_3$)GeBr$_3$	0.194	−0.037	−0.052
(CF$_3$)GeI$_3$	0.148	−0.097	−0.017
(CF$_3$)$_2$GeF$_2$	0.240	0.022	−0.142
(CF$_3$)$_2$GeCl$_2$	0.206	−0.022	−0.081
(CF$_3$)$_2$GeBr$_2$	0.191	−0.041	−0.055
(CF$_3$)$_2$GeI$_2$	0.163	−0.077	−0.005
(CF$_3$)$_3$GeF	0.209	−0.018	−0.154
(CF$_3$)$_3$GeCl	0.196	−0.036	−0.089
(CF$_3$)$_3$GeBr	0.189	−0.044	−0.056
(CF$_3$)$_3$GeI	0.176	−0.061	0.006
(CF$_3$)$_4$Ge	0.188	−0.047	
(CH$_3$)GeF$_3$	0.261	0.141	−0.134
(CH$_3$)GeCl$_3$	0.184	0.102	−0.095
(CH$_3$)GeBr$_3$	0.156	0.087	−0.081
(CH$_3$)GeI$_3$	0.138	0.078	−0.072
(CH$_3$)$_2$GeF$_2$	0.163	0.091	−0.172
(CH$_3$)$_2$GeCl$_2$	0.123	0.070	−0.132
(CH$_3$)$_2$GeBr$_2$	0.108	0.063	−0.117
(CH$_3$)$_2$GeI$_2$	0.097	0.057	−0.106
(CH$_3$)$_3$GeF	0.074	0.045	−0.208
(CH$_3$)$_3$GeCl	0.059	0.037	−0.171
(CH$_3$)$_3$GeBr	0.054	0.035	−0.158
(CH$_3$)$_3$GeI	0.049	0.032	−0.146
(CH$_3$)$_4$Ge	−0.008	0.002	

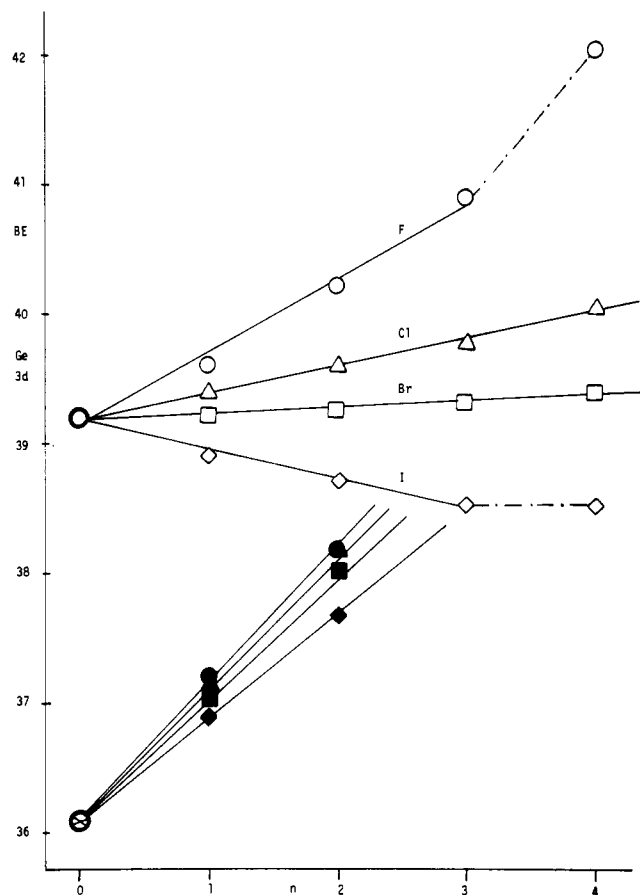[a] Values of a and b for $X = a + b\delta$ are given in the text.

Figure 3. Fluorine 1s, carbon 1s, and halogen levels plotted as a function of n in the series (CF$_3$)$_{4-n}$GeX$_n$, where X = F (O), Cl (△), Br (□), I (◇). O = (CF$_3$)$_4$Ge.

