Electronic Structure of $B_4H_8Fe(CO)_3$. Comparison of SCF-Xα-SW Molecular Orbital Theory with the Ultraviolet Photoelectron Spectrum

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Summary The good agreement between the results of SCF-Xα-SW M.O. calculations and the experimental u.v. photoelectron spectrum of $B_4H_8Fe(CO)_3$ demonstrates (in contrast to the conclusions for similar molecules based on the Hartree–Fock model), that a first-principles one-electron treatment is capable of providing accurate results for this type of compound.

ULMAN *et al.*[1] have recently synthesized and characterized, by way of their u.v. photoelectron spectra, a number of compounds containing a borane, hydrocarbon, or carbaborane framework and an iron tricarbonyl group and have given interpretations of the spectra based on simple M.O. arguments and on observed intensity changes as a function of photon energy. For two of these molecules, $C_4H_4Fe(CO)_3$ and $B_3C_2H_7Fe(CO)_3$, the results of *ab initio* calculations have been reported.[2] These calculations (using Koopmans' theorem[3]) give assignments for the spectra which differ markedly from those deduced experimentally, the most noteworthy difference being that the experimental deductions place three orbitals which are primarily derived from the *d* orbitals of the $Fe(CO)_3$ species under the first experimental peak, whereas the calculations show one [$B_3C_2H_7Fe(CO)_3$] or no [$C_4H_4Fe(CO)_3$] metal-derived levels near the Fermi level (energy of the highest occupied M.O.). The remaining orbitals with a high metal character are calculated to be about 4 or 5 eV deeper. In the case of $C_4H_4Fe(CO)_3$ this discrepancy has been ascribed to a failure of Koopmans' theorem although ΔSCF calculations still do not give the correct assignment, the obvious conclusion (aside from the possibility of basis set problems) being that many-electron effects (*i.e.*, configuration interaction) are important.

We have performed M.O. calculations on the related metalloborane $B_4H_8Fe(CO)_3$ using the SCF-Xα-SW method.[4] Computational details will be given elsewhere.[5] The Figure shows (a) the experimental photoelectron spectrum[1] taken with He (I) radiation and (b) a simulated spectrum generated from our calculated M.O. energy levels by replacing each discrete level by a gaussian in order to generate a continuous curve.† The agreement in the relative positions of the peaks and even the relative intensities (assumed proportional to the number of contributing levels, *i.e.*, equal weights for the gaussians) is indeed striking. Moreover, analysis of the charge distribution in each M.O. yields an interpretation in substantial agreement with that deduced experimentally by Ulman *et al.* Briefly, peak 1 is assigned to three M.O.s which are predominantly *d* functions on the iron atom, peaks 2 and 3 are assigned, respectively, to two and four M.O.s with substantial contributions from the iron and the borane framework, and peak 4 is assigned to eleven M.O.s derived primarily from the carbonyl 1π and 5σ levels interacting with the iron *s* and *d* orbitals. The details of these interactions and of the construction of $B_4H_8Fe(CO)_3$ from its various fragments are important in the use of this molecule as a model for a supported transition metal catalyst and will be discussed fully elsewhere.[5] The good agreement shown in the Figure demonstrates that a reasonable description of the electronic structure of this type of molecule can be obtained from a first-principles one-electron treatment, without recourse to configuration interaction, and will lend confidence to subsequent conclusions based on the analysis of the wave functions.[5] As an indication that the present results are probably not fortuitous, the reader is referred to a very recent paper by Cotton and Stanley[6] where similar conclusions are reached concerning the comparison of Xα, Hartree–Fock, and configuration interaction results

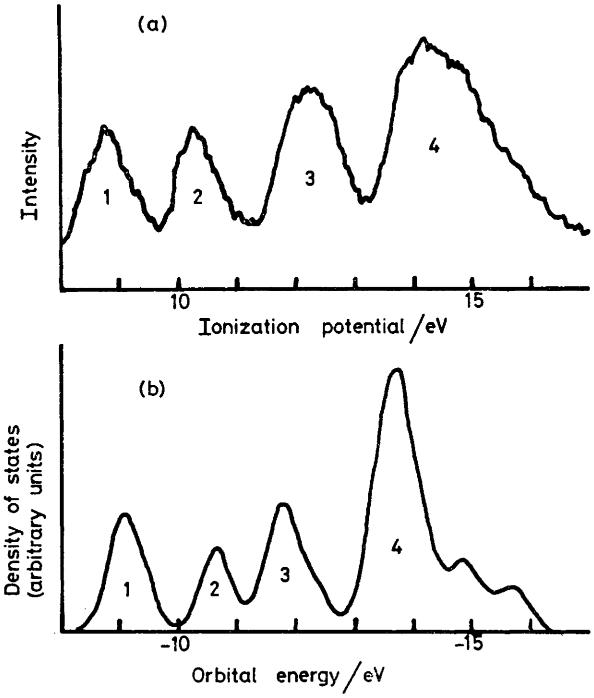

FIGURE. (a) The photoelectron spectrum of $B_4H_8Fe(CO)_3$ taken with He(I) radiation (from ref. 1) and (b) calculated density of states for $B_4H_8Fe(CO)_3$ *vs.* orbital energy, generated by replacing each discrete energy level by a gaussian function.

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† For a strict comparison to be made, the Slater transition state (ref. 4a) energies rather than the orbital energies should be used. This would involve a separate calculation for each level and is beyond our resources. However, the shifts involved usually differ very little from orbital to orbital [see, for example, the recent calculations on $Cr(CO)_6$, J. B. Johnson and W. G. Klemperer, *J. Amer. Chem. Soc.*, 1977, **99**, 7132, where the displacements are all between 2·1 and 2·4 eV] so that 'differential relaxation' is unlikely to be important.

for the question of the existence of a quadruple bond in $Cr_2(O_2CH)_4$.

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