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Electronic Structure in Methyl and Silyl Halides: Jahn-Teller Distortions and Ionisation Potentials

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For a wide range of pairs of methyl and silyl compounds $(CH_3)_nX$ and $(SiH_3)_nX$ the first ionisation potential is greater for the silyl derivative than for the methyl, and this has been regarded as strong evidence for the occurrence of pπ–dπ bonding involving lone pairs on X and 3d orbitals on silicon [1–5] : this view has been criticised [6] on the grounds that if the parent hydrides H_nX are also considered, the order of the ionisation potentials is always $(CH_3)_nX < (SiH_3)_nX < H_nX$, and it was suggested that a π perturbation was operative *via* the *n*p orbitals on carbon or silicon, and that the differing electronic properties of methyl and silyl groups were intimately connected with the different polarities of CH and SiH bonds.

Subsequently, it was noted from MNDO calculations [7] that in MH_3Cl (M = C, Si) the HOMO of *e* symmetry was much more delocalised from Cl onto MH_3 when M was silicon than when M was carbon, even using s and p orbitals only: this is consistent with the view put forward earlier [6], and in fact it is possible to reproduce the correct order of ionisation potentials $(CH_3)_nX < (SiH_3)_nX < H_nX < (CF_3)_nX < (SiF_3)_nX$ for a range of atoms X by *ab initio* calculations, using split basis sets but without d orbitals [8].

The greater delocalisation of the HOMO from the halogen atom in MH_3X when M is silicon implies that there should necessarily be a greater change in the molecular geometry of these species consequent upon ionisation. Here we report MNDO calculations of the molecular geometries of some radical cations $(X_3MY)^+$ (M = C, Si; Y = F, Cl; X = H, F) and also of some formally isoelectronic neutral radicals H_3MY (M = C, Si; Y = O, S). The structures of the cations $(X_3MY)^+$ are given in Table I, and those for the radicals $H_3MY^\bullet$ and their parent anions $(H_3MY)^-$ in Table II.

The cations $(X_3MY)^+$ all have C_s symmetry, as do the radicals $H_3MY^\bullet$, while the anions $(H_3MY)^-$ have C_{3v} symmetry as expected: in all the closed shell species, the HOMO has *e* symmetry, and ionisation is therefore expected to lead to a Jahn-Teller distortion along one of the *e* vibrations, ν_4, ν_5 or ν_6. The predominant motion appears always to be along a component of ν_5, the X_3M deformation mode. For a better assessment of the changes of structure, the data for the C_s species in Tables I and II have been recast in terms of the angles a_i and distances d_i defining the MX_3 group in terms of the local top-axis and its orientation with respect to the MY vector [9]; these data are given in Table III. Of these parameters [9], a_1 is the angle between the MY vector and the local top-axis of the MX_3 group, and is a close approximation to the 'tilt' angle usually employed when the MX_3 group is constrained, *e.g.* in electron diffraction analyses, to local C_{3v} symmetry; d_1 is the perpendicular distance from M to the top-axis (which rarely, if ever, actually passes through the atom M); d_2 and a_4 are the idealised bond distance and bond angle referred to the top-axis; and a_5 and a_6 are the dihedral angles of two of the X atoms referred to the

TABLE I. Geometries of Cations $(X_3MY)^+$.

$(X_3MY)^+$	d(MX)/A	d(MY)/A	<(XMY)/°	<(XMX)/°
$(CH_3F)^+$	1.2938	1.1119(×1) 1.2088(×2)	115.75(×1) 114.68(×2)	75.42(×1) 115.07(×2)
$(SiH_3F)^+$	1.5961	1.4604(×1) 1.5574(×2)	113.48(×1) 109.42(×2)	63.07(×1) 125.96(×2)
$(CH_3Cl)^+$	1.7492	1.1083(×1) 1.1400(×2)	108.79(×1) 108.48(×2)	101.47(×1) 114.60(×2)
$(SiH_3Cl)^+$	2.0536	1.4533(×1) 1.5333(×2)	115.03(×1) 108.89(×2)	73.55(×1) 121.78(×2)
$(CF_3Cl)^+$	Dissociates to $(CF_3)^+ + Cl^\bullet$			
$(SiF_3Cl)^+$	2.3305	1.6090(×1) 1.6078(×2)	103.90(×1) 104.16(×2)	113.45(×1) 114.71(×2)

TABLE II. Geometries of Anions $(H_3MY)^-$ and radicals H_3MY.

