

The breakdown of the oneelectron picture in the ligand XPES of Mo₂(O₂CH)₄, Mo₂(O₂CCH₃)₄, and Cr₂(O₂CCH₃)₄

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The breakdown of the one-electron picture in the ligand XPS of $\text{Mo}_2(\text{O}_2\text{CH})_4$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$

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The C1s and O1s photoelectron spectra of gaseous $\text{Mo}_2(\text{O}_2\text{CH})_4$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ are reported. An intense satellite peak is associated with C1s ionization in $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, but is absent in the other spectra. These observations are interpreted using *ab initio* MO calculations, together with initial and final state correlation effects. The intense satellite is associated with the transition $\delta \rightarrow Lp\pi$, where δ is a metal-metal bonding orbital and $Lp\pi$ is an orbital of the same symmetry localized on the ligand from which ionization has occurred.

I. INTRODUCTION

The change in the ionization energies (I.E.) of the core electrons of a ligand upon formation of a transition metal complex is a potential source of information concerning the electronic charge distribution within the complex. Thus, in simpler molecules, the core electron (ESCA) chemical shifts can often be interpreted in terms of the simple point charge potential model, which contains the formal atomic charges of the molecule.¹ However, such an approach requires the assumption that the relaxation energy accompanying core electron ionization is the same in the free and in the complexed ligand. In the most extensively studied case to date, that of mononuclear transition metal carbonyls, the use of Koopmans's theorem (KT) predicts the incorrect sign for the change in the carbon 1s I.E. on complex formation.² The inclusion of orbital relaxation, which is found to be greater in complexed than in free CO, yields the correct sign and magnitude for the chemical shift.³ A further complication is present in the ESCA spectra of transition metal carbonyls, the occurrence of an intense satellite peak close to the primary O1s and C1s lines, which is absent in the spectra of free CO.⁴ This intense peak has been attributed to a $M(3d) \rightarrow L(\pi^*)$ valence charge transfer transition which accompanies core electron ionization.³ Thus, the ESCA spectra of ligands complexed to transition metal atoms are potentially complicated, and their interpretation is often far from straightforward. An understanding of such spectra is particularly important since analogous spectra are often observed in surface chemistry studies. For example, satellite spectra similar to those found in transition metal carbonyls are found in the ESCA spectra of CO chemisorbed on metal surfaces.⁵

In this paper, we present a study of the core electron I.E.'s of the ligands in the molecules $\text{Mo}_2(\text{O}_2\text{CH})_4$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$. For the molybdenum containing molecules, an intense C1s satellite peak is found, which is considerably weaker or absent in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$. In none of the molecules studied here are intense satellites observed in the O1s spectra. Following a description of the observed spectra, we

report *ab initio* calculations of the core I.E.'s and of the position and intensities of the satellite peaks.

II. EXPERIMENTAL DETAILS AND RESULTS

Gas phase x-ray photoelectron spectra (XPS) of $\text{Mo}_2(\text{O}_2\text{CH})_4$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ were measured using AlK α radiation. The spectrometer described earlier⁶ was fitted with an x-ray gun having a heatable gas cell attached at its end. Noninductively wound resistance heaters allow temperatures up to 400 °C to be attained. Gaseous samples and calibrant gases enter the gas cell *via* a small side tube. The spectra described in this paper were calibrated using CO_2 and C_6H_6 , which have I.E.'s close to those being measured.⁷ Count rates of $\sim 3000 \text{ cs}^{-1}$ are typical for the neon 1s line when irradiated by AlK α radiation (10 kV, 40 mA). Repeated scanning and data accumulation is carried out using an Ino Tech 5300 multichannel analyzer.

The molybdenum and chromium complexes were prepared by standard methods,⁸ the spectra being recorded at the following approximate temperatures: $\text{Mo}_2(\text{O}_2\text{CH})_4$, 150 °C; $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 135 °C; $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, 200 °C. The measured C1s and O1s I.E.'s and relative peak areas are listed in Table I, and the spectra are shown in Figs. 1 and 2. It can be seen that in the case of

TABLE I. C and O1s ionization energies (eV) in $\text{Mo}_2(\text{O}_2\text{CH})_4$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

	C1s ^a	O1s
$\text{Mo}_2(\text{O}_2\text{CH})_4$	293.8 (1.0)	538.5
	296.1 (1.1)	
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	291.1 (1.9)	537.9
	293.4 (1.0)	
	295.7 (1.1)	
$\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$	294.3	537.8
	291.1	

^aThe relative peak intensities are given in parentheses.

