

Molecular Core Binding Energies for Thiophen and a Comparison with *Ab Initio* Calculations

By D. T. CLARK

(Department of Chemistry, University of Durham, South Road, Durham)

Summary Molecular core binding energies have been measured for thiophen, and are interpreted in terms of non-empirically calculated energy levels assuming Koopmans' theorem.

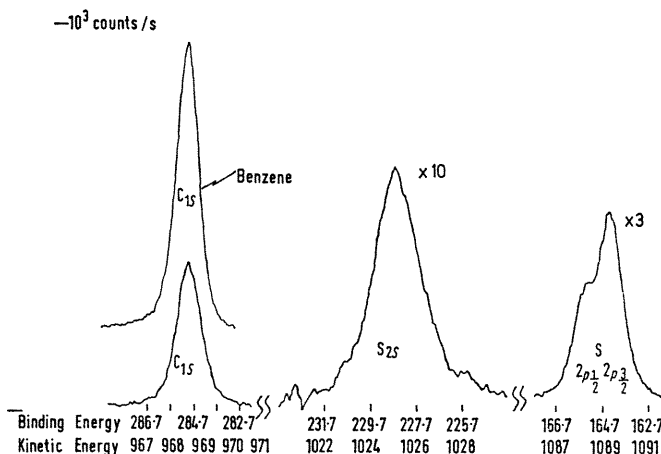
IN a recent communication¹ the sulphur core binding energies for a series of molecules including thiophen have been reported. We report here molecular core binding

contracted gaussian basis sets and differing strikingly in their predictions concerning the carbon 1s levels. Whereas the calculation by Clark and Armstrong predict essentially the same binding energies for C-1(C-4) and C-2(C-3), Gelius, Roos, and Siegbahn's¹ calculations shows a split of 0.7 eV.

The Figure shows the X-ray photoelectron spectrum of thiophen studied as a thin film on gold using Mg- $K_{\alpha 1,2}$ radiation. For comparison the carbon 1s levels for benzene are also shown. The carbon 1s levels for thiophen are little different in both binding energies and line widths from those of benzene (1.2 eV half width, and 1.1 eV half width respectively). Under the same condition the gold $4f_{7/2}$ core level has half width 0.95 eV. The linewidths for the sulphur ($2p_{3/2}, 2p_{1/2}$) spin doublet are similar to that observed by Gelius and his co-workers in their gas phase measurements.¹ Measurements have shown that for covalent compounds the binding energies in thin films of the solid and gaseous samples differ little when standardized to the same energy reference. (For gas phase measurements this will be the vacuum level, whilst for thin films on a conducting backing it will be the Fermi level). The spin-orbit splitting of 1.0 eV for the sulphur 2p level is clearly evident so that a split of this magnitude in the carbon 1s levels of thiophen would have been readily discernible. However, from the line width of the carbon 1s peak the split in the core levels must be *ca.* 0.1 eV, in good agreement with ref. 2. Since the two calculations differ only in the number of gaussian functions and their contraction experimental measurements of molecular core binding energies may be useful in obtaining balanced wavefunctions from limited basis set calculations.

We thank the S.R.C. for equipment.

(Received, January 6th, 1971; Com. 022.)



FIGURE

energies for both carbon 1s and sulphur 2s, 2p, for thiophen and comparison with non empirical calculations. There have been two 'ab initio' studies of thiophen^{1,2,3} both using

¹ U. Gelius, B. Roos, and P. Siegbahn, *Chem. Phys. Letters*, 1970, 4, 471.

² D. T. Clark and D. R. Armstrong, *Chem. Comm.*, 1970, 319.

³ D. T. Clark, "Organic Compounds of Sulphur, Selenium, and Tellurium," *The Chemical Society*, 1970, 1, 1.