	d(MH)/A	d(MY)/A	<(HMY)/°	<(HMH)/°
(a) Anions				
$(H_3CO)^-$	1.2878	1.1545	116.21	101.97
$(H_3SiO)^-$	1.6387	1.4692	115.94	102.29
$(H_3CS)^-$	1.6710	1.1173	112.87	105.86
$(H_3SiS)^-$	1.9813	1.4540	115.55	102.77
(b) Radicals				
$H_3CO^{\cdot}$	1.3531	1.1180(×1) 1.1141(×2)	109.62(×1) 111.76(×1)	107.09(×1) 108.24(×2)
$H_3SiO^{\cdot}$	1.6839	1.4425(×1) 1.4567(×2)	109.33(×1) 107.78(×2)	109.17(×1) 111.32(×2)
$H_3CS^{\cdot}$	1.6912	1.1065(×1) 1.1090(×2)	111.50(×1) 109.38(×2)	108.55(×1) 108.98(×2)
$H_3SiS^{\cdot}$	2.0622	1.4382(×1) 1.4398(×2)	108.68(×1) 107.43(×2)	111.13(×1) 111.00(×2)

TABLE III. Structural Parameters for $(X_3MY)^+$ and $H_3MY^{\cdot}$.

	a_1/°	a_5, a_6/°	d_1/Å	d_2/Å	a_4/°
$(CH_3F)^+$	−0.69	± 135.65	−0.0501	1.1683	115.14
$(SiH_3F)^+$	+1.43	± 144.73	−0.0845	1.5122	111.11
$(CH_3Cl)^+$	−0.15	± 124.39	−0.0194	1.1285	108.60
$(SiH_3Cl)^+$	+2.78	± 138.81	−0.1020	1.4960	111.28
$(SiF_3Cl)^+$	−0.16	± 120.49	+0.0031	1.6082	104.07
$CH_3O^{\cdot}$	−1.37	± 120.60	+0.0220	1.1151	111.01
$SiH_3O^{\cdot}$	+0.90	± 120.54	−0.0242	1.4517	108.29
$CH_3S^{\cdot}$	+1.38	± 120.11	−0.0200	1.1080	110.07
$SiH_3S^{\cdot}$	+0.82	± 119.70	−0.0174	1.4420	107.80

third (which lies on the mirror plane) in a plane perpendicular to the top-axis.

For the cations $(H_3MY)^+$ (M = C, Si; Y = F, Cl) there is in each case a substantial change in geometry from the C_{3v} structure of the neutral parents, the major change being a sharp decrease in one of the H···H distances, characterised by <(HMH) (Table I) and a_5 and a_6 (Table III). For each Y, the magnitude of this distortion is greater for M = Si than for M = C: similarly within each Y pair, a_1 and d_1 are both greater in magnitude for silicon than for carbon, although the values of a_1 are negative for carbon and positive for silicon: for given M, the distortions, particularly as characterised by a_5 and a_6 are bigger for Y = F than for Y = Cl. The variations in the magnitudes of the distortions can be neatly correlated with the coefficient c_Y of the np_π orbitals on atom Y in the HOMO from which ionisation occurs in the neutral parent H_3MY (Table IV).

TABLE IV. HOMO Coefficients c_Y and Valence Electron Populations q_Y in Diamagnetic Molecules and Anions.

X_3MY	c_Y	q_Y	$(X_3MY)^-$	c_Y	q_Y
CH_3F	0.630	7.246	$(CH_3O)^-$	0.849	6.753
SiH_3F	0.534	7.475	$(SiH_3O)^-$	0.901	6.836
CH_3Cl	0.896	7.215	$(CH_3S)^-$	0.963	6.896
SiH_3Cl	0.812	7.358	$(SiH_3S)^-$	0.956	6.873
CF_3Cl	0.988	7.105			
SiF_3Cl	0.979	7.217			

These coefficients in H_3MY are lower for silicon than for carbon and lower for fluorine than for chlorine, and hence the magnitude of the Jahn-Teller distortions in $(H_3MY)^+$ is well correlated to the value of c_Y in the HOMO of H_3MY. The natural corollary is that where the HOMO is heavily localised on the atom Y and c_Y approaches unity the magnitude of the Jahn-Teller distortion will be much smaller. This is amply born out by trifluoro species F_3SiCl and by the Group VI derivatives $(H_3MY)^-$ (Y = O, S), where in particular a_5, a_6 are significantly smaller in the cation $(F_3SiCl)^+$ and the radicals $H_3MY^\cdot$ than for the cations $(H_3MY)^+$, while the values of c_y are rather greater.

It is interesting to note that there is no correlation whatever between c_y and the valence electron population on atom Y, q_y (Table IV): c_y contains information only about the HOMO, while q_y is the resultant of all the populated molecular orbitals in the valence shell. (Inner shells cause insignificant variations to the overall populations q'_y). The electron-donor or -acceptor properties of X_3M are manifested in q_y, but not in c_y and it is therefore inappropriate to interpret ionisation energies in terms of such properties: for this purpose, accurate values of q_y are required, and we shall return to the calculational aspects of this point in a subsequent publication.

Experimentally, because of the dependence of the extent of structural relaxation after ionisation on the magnitude of c_y, there should be a correlation between c_y and the difference between the vertical and adiabatic ionisation potentials.

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