$\text{Mo}_2(\text{O}_2\text{CH})_4$ there are two main C1s peaks, in spite of the four carbon atoms in the molecule being equivalent. Similarly, for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, there are three C1s lines, with only two distinct types of carbon atoms in the molecule. For $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, it is clear from the intensity profile that the most intense peak at low I.E. is due to

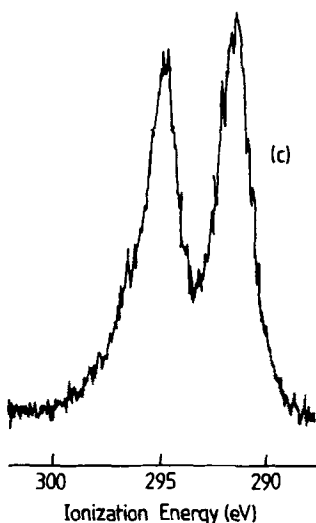
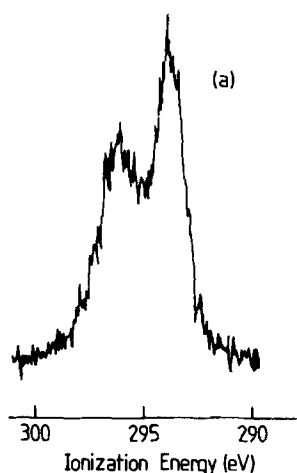


FIG. 1. C1s XPES of (a) $\text{Mo}_2(\text{O}_2\text{CH})_4$, (b) $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and (c) $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

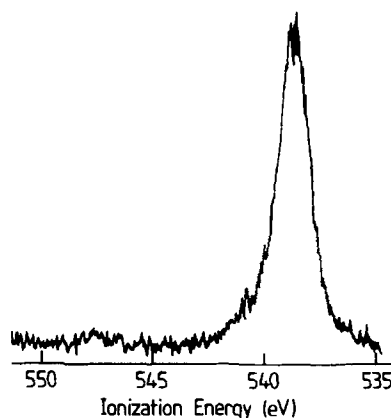


FIG. 2. O1s XPES of $\text{Mo}_2(\text{O}_2\text{CH})_4$.

$-\text{CH}_3$ C1s ionization and that the other two peaks, whose summed intensities are approximately equal to that of the first peak, arise from $-\text{CO}_2$ C1s ionization. Similarly, the two C1s peaks observed for $\text{Mo}_2(\text{O}_2\text{CH})_4$ arise from core ionization of the equivalent carbon atoms in this molecule. In the case of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, the C1s peak to low I.E., which corresponds to the same I.E. as that in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, is assigned to $-\text{CH}_3$ C1s ionization. In contrast to $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, only a second C1s peak is found, having a shoulder to high I.E. The intensity of this second peak is approximately equal to that of the first. From these results, it is clear that in both $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ the total intensity for $-\text{CO}_2$ C1s ionization is the same as that for $-\text{CH}_3$ C1s ionization. In $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, intensity is essentially equally distributed between two peaks, whilst in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ most of the intensity is contained in the primary $-\text{CO}_2$ C1s line. In all three molecules studied here, the O1s region of the photoelectron spectrum shows no such intense satellite peaks (Fig. 2).

In order to understand these carbon and oxygen XPES, we now describe theoretical treatments of the C1s and O1s ionic states of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$. In view of the similarities between the spectra of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, calculations on $\text{Cr}_2(\text{O}_2\text{CH})_4$ will be relevant to an understanding of the spectra of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

III. COMPUTATIONAL DETAILS AND RESULTS

Our previous experience in the computation of core electron I.E.'s,⁹ and in the assignment of satellite states,¹⁰ suggested that a series of calculations of increasing complexity would be useful in the present studies, including first orbital relaxation, to be followed by the inclusion of correlation effects. An additional complication which was not present in studies on other molecules is that in these complexes which contain formal metal-metal quadruple bonds, a single determinant is a poor description of the ground state.^{11,12} Thus, in $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$, the quadruple bond configuration contributes only 67% and 6%, respectively, to the ground state wave function.¹² Thus, correlation effects in both the ground and ionic states, which have previously been found to be important in

TABLE II. Calculated and experimental C1s and O1s ionization energies (eV) in HCO_2H , $\text{Cr}_2(\text{O}_2\text{CH})_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$.

	Experimental I. E.		Calculated I. E.			
	C1s ^a	O1s	Koopmans' theorem		ΔSCF	
			C1s	O1s	C1s	O1s
HCO_2H^b	296.0 (295.6)	538.9, 540.6	311.6	560.0, 561.7	299.5	540.3, 542.7
$\text{Mo}_2(\text{O}_2\text{CH})_4$	293.8 (293.4)	538.5	311.3	560.3	297.9	539.8
$\text{Cr}_2(\text{O}_2\text{CH})_4$	(294.3)		311.6		298.9	

^aThe value in parentheses is for the corresponding acetate.^bThe I. E. for the carbonyl oxygen 1s orbital is given first, experimental values from Ref. 22.

calculations of the satellites of small molecules such as HF , ^{13}CO , and N_2 ,¹⁰ are expected to be of greater importance in the studies described here.

A. Basis sets and ground state SