A New Assignment of the Metal Ionizations in the Photoelectron Spectrum of $Mo_2(O_2CH)_4$

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Summary A new assignment of the metal ionizations in the photoelectron spectrum of $Mo_2(O_2CH)_4$ is proposed on the basis of *ab initio* SCF-MO calculations; such an assignment is consistent with the experimental spectrum and differs from that proposed on the basis of SCF-Xα-SW calculations.

Low energy photoelectron (p.e.) spectroscopy is potentially the most direct method of obtaining information on the ordering and separation of the valence metal levels in complexes possessing metal–metal bonds. For Mo^{II} dimeric species, the ordering of the metal–metal bonding molecular orbitals, $\sigma(d_{z^2}) < \pi(d_{xz},d_{yz}) < \delta(d_{xy})$ is commonly assumed,[1] following qualitative bonding arguments. Quantitative calculations have been performed in the case of $Mo_2(O_2CH)_4$ by the SCF-Xα-SW method.[2]

The p.e. spectrum of $Mo_2(O_2CH)_4$ shows two low energy bands corresponding to ionization potentials (i.p.) of 7·6 and 9·4 eV with intensity ratios of 1 : 5 and 1 : 3 for these bands using He(I) and He(II) ionizing radiation, respectively.[3,4] To date it has been suggested that these two bands correspond to ionization from the δ and π metal–metal bonding orbitals respectively,[2,3] and that the σ ionization occurs at 12·7 eV, appearing as a peak to higher i.p. of the broad band arising from ligand ionizations.[2] We here report *ab initio* SCF-MO calculations on $Mo_2(O_2CH)_4$ which cast doubt on such an assignment.

The calculations were performed using the molybdenum basis of Huzinaga[5] (17*s*11*p*8*d* contracted to 7*s*3*p*2*d*). The oxygen and carbon 1*s* and 2*s* orbitals were represented by best atom Slater type orbitals[6] (STO) each fitted by three gaussian type functions (GTF), the 2*p* orbitals being atomic Hartree–Fock functions each represented by 4GTF's.[7] The hydrogen 1*s* orbital was an STO of exponent 1·2 fitted by three GTFs. The calculation was performed at the experimental geometry.[8] In the Table we show the i.p.s corresponding to removal of an electron from the $2b_{2g}(d_{xy})$, $5a_{1g}(d_{z^2})$, and $6e_u(d_{xz},d_{yz})$ metal–metal bonding orbitals (all these orbitals have >75% Mo 4*d* character). These i.p.s were calculated both by the use of Koopmans' theorem and by the ΔSCF method, the latter allowing for

Table. Calculated i.p.s. (eV) of $Mo_2(O_2CH)_4$.

Ionic state	i.p. (Koopmans' theorem)	i.p. (ΔSCF method)
$^2B_{2g}(2b_{2g})$	9·4	8·6
$^2A_{1g}(5a_{1g})$	11·5	10·3
$^2E_u(6e_u)$	11·6	10·4

orbital relaxation upon ionization. As expected, the lowest i.p. corresponds to the $2b_{2g}(d_{xy})$ M.O. However, both approximations predict that the σ and π ionizations are separated by only 0·1 eV. We thus suggest that the second peak in the p.e. spectrum contains both the σ and π ionizations, and not as is commonly assumed just the π ionization. With our new assignment, the calculated separation between the first two peaks in the spectrum is 2·2 eV (Koopmans' theorem) or 1·8 eV (ΔSCF method), in good agreement with the experimental value (1·8 eV). In this communication we do not present the complete assignment of the p.e. spectra of $Mo_2(O_2CR)_4$ species, but we do note that the peak at 12·7 eV previously assigned[2] to the σ ionization can be correlated with the $4b_{1g}$ and $4a_{1g}$ M.O.s, both of which have significant (*ca.* 20%) metal character, and which contribute to the Mo–O bonds. It is also noteworthy that the experimental intensity ratio of the first two peaks is substantially greater then the value near 1:2 expected on degeneracy grounds alone if the first two peaks arose from δ and π ionizations respectively. However, in view of the substantially different intensity ratios found for He(I) and He(II) we do not cite such ratios as giving strong support to our new assignment, but note that they are not inconsistent with more than one ionization being contained in the second band.

The use of a near minimal basis and the neglect of correlation effects in these calculations, might cast doubts upon the validity of the interpretation thus derived. However, we have shown that a basis of this quality has been successful in interpreting the spectra of a wide range of transition metal complexes.[9] Also *ab initio* calculations have been performed on $Mo_2(OH)_6$ to interpret the p.e. spectrum of $Mo_2(OCH_2CMe_3)_6$ reported by Cotton *et al.*,[10] an SCF-Xα calculation having also been reported by these authors on this hypothetical molecule.[10] The p.e. spectrum of $Mo_2(OCH_2CMe_3)_6$ shows two low energy bands at 7·4 and 8·1 eV which can confidently be assigned to metal–metal π and σ ionizations of this molecule which possesses a metal–metal triple bond. Calculations carried out as described above predict the first i.p. to arise from the metal–metal π ionization, the σ ionization being calculated to be 1·9 eV to higher i.p. This compares with the experimental separation of 0·7 eV. Although the difference between the theoretical and experimental splitting is rather large, it may in some measure be associated with the calculation being performed not on the actual molecule studied experimentally. However, this calculation on $Mo_2(OH)_6$ does suggest that we overestimate the σ–π separation. For our new assignment of the p.e. spectrum of $Mo_2(O_2CH)_4$ to be incorrect our calculation must significantly underestimate this separation. There is thus good reason to suspect the usefulness of the SCF-Xα-SW method in assigning the p.e. spectra of molecules containing Mo–Mo bonds. This conclusion suggests that any assignment by this method, of the spectra of molecules containing Cr–Cr bonds, where the bonding is undoubtedly more complex[11] should also be undertaken with caution.

(*Received, 14th November* 1977; *Com.* 1172.)

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