Hydrogen Bonding in the Hydrogen Difluoride Anion. A Comparison of the Predicted Bonding Role of Fluorine $2p$ Orbitals with that Observed using X-Ray Emission Spectroscopy

By E. I. Esmail and D. S. Urch*

(*Chemistry Department, Queen Mary College, Mile End Road, London* E1 4NS)

Summary A shoulder, which is absent in potassium fluoride, is observed on the low energy side of the main fluoride K_α emission peak from potassium hydrogen difluoride, and is equated with fluorine $2p$ character in the orbital engaged in hydrogen bonding; relative peak intensities and energies correlate well with the SCF–LCAO–MO calculations of Clementi and McLean.

The fluorine K_α emission spectra[1] from potassium fluoride and potassium hydrogen difluoride were measured by irradiating the samples with X-rays (2·7 kW, Cr anode) in a Philips 1410 spectrometer using a rubidium acid phthalate diffracting crystal ($2d = 2612$ pm). The compounds were mounted by pressing them into discs with terephthalic acid. The spectra were scanned automatically by counting for 3 min periods at pre-set angular positions in the range $2\theta = 89$—$91°$, with 25 steps per degree change in 2θ.

The spectra are shown in Figure 1; the most striking difference between the two is the presence of a shoulder on the low energy side of the main peak in the hydrogen difluoride spectrum, separated from the main peak by *ca.* 4 eV or a little less. The simplest explanation for this shoulder is that it arises from fluorine $2p$ contributions to the MO which is involved in hydrogen bonding.

Clementi and McLean[2] have carried out SCF–LCAO MO calculations using Slater-type orbitals for a variety of basis sets. Using their tabulated AO coefficients for fluorine $2p$ orbitals in the various valence bond MOs and, taking into account the values of ζ used, it is possible to estimate the shape of the fluorine K_α emission peak. This is because the intensity of the fluorine K_α emission from any MO is proportional to the square of the fluorine $2p$ orbital coefficient in that MO.[3] Figure 2 (solid-line) shows the fluorine K_α peak (assuming a width at half-height of 3 eV for each orbital) for the basis set IV. This set includes double ζ functions for F$2p\sigma$ and F$2p\pi$ and also the hydrogen $2p\sigma$, $2p\pi$, and $3d\sigma$ orbitals; it also gave the lowest total energy. The other extended basis sets give quite similar K_α spectra. Figure 2 (dashed line) shows the fluorine K_α spectrum expected using the minimal basis set I. Figure

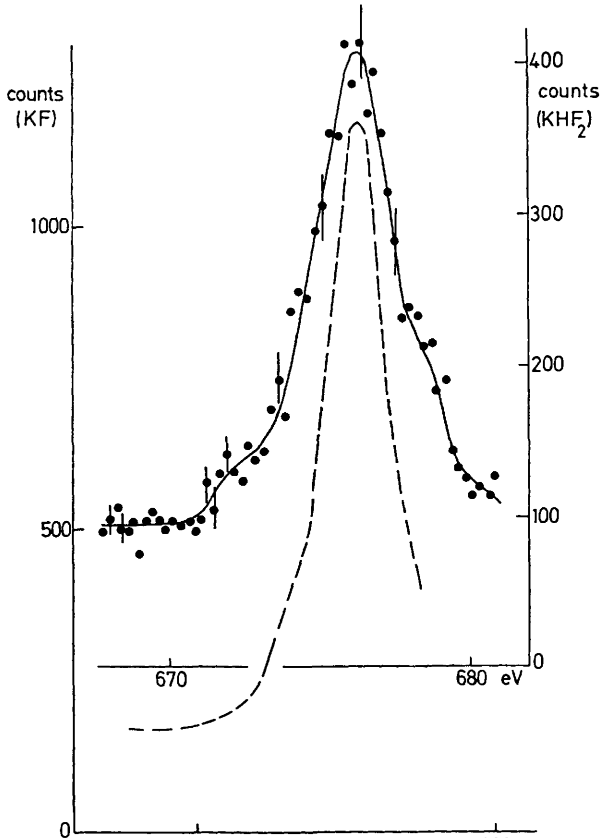

Figure 1. Dots, linked by solid line, show the actual counts recorded (right hand scale) at particular energies, for the fluorine K_α X-ray emission from potassium hydrogen difluoride. Typical errors are indicated by vertical lines at various points in the spectrum. The additional structure in the region >677 eV is probably due to X-ray emission from doubly ionised species. The fluoride K_α X-ray emission spectrum from potassium fluoride is shown by the dashed line and the number of counts is given on the left hand scale.

2 appears to show a greater difference in intensity of the low energy feature than could be explained merely by the somewhat larger F2$p\sigma$ coefficients that are found using basis set IV. This is due to the overlap that occurs between the main peak and the low energy satellite when a width of 3 eV is used for set IV; the peak separation for set I is greater and so this overlap is much less.

Comparison of Figures 1 and 2 (set IV) is most satisfactory with regard to both the energy separation between the main peak and the low energy shoulder, and also the relative intensities of the two features but similar comparison of Figures 1 and 2 (set I) shows that the minimal basis set gives a poor prediction of the K_α emission spectrum. That agreement between Figure 1 and 2 (set IV) is not better could be due to a variety of reasons, *e.g.*, poor statistics in the hydrogen difluoride spectrum, perturbations of calculated energy levels caused by potassium ions, and by solid state effects, *etc.* Despite these limitations the spectrum shown in Figure 1 confirms the theoretical predictions using the extended basis sets and demonstrates the value of X-ray emission spectroscopy in providing data by means of which theoretical calculations of both orbital energies and coefficients can be checked. It also demonstrates that this type of spectroscopy can be used to judge the quality of calculations using different degrees of approximation.

The authors thank the Royal Society and the University of London Central Research Fund for generous financial support, and Professor K. W. Sykes for helpful comments.

(*Received*, 12*th December* 1973; *Com.* 1681.)

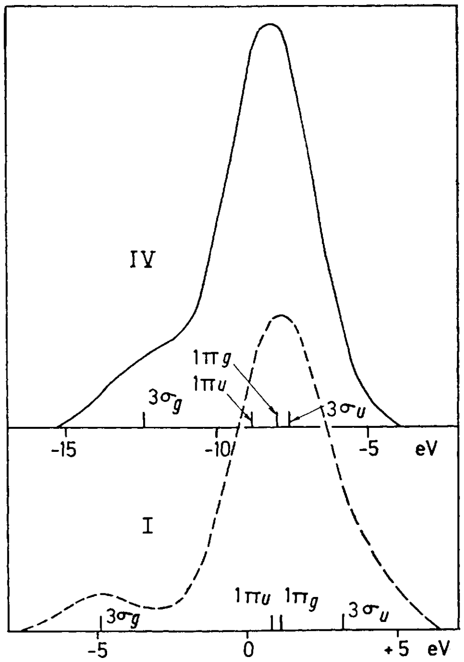

Figure 2. Fluorine K_α X-ray emission spectra for the hydrogen difluoride anion, from the calculations of Clementi and McLean[2] (basis set IV, solid line and basis set I, dashed line), assuming a half-height peak width of 3 eV.

---

[1] D. S. Urch, *Quart. Rev.*, 1971, **25**, 343.
[2] E. Clementi and A. D. McLean, *J. Chem. Phys.*, 1962, **36**, 745.
[3] D. S. Urch, *J. Phys.* (*C*)*-Solid State Physics*, 1970, **3**, 1275.