E.S.R. Spectra and Structure of the Tetramethylsilane and Tetramethylgermane Radical Cations

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Solid-state e.s.r. studies show that $SiMe_4^+$ and $GeMe_4^+$ adopt C_{2v} symmetry rather than the D_{2d} or C_{3v} symmetries allowed by Jahn–Teller distortions from the T_d symmetry of the parent molecules.

The vapour phase photoelectron spectra of tetrahedral molecules[1-3] indicate that the positive ions distort from T_d to lower symmetries as a result of the Jahn–Teller effect.[4-6] In view of recent developments[7-10] showing that positive ions of saturated molecules can also be generated by γ-irradiation of solid solutions† and detected by e.s.r. spectroscopy, we have investigated the structure of the tetramethylsilane and tetramethylgermane radical cations to determine what kind of distortion, if any, takes place from tetrahedral symmetry under solid-state conditions.

The e.s.r. spectra of $SiMe_4^+$ and $GeMe_4^+$ in Figures 1 and 2, respectively, possess a similar overall hyperfine structure, each spectrum consisting of a partially resolved multiplet with at least 19 almost evenly spaced components in the absorption envelope. Assuming that the methyl groups are rotating freely as observed for $Si_2Me_6^+$ and $Ge_2Me_6^+$ at low temperatures,[11] only 13 lines would be expected from isotropic coupling to 12 equivalent hydrogens if the 4 methyl groups were equivalent as in T_d, D_{2d}, or D_{4h} symmetries. Consequently, a tetragonal distortion from T_d to the D_{2d} or D_{4h} point groups can be eliminated.

Distortions to C_{2v} and C_{3v} symmetries would in either case give rise to many more lines in the spectrum, and a reconstruction of the spectral patterns was therefore attempted for each of these possibilities. For both $SiMe_4^+$ and $GeMe_4^+$, a satisfactory fit was obtained only in terms of C_{2v} symmetry, the two pairs of equivalent methyl groups giving a septet of overlapping septets with binomial intensity ratios originating from two sets of six equivalent hydrogens. Stick diagrams corresponding to this analysis are shown in Figures 1 and 2,

