Theoretical and Experimental Compton Profiles of Decaborane (14)

By IRVING R. EPSTEIN*
(*Department of Chemistry, Brandeis University, Waltham, Massachusetts* 02154)
and PHILIP PATTISON, MALCOLM G. H. WALLBRIDGE,† and MALCOLM J. COOPER
(*Department of Physics and Department of Molecular Sciences,*† *Warwick University, Coventry*)

Summary Measurement of the Compton profile of decaborane(14) using ^{241}Am γ-rays yields results in excellent agreement with a calculation employing localized molecular orbitals from smaller boron hydrides.

RECOGNITION of the potential chemical significance of Compton scattering, a technique which affords a direct experimental determination of electron momentum distributions and hence a stringent test of electronic wavefunctions, particularly for valence electrons, has been growing rapidly.[1] Chemical studies in this area have been devoted to metals, ionic solids, and a few molecules, mainly hydrocarbons and diatomic gases. The boron hydrides, with their complex three-centre bonding, played an important role in the first applications of *ab initio* localized molecular orbital (LMO) theory[2] to the analysis of Compton profiles and electronic momentum distributions in molecules.[3] However, until the present no experimental studies of boron hydride Compton profiles had been performed with which to test the theoretical predictions.

We present here a preliminary report of the first measurement of the Compton profile of a boron hydride, polycrystalline decaborane(14). We have also calculated the Compton profile of $B_{10}H_{14}$ by 'synthesizing' its momentum distribution from bridge and terminal BH bonds, two- and three-centre boron framework bonds, and boron inner shell LMO's taken from calculations on hexaborane(10).[4]

The experimental system, which is described in detail elsewhere,[5] consisted of a 300 mCi ^{241}Am source of 59·54 keV γ-rays, which were scattered by the sample through an angle of 150° into a Ge(Li) detector coupled to a multichannel analyser. The resolution of the detector at 60 keV was 390 eV FWHM (430 eV including beam divergence). Standard procedures were used for energy dependent corrections[5] and deconvolution of the instrumental resolution,[6] and a small contribution to the profile from multiply-scattered photons was removed by the Monte Carlo procedure of Felsteiner *et al.*[7]

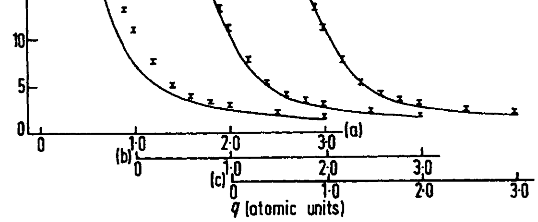

FIGURE. Experimental (I) and theoretical (———) Compton profiles of decaborane (14). (a) Experimental *vs.* Hartree-Fock free atoms (R. J. Weiss, A. Harvey, and W. C. Phillips, *Phil. Mag.*, 1968, **17**, 241); (b) experimental *vs.* LMO; (c) experimental *vs.* LMO after convolution with residual instrument function.

As the Figure shows, agreement of the LMO theory with experiment is excellent, far better than with a more elaborate calculation based on non-interacting boron and hydrogen atoms. We also see that the agreement is further improved when the theoretical profile is convoluted with the residual instrument function. This procedure takes account of the residual smearing of the experimental profile which remains after deconvolution.[8]

In summary, in addition to its success in dealing with structure and reactivity, the simple three-centre bond approach to boron hydride chemistry, quantified through the application of LMO's,[9] has now shown itself capable of accurately describing the spherically symmetric part of the electron momentum distribution in decaborane(14). The results presented here therefore provide a unique experimental verification of the validity of the LMO theory applied to a complex molecule other than a hydrocarbon, and give confidence to the application of such theories to other boron hydrides and electron-deficient molecules.

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