Figure 2. Germanium 3d levels plotted as a function of n in the two series of compounds (CF$_3$)$_{4-n}$GeX$_n$, where X = F (O), Cl (△), Br (□), and I (◇), and (CH$_3$)$_{4-n}$GeX$_n$, where X = F (●), Cl (▲), Br (■), and I (♦). O = (CF$_3$)$_4$Ge; ⊗ = (CH$_3$)$_4$Ge.

pronounced for the perfluoro than for the methyl series, and whereas the binding energies increase significantly with increasing halide substitution for all halides in the methyl series, a large increase is only observed for the fluorides in the
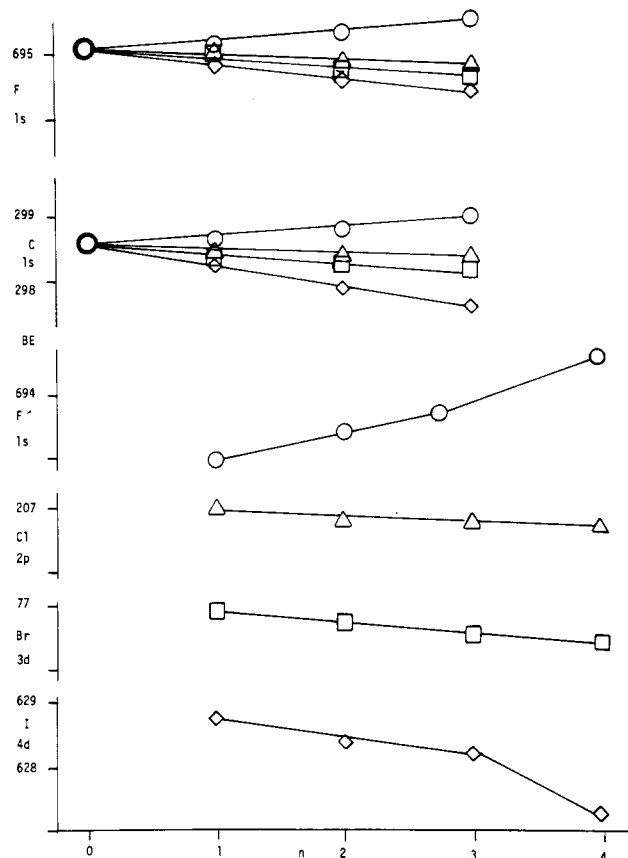
CF$_3$–germanes and, indeed, a decrease is observed for the iodide series. The increase in the chloride series is only slight and in the bromide series the binding energies are essentially independent of subsitution. These trends are predictable in terms of a simple inductive model. The group electronegativity of a CF$_3$ group is expected to be considerably higher than that of a CH$_3$ group, and vibrational studies[4] suggest its electronegativity, χ_{CF_3}, is probably close to that of a chlorine atom, χ_{Cl}.

It can be seen from Figure 3 that all of the other binding energies, C 1s, F 1s (attached to C) and F 1s, Cl 2p$_{3/2}$, Br 3d, and I 4d$_{5/2}$ essentially display a similar pattern of behavior. Thus increasing fluorine substitution on germanium increases the binding energies of core levels of *all* atoms in the molecule while increasing iodine substitution decreases them. This suggests very strongly that the introduction of a more electronegative group increases the relative positive charge on *all* of the other atoms (i.e., $^{\delta\delta+}$F–$^{\delta\delta+}$C–$^{\delta+}$Ge–$^{\delta}$F). The introduction of a second fluorine atom further increases the effective positive charge "down the chain", but because of competition from the fluorine atom already there, the fluorine atoms themselves become relatively less electronegative (hence also relatively more positive). The converse is the case for the introduction of the iodine atoms. In the bromide and chloride cases, the trends, although similar, do not match exactly, suggesting that some factors other than purely inductive may be evident when the electronegativity differences are small.

