PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

General Discussion: Electronic Emission Spectroscopy of CF $_{4}^{+}$ and SiF$_{4}^{+}$: Appendix. The Sign of the Spin-Orbit Coupling Constant in (t $_{2})^{52}T_{2}$ States of AX$_{4}^{+}$ Ions

S. M. Mason, R. P. Tuckett and R. N. Dixon

Phil. Trans. R. Soc. Lond. A 1988 **324**, 293-294
doi: 10.1098/rsta.1988.0019

REFERENCES

Aarts, J. F. M. 1985 *Chem. Phys. Lett.* **114**, 114.
Aarts, J. F. M., Mason, S. M. & Tuckett, R. P. 1987 *Molec. Phys.* **60**, 761.
Carrington, A. & Tuckett, R. P. 1980 *Chem. Phys. Lett.* **74**, 19.
Mason, S. M. & Tuckett, R. P. 1987*a* *Molec. Phys.* **60**, 771.
Mason, S. M. & Tuckett, R. P. 1987*b* *Molec. Phys.* (In the press.)
Watson, J. K. G. 1984 *J. molec. Spectrosc.* **107**, 124.

APPENDIX. THE SIGN OF THE SPIN–ORBIT COUPLING CONSTANT IN $(t_2)^5\,{}^2T_2$ STATES OF AX_4^+ IONS

By R. N. Dixon, F.R.S.

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

The spin–orbit splitting in orbitally degenerate systems with one open shell usually conforms to Hund's third rule: that is, the splitting is regular for a less than half-filled shell, and inverted for a more than half-filled shell. The $\tilde{C}\,{}^2T_2$ states of CF_4^+ and SiF_4^+ reported by Mason & Tuckett violate this expectation. We show below how this may occur in AX_4^+ ions where the dominant atomic spin-orbit coupling arises from motion around the X atoms.

For $(t_2)^5\,{}^2T_2$ states we consider only the spin–orbit coupling matrix elements within the t_2 shell, and use a basis of symmetry-adapted components which transform as translations parallel to the three cubic axes (Dixon *et al.* 1971). There are three types of t_2 basis function involving atomic p-orbitals, one localized on A and two on X_4:

$$\left.\begin{aligned} 1t_{2x} &= x_A, \\ 1t_{2y} &= y_A, \\ 1t_{2z} &= z_A. \end{aligned}\right\} \qquad \text{(A 1)}$$

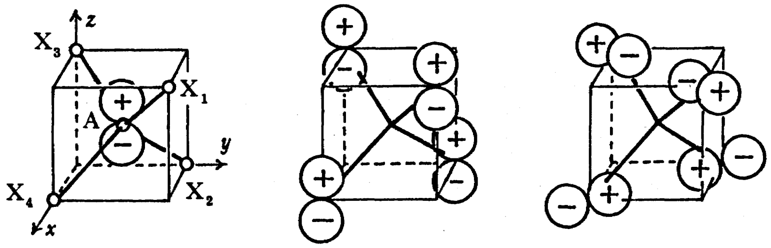
$$\left.\begin{aligned} 2t_{2x} &= \tfrac{1}{2}(x_1+x_2+x_3+x_4), \\ 2t_{2y} &= \tfrac{1}{2}(y_1+y_2+y_3+y_4), \\ 2t_{2z} &= \tfrac{1}{2}(z_1+z_2+z_3+z_4). \end{aligned}\right\} \qquad \text{(A 2)}$$

$$\left.\begin{aligned} 3t_{2x} &= \tfrac{1}{2\sqrt{2}}(y_1-y_2+y_3-y_4+z_1+z_2-z_3-z_4), \\ 3t_{2y} &= \tfrac{1}{2\sqrt{2}}(x_1-x_2+x_3-x_4+z_1-z_2-z_3+z_4), \\ 3t_{2z} &= \tfrac{1}{2\sqrt{2}}(x_1+x_2-x_3-x_4+y_1-y_2-y_3+y_4). \end{aligned}\right\} \qquad \text{(A 3)}$$

Note that for $3t_2$ the p-orbitals at each atomic centre can be combined into a single p-orbital directed at 90° to the translation axis of the basis function (see figure A 1), whereas it is parallel to this axis for $1t_2$ and $2t_2$.