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† The radical cations are generated in a Freon (CCl_3F) matrix by a mechanism which involves ionization of the solvent molecules followed by charge transfer to the solute (refs. 8—10).
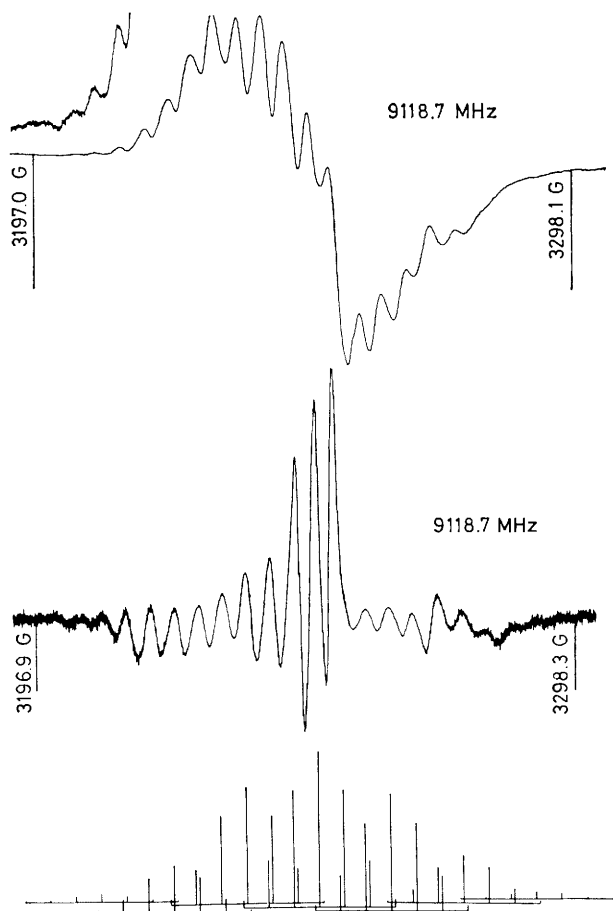
Figure 1. First-derivative (upper) and second-derivative (lower) e.s.r. spectra of a γ-irradiated (dose, 1 Mrad) solid solution of 8 mol % tetramethylsilane in trichlorofluoromethane at 90 K. The stick diagram reconstruction consisting of a septet of septets shows the line components assigned to the tetramethylsilane radical cation.
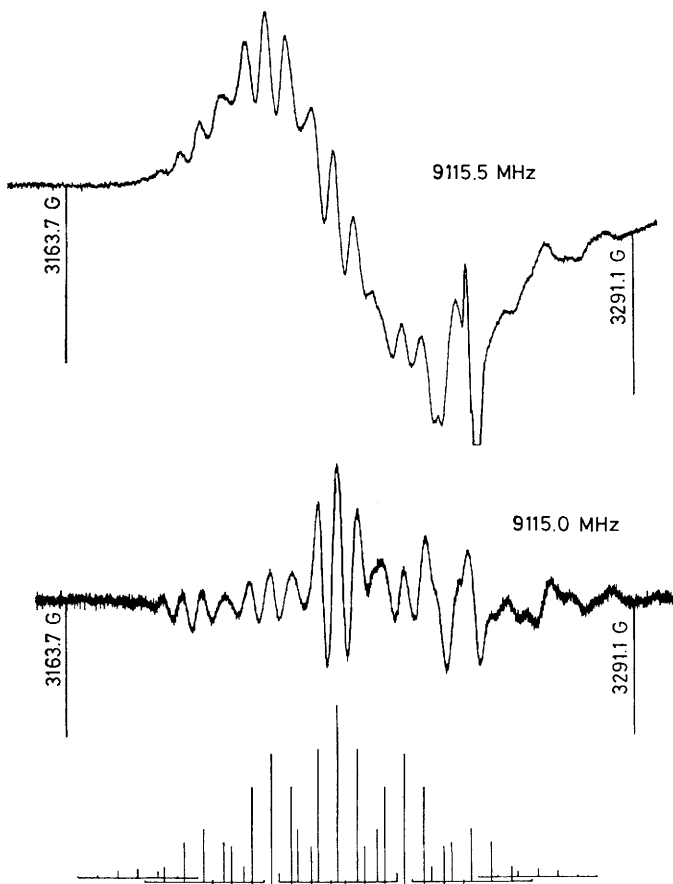
Figure 2. First-derivative (upper) and second-derivative (lower) e.s.r. spectra of a γ-irradiated (dose, 1 Mrad) solid solution of 8 mol % tetramethylgermane in trichlorofluoromethane at 85 K. The stick diagram reconstruction consisting of a septet of septets shows the line components assigned to the tetramethylgermane radical cation. A much better fit is apparent for the low-field side of the spectrum because this region is free from signals due to extraneous radicals.

Table 1. E.s.r. parameters for MMe_4^+ (M = C, Si, Ge) radicals.

Radical	¹H Hyperfine coupling/G	g-factor
CMe_4^+	$a(3H) = 42$ [a]	2.002—2.003 [a]
$SiMe_4^+$	$a_1(6H) = 13.6$ [b,c]; $a_2(6H) = 4.8$ [b,c]	$g_{iso} = 2.0050$ [b]
$GeMe_4^+$	$a_1(6H) = 14.7$ [b,c]; $a_2(6H) = 4.2$ [b,c]	$g_{iso} = 2.0196$ [b]

[a] Ref. 10. [b] This work. [c] If the major contribution to the hydrogen couplings in $SiMe_4^+$ and $GeMe_4^+$ arises from hyperconjugation with the unpaired electron localized mainly in the p orbital of the central atom directed along the C_2 axis (see the $2a_1$ molecular orbital in the diagram), the larger coupling $a_1(6H)$ is probably associated with the methyl groups in the apical sites of the trigonal bipyramidal (C_{2v}) structure.

and the e.s.r. parameters are given in Table 1. The observation that some of the components in the $GeMe_4^+$ spectrum (Figure 2) appeared to be broadened greatly assisted the above analysis, and these features are in turn well reproduced by computer simulation as shown in Figure 3.

