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A RELATION BETWEEN ^{73}Ge CHEMICAL SHIFTS AND CNDO/2 CHARGES IN TETRAHALOGENOGERMANES

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Summary

Using Hojer and Meza's extension of the CNDO/2 method to third row elements, a linear relationship is established between the calculated atomic charges on the Ge atom in germanium tetrahalides $GeCl_nBr_{4-n}$ ($n = 0, 1, 2, 3, 4$) and their recently measured ^{73}Ge chemical shifts.

Recently, Kidd and Spinney [1] reported for the first time ^{73}Ge chemical shift measurements. They found that the pattern and range of ^{73}Ge chemical shifts in $GeCl_4$, $GeBr_4$, GeI_4 and in all the twelve corresponding mixed tetrahalogenogermanes were analogous with the corresponding shifts in tetrahalogeno compounds of two other group IV elements: ^{13}C [2] and ^{119}Sn [3]. Furthermore, the halogen dependence pattern for the ^{73}Ge shifts was the same as that observed for halogeno compounds of other main group elements, the central atom nucleus shielding increasing in the order $Cl < Br < I$ [4]. Using a pairwise additivity model of the type already used by Litchman and Grant in the investigations on the ^{13}C chemical shifts in tetrahalogeno-methanes [2], Kidd and Spinney fitted a ten parameter equation of the form:

$$\delta(^{73}\mathrm{Ge}) = a + \sum_{i} b_i\delta_i + \sum_{ij} c_{ij}\delta_{ij} \qquad (1)$$

where $\delta(^{73}\mathrm{Ge})$ is the ^{73}Ge chemical shift, taken relative to $GeCl_4$; δ_i represents the direct effect of the ith halogen substituent and the pair interaction δ_{ij} accounts for the combined effect of two halogens i and j; b_i and c_{ij} are simple population factors; a is a scale factor. On the other hand it is currently known that [5] a simple relationship can be established between ^{13}C chemical shifts and the electronic valence charge on the carbon atom involved. Until recently,

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TABLE 1

EXPERIMENTAL ^{13}C [2] and ^{73}Ge [1] CHEMICAL SHIFTS (IN ppm) IN TETRAHALOGENO COMPOUNDS MCl$_n$Br$_{4-n}$ (M = C, Ge) RELATIVE TO THE TETRACHLORO COMPOUND

n	C	Ge
0	125.1	343
1	91.5	259
2	—	101
3	28.9	78
4	0	0

however, no all valence semi-empirical method of the NDO-type including third row elements was available. The extension of the CNDO/2 method [6,7] by Hojer and Meza [8] to the elements K, Ca and Ga up to Br, makes it now possible to test the existence of a simple two parameter linear relationship between the calculated charge on the Ge-atom and the reported ^{73}Ge chemical shifts for the series of tetrahalogenogermanes of the form GeCl$_n$Br$_{4-n}$; n = 0, 1, 2, 3, 4. For the sake of comparison and as a test for the reparametrisation of this CNDO/2 method, we also calculated the charges on the carbon in the corresponding tetrahalogeno compounds. The experimental ^{13}C and ^{73}Ge chemical shifts [1,2] relative to the tetrachloro compounds are summarized in Table 1. The cartesian coordinates for the above-mentioned molecules were calculated assuming tetrahedral angles. The M—X distances (X = Cl, Br; M = C, Ge) were set equal to the experimental values obtained for MX$_4$ compounds: C—Cl = 1.766 Å [9], C—Br = 1.942 Å [10], Ge—Cl = 2.113 Å [11], Ge—Br = 2.29 Å [12]. Atomic charges were first calculated using the diagonal elements of the bond order matrix. However, as was pointed out by Shillady [13] and Figeys [14] a deorthogonalisation of the NDO wave functions as proposed by Giessner and Pullman [15] yields charge distributions which are in better agreement with ab initio calculations. So, we also calculated the atomic charges from the deorthogonalised wave function using a Mulliken population analysis [16]. The results from both procedures are summarised in Table 2. Also listed are the co-

TABLE 2

CHARGES (IN ELECTRONS) ON C AND Ge TETRAHALOGENO COMPOUNDS MCl$_n$Br$_{4-n}$ (M = C, Ge) BEFORE AND AFTER DEORTHOGONALISATION, AND COEFFICIENTS OF THE $y = ax + b$ EQUATION AND STANDARD DEVIATION

	Charge					*a*	*b*	s.d.
	n = 4	*n* = 3	*n* = 2	*n* = 1	*n* = 0			
Before deorthogonalisation								
C	0.284	0.246	0.209	0.174	0.138	— 862.6	243.5	2.2
Ge	0.155	0.110	0.067	0.026	—0.014	—2030.9	306	9.2
After deorthogonalisation								
C	0.213	0.166	0.121	0.079	0.035	— 706.1	148.4	2.4
Ge	1.454	1.374	1.296	1.220	1.147	—116.1	1615.4	8.3

efficients *a* and *b* and standard deviations of the fitted relations of the form $y = ax + b$ where y represents the experimental chemical shift relative to the tetrachloro compounds and x is the atomic charge on the C or Ge atom. The results show that the ^{73}Ge chemical shift can rather well be predicted from the calculated charges with an accuracy comparable to the results obtained by using [1]. We also see that, although the atomic charges on the Ge atom are clearly exaggerated, the results are slightly improved for third row elements when de-orthogonalised wave functions are used. For the two elements C and Ge the same sequence is observed, namely the decrease of the atomic charge on the central atom with increasing n, in agreement with common expectations.

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