In calculating spin–orbit matrix elements we shall only include integrals involving two atomic orbitals of the same atom. It is then sufficient to use a pseudo one-electron hamiltonian of the following form

$$H'_{\text{S-O}} = \sum_{i=1}^{5} \sum_{k} \xi_k\, l_k(i) \cdot s(i), \qquad \text{(A 4)}$$



$1t_{2z}$ $2t_{2z}$ $3t_{2z}$

FIGURE A 1. Symmetry-adapted p-orbital basis functions that transform as a translation parallel to the cubic z-axis.

where l_k is the one-electron angular momentum operator with origin at nucleus k, and ξ_k is the appropriate (positive) atomic-orbital coupling parameter. Let a molecular orbital be expanded as

$$\psi = c_1|1t_2\rangle + c_2|2t_2\rangle + c_3|3t_2\rangle. \tag{A 5}$$

It may then be shown that the splitting of the $^2T_2$ state into its $G_{\frac{3}{2}}$ and $E_{\frac{5}{2}}$ components is isomorphic with that for the effective hamiltonian $\xi_0 \Lambda \cdot S$, where

$$\xi_0 = -[c_1^2 \xi_A + (c_2^2 - \tfrac{1}{2}c_3^2)\, \xi_X]. \tag{A 6}$$

The global negative sign arises from the summation over five electrons, in accordance with Hund's third rule, whereas the additional negative sign to the $3t_2$ contribution is directly related to the atomic orbital orientation commented on above. With $\xi_X > \xi_A$ the limits are $\xi_0 = -\xi_X$ ($c_2 = 1$) and $\xi_0 = +\frac{1}{2}\xi_X$ ($c_3 = 1$).

If we assume pσ/pπ separability at the X atoms with respect to the AX bonds, the open shell for the $\tilde{C}^2T_2$ states of CF_4^+ or SiF_4^+ involves the pσ combination of $2t_2$ and $3t_2$, with $c_3 = \surd 2\, c_2$. In that approximation there would be no diagonal spin–orbit contribution from the X atoms, and Hund's third rule would be obeyed for the A atom contribution. However, an *ab initio* SCF–MO calculation at the double-zeta level of accuracy for the ground state of neutral CF_4 shows substantial pσ/pπ mixing (Snyder & Basch 1972), with small positive coefficients (c_2) for both basis functions of type $2t_2$, and much larger negative coefficients (c_3) for those of type $3t_2$. There may be some reorganization of the orbitals on ionization to CF_4^+. Nevertheless, it is clear that the multiplier of ξ_F within the bracket in (A 6) must be negative. The overall fluorine contribution to ξ_0 is therefore positive in the $\tilde{C}^2T_2$ state, and will outweigh the negative carbon contribution given that $\xi_F = 269\ \mathrm{cm}^{-1}$ and $\xi_C = 29\ \mathrm{cm}^{-1}$ (2p orbitals). A very similar reasoning applies to the Coriolis constant ζ, except that there are no scaling parameters ξ_F and ξ_C that give heavier weight to the fluorine orbital contribution. The carbon contribution will therefore be positive, but partly offset by a negative fluorine contribution, substantially reducing ζ from its limiting value of $+1$.

In conclusion, we should remember that Hund's rules were formulated for the lowest energy configuration of atoms with one open shell. Their extension to polyatomic molecules may go beyond the range of their validity.

REFERENCES

Dixon, R. N., Murrell, J. N. & Narayan, B. 1971 *Molec. Phys.* **20**, 611.
Snyder, L. C. & Basch, H. 1972 *Molecular wavefunctions and properties*, p. 362. New York: Wiley and Son.