This point is also illustrated in Figure 4. A plot of BE(C 1s) vs. BE(F 1s) for the CF$_3$ groups in various species shows an essentially linear correlation (Figure 4a). The corresponding plots of BE(C 1s) vs. BE(Ge 3d) for the (CF$_3$)$_{4-n}$GeF$_n$ and (CF$_3$)$_{4-n}$GeI$_n$ series show linear correlations of positive but different slopes whereas the (CF$_3$)$_{4-n}$GeCl$_n$ and (CF$_3$)$_{4-n}$GeBr$_n$ series show somewhat different correlations
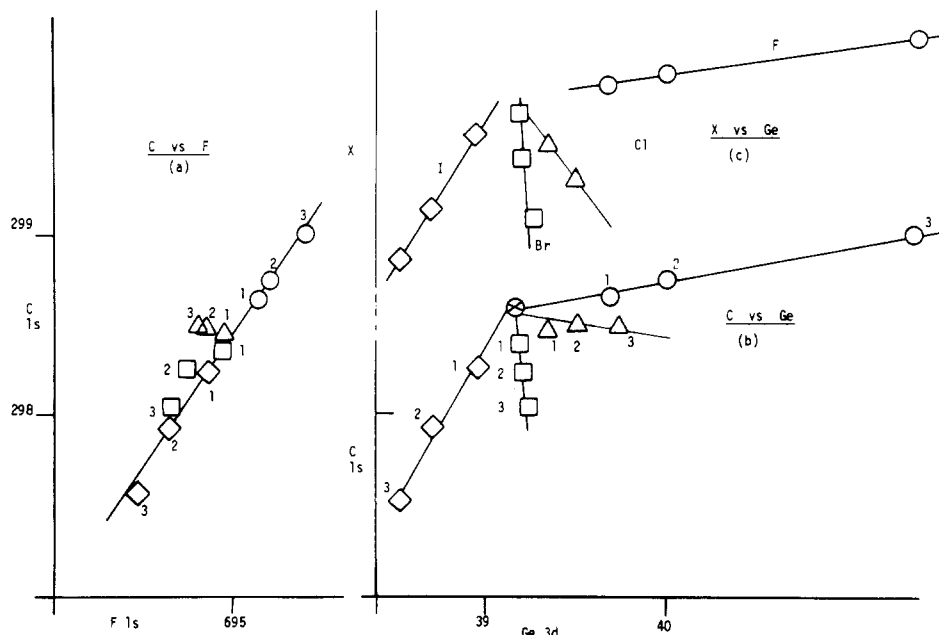
Figure 4. (a) Carbon 1s level plotted as a function of the fluorine 1s level of the CF_3 group and (b) the halogen levels and the carbon 1s levels plotted as functions of the germanium 3d level for the series $(CF_3)_{4-n}GeX_n$.
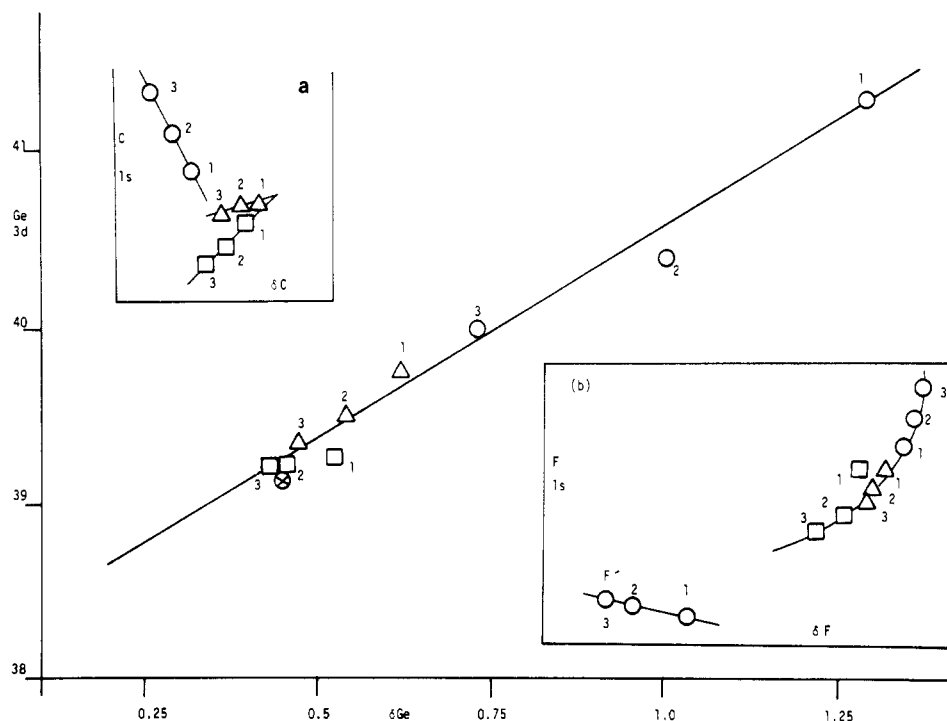
Figure 5. Germanium 3d levels plotted as a function of the CNDO/2 calculated charge on germanium. The inserts show corresponding plots for carbon 1s and fluorine 1s for the series $(CF_3)_nGeX_{4-n}$, where X = F (O), Cl (△), and Br (□).