Although only tetragonal and trigonal distortions to the D_{2d} and C_{3v} point groups, respectively, are allowed from tetrahedral symmetry by the theory of the Jahn–Teller effect,[5] such restrictions may not apply to the solid state where suitable vibronic perturbations can arise from intermolecular (matrix) effects. That a distortion to C_{2v} symmetry is likely to be energetically favourable for the radical cation can be seen qualitatively from the energy level diagram of Gimarc
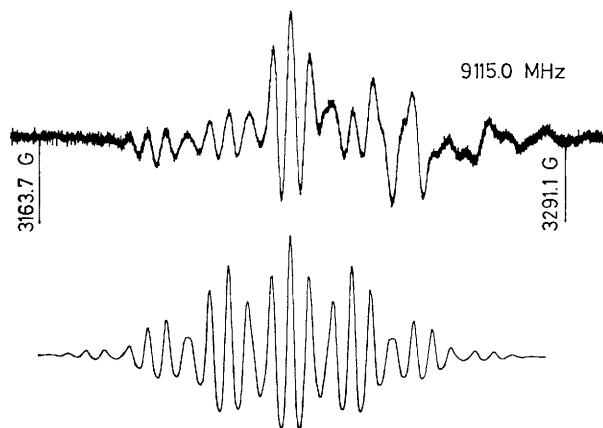
Figure 3. Observed (upper) and computer-simulated (lower) second-derivative e.s.r. spectra of the tetramethylgermane radical cation. The simulation was carried out using the parameters given in Table 1 and a line-width of 2.0 G. Only the low-field side of the observed spectrum is relatively free from interfering signals. It should also be noted that while the intensity ratios for the components present within each of the septet substructures are largely as expected, the intensity ratios between the individual septets are distorted from their theoretical values in a second-derivative presentation by the effect of the background envelope (see Figure 2).
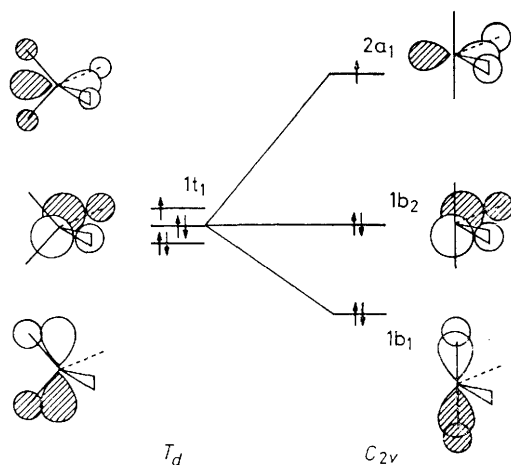
and Khan[12] for the central atom–ligand orbitals which is reproduced here, the effect of lowering the *occupied* 1 b_1 orbital more than cancelling the opposite effect resulting from the raising of the *half-occupied* 2 a_1 orbital.

The findings reported here contrast with the recent report[10] of a $T_d \rightarrow C_{3v}$ distortion for the radical cation of neopentane.‡ However, this difference could well be due to a greater mixing of the central atom–ligand σ-orbitals with the σ_{C-H} orbitals of the methyl groups in neopentane, as suggested by the interpretation of the photoelectron spectra of the Group 4B tetramethyls.[3] Moreover, the large hyperfine coupling (42 G)

‡ A similar e.s.r. spectrum for CMe_4^{+} showing coupling to three equivalent hydrogens has been obtained in our laboratory (J. T. Wang and F. Williams, unpublished work).

to only three equivalent hydrogens and the apparent formation of a preferred conformation in CMe_4^{+} also indicate a stronger delocalization of the positive hole away from the central atom in the case of neopentane. Just this kind of difference has been noted previously between the radical cation of hexamethylethane and those of hexamethyldisilane and hexamethyldigermane.[11]

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