(Figure 4b). Similar features are evident in correlating the Ge 3d levels with the halogen levels (adjusting the scale to superimpose the various series, Figure 4c).

At this point it seems appropriate to examine the changes in binding energies relative to the changes in calculated charge. A frequently used method of correlation is that which simply correlates the binding energy with the calculated charge on the atoms. In Figure 5, the correlation of BE(Ge 3d) with q_{CNDO} (listed in Table II) is displayed. It can be seen that the correlation is essentially linear, with the expected positive slope reflecting increase in BE with increase in charge. However, the inserts a and b demonstrate that some correlations for the BE of the carbon 1s and halide levels in fact have *negative* slopes, whereas the F 1s levels of the CF_3 group once

again have a positive slope. This pattern emerges because of CNDO/2 calculations produce an "alternating" charge effect on the introduction of a group of different electronegativity (i.e., $^{\delta\delta+}F-^{\delta\delta-}C-^{\delta+}Ge-^{\delta-}X$). These plots indicate that this does not reflect the true rearrangement of electron density. The Ge and F binding energies are correctly predicted because an increased positive charge is indicated, but the C 1s level does not fit because the calculations incorrectly predict an increased negative charge. Moreover, the prediction of the CNDO model suggests an increase in negative charge on increased substitution of a fluorine atom (Table II), whereas the experimental evidence suggests the opposite. Thus the more simplistic inductive effect suggesting $^{\delta\delta\delta+}F-^{\delta\delta+}C-^{\delta+}Ge-^{\delta-}X$ appears to reflect more accurately the changes taking effect
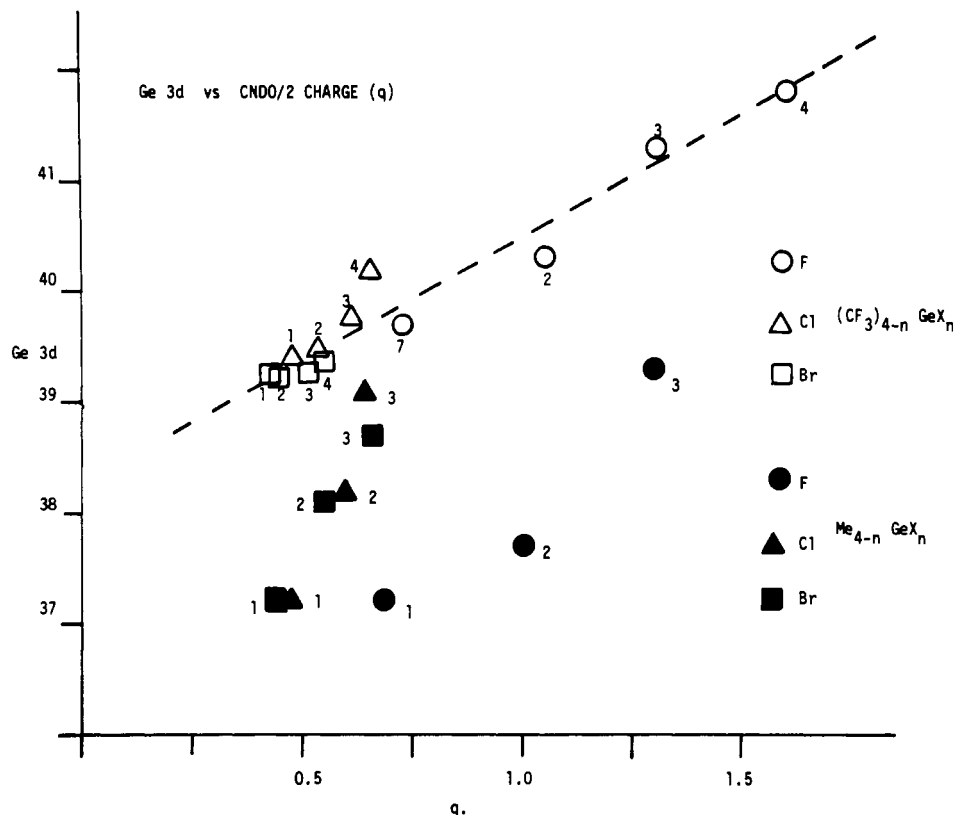
Figure 6. Germanium 3d levels plotted as a function of the CNDO/2 calculated charge on germanium for the $(CF_3)_nGeX_{4-n}$ and $(CH_3)_nGeX_{4-n}$ series.

and emphasizes the importance of looking at the binding energies of several atoms in a molecule rather than just the one of central interest. The CNDO calculated charges for the $(CH_3)_{4-n}GeX_n$ series are displayed in Figure 6, and this demonstrates the lack of consistency between the two series. It defies chemical sense that the charges on germanium should be essentially independent of whether CH_3 or CF_3 groups are attached.

It may be argued that these correlations failed because the potential term (as defined by $BE = kq + V + l^{16}$) was not included. The effect of substitution within a series of compounds is given by $\Delta BE = kq_1 + \Delta V$, and the results of the inclusion of the ΔV term are shown in Tables III–V.

For the carbon 1s levels, the inclusion of the potential terms does improve the correlation with the experimental binding energy shifts, ΔE_c, although the experimental observations still show different trends on halide substitution from those predicted (Table III). The experimental ΔE_F values are of the same magnitude and change in the same direction on halide substitution as do the values calculated from $kq_F + V + l$ (Table IV) for the CF_3 group fluorine atoms. However, for the fluorine atoms attached to germanium, the trends do not correlate. This is essentially as observed for the plots of binding energy against calculated charge and is not surprising in view of the similarity of the potential term for the CF_3 group in all compounds. This is not the case for the germanium 3d levels (Table V). The lack of general fit can be illustrated by a specific example. In the compound CF_3GeF_3, the CNDO/2 charge (positive) on Ge is overestimated at least in part because of the overestimation of large negative charge on the fluorine atoms. In turn, the overlarge negative charges on fluorine give overlarge values for V which overcorrects the binding energies to predict a decrease with increasing substituion rather than an increase. Thus, the potential term, which is essentially acting as a correcting factor for the overestimation of the charge in the first place, in this case overcorrects so that its inclusion incorrectly predicts that the germanium 3d binding
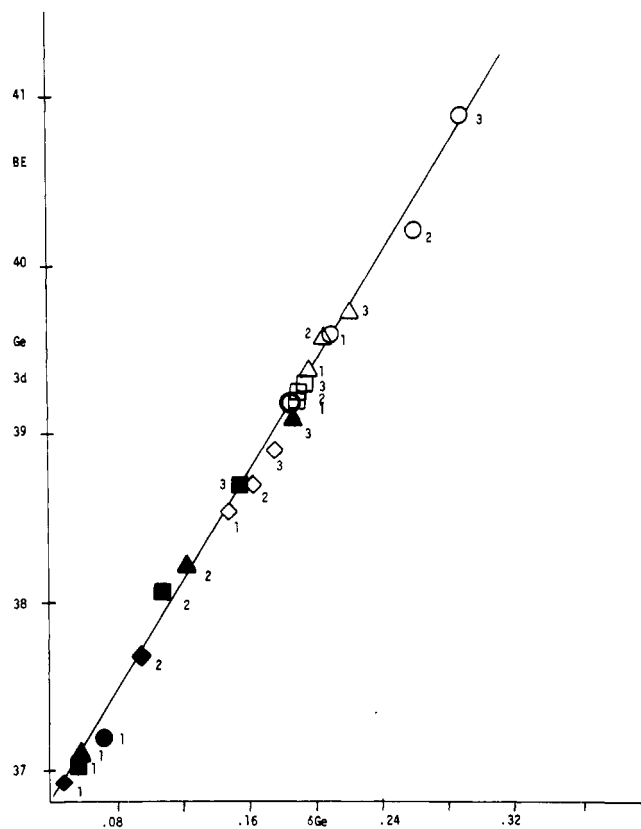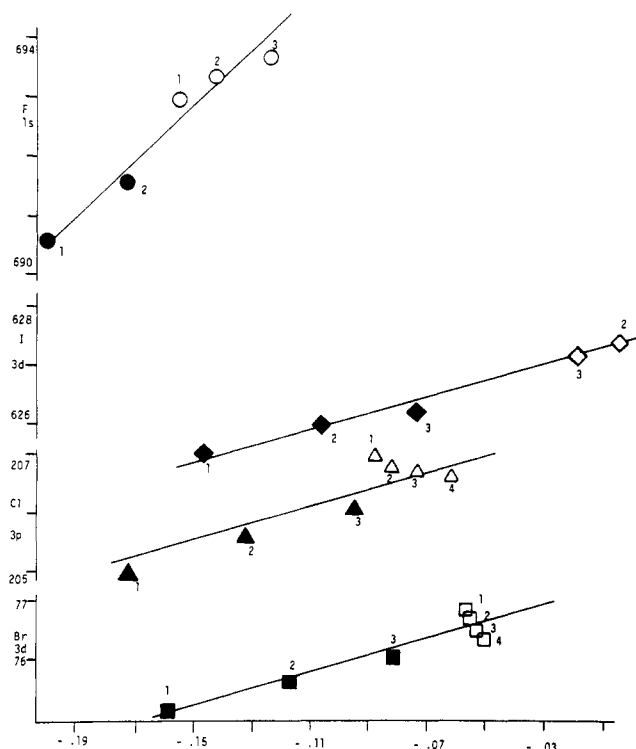

Figure 7. Germanium 3d levels plotted as a function of EESOP calculated charge on germanium.

energies decrease with increasing fluorine or chlorine substitution. We find that the inclusion of a relaxation term[17] recorrects back toward the observed trend but not sufficiently to correlate with experimental data. This serves to emphasize

Figure 8. Halogen levels plotted as a function of EESOP calculated charge on the halogen.

that increasing the degree of sophistication of calculations is meaningless if the orginal charges are being calculated incorrectly by the CNDO/2 method.

Thus we returned to our EESOP calculations[5,6] based on electronegativity-equalization methods.[18] This method shows reasonable agreement in the trends on plotting BE vs. charge (Figures 7 and 8). It should be noted that the methyl analogues fit the same correlation. The limitation in this case is the requirement of treating the CF_3 moiety as a group so that correlations can only be made for BE (Ge 3d) vs. q_{EESOP} (Figure 7) and BE (halogens) vs. q_{EESOP} (Figure 8). For the germanium 3d levels, the smooth changes in the charge distribution within a series of compounds suggests that the

changes are basically controlled by inductive effects. The absolute value of the charge depends on the relative participation of the s and p orbitals of the halogens which have been assumed to remain constant throughout both the methyl and perfluoromethyl series. The "best fit" value for the electronegativity of the CF_3 group, $\chi_{CF_3} = 9.6 + 5.32\delta_{CF_3}$, implies an overall electronegativity very similar to that of bromine which in EESOP calculation was assumed to have 15% s orbital participation in the bond to germanium. Any attempt to involve the potential term gave poorer fits with the experimental data, though the changes caused by the V term are much less pronounced than in the CNDO calculations because of the smaller calculated charges.

The halogen correlations show a reasonable fit, given our gross assumptions, except for the chlorides and, to some extent, the bromides in the CF_3 series. This is, no doubt, indicative that the oversimplified concept works least well when there are only slight changes in inducitve effects and parameters that have been ignored are coming into play.

Nevertheless, our results, in general, show, as they did for the methyl series, that changes in the binding energies of the various atoms in a molecule parallel each other. Thus if all binding energies are increasing along the series $(CF_3)_4Ge > (CF_3)GeF > (CF_3)_2GeF_2 > (CF_3)GeF_3$, GeF_4, it seems reasonable to assume that the atoms as a whole are more tightly bound together. It is interesting that the force constants of *all* bonds also increase along this particular series, and indeed the plots of force constant (C–Ge) vs. increasing substitution of halide[4] bear a remarkable similarity to Figures 3 and 4.

Registry No. $(CF_3)_4Ge$, 55642-43-8; $(CF_3)_3GeF$, 66348-16-1; $(CF_3)_3GeCl$, 66348-17-2; $(CF_3)_3GeBr$, 65094-18-0; $(CF_3)_3GeI$, 66348-18-3; $(CF_3)_2GeF_2$, 56592-86-0; $(CF_3)_2GeCl_2$, 56593-14-7; $(CF_3)_2GeBr_2$, 56593-16-9; $(CF_3)_2GeI_2$, 754-36-9; $(CF_3)GeF_3$, 1512-15-8; $(CF_3)GeCl_3$, 1495-36-9; $(CF_3)GeBr_3$, 56593-15-8; $(CF_3)GeI_3$, 1512-08-9; GeF_4, 7783-58-6; $GeCl_4$, 10038-98-9; $GeBr_4$, 13450-92-5; $(CH_3)_3GeF$, 661-37-0; $(CH_3)_2GeF_2$, 811-70-1; $(CH_3)GeF_3$, 753-69-5; $(CH_3)_3GeCl$, 1529-47-1; $(CH_3)_2GeCl_2$, 1529-48-2; $(CH_3)GeCl_3$, 993-10-2; $(CH_3)_3GeBr$, 1066-37-1; $(CH_3)_2GeBr_2$, 1730-66-1; $(CH_3)GeBr_3$, 6558-57-2; $(CH_3)GeI_3$, 1111-91-7; $(CH_3)_2GeI_2$, 1184-77-6; $(CH_3)_3GeI$, 1066-38-2; $(CH_3)_4Ge$, 865-52-1.

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Solid-State High-Resolution Carbon-13 Spectra of Some Tellurium Coordination Complexes. Correlations with X-ray Crystallography

N. ZUMBULYADIS* and H. J. GYSLING

High-resolution solid-state ^{13}C NMR spectra were obtained for several tellurium coordination complexes $[Te(S_2CNEt_2)_n$, $n = 2, 4, Te(S_2COEt)_2$, and $AsPh_4[Te(S_2COEt)_3]]$ by using cross polarization, dipolar decoupling, and magic-angle spinning. The spectra display solid-state effects that are intermolecular in origin. Methyl group chemical shifts are particularly sensitive probes of crystal symmetry, which is often reduced compared to molecular symmetry.

The combination of cross polarization,[1] dipolar decoupling, and magic-angle spinning[2] has allowed the observation of solid-state ^{13}C NMR spectra with resolution approaching that

obtained from liquid samples. The solid-state spectra often differ from the corresponding solution spectra both in the number of individual carbon resonances and in their chemical shifts. Two main factors determine such differences: (a) the freezing of the molecules into a particular conformation generally reduces the effective molecular symmetry and (b)

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(2) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976,** *98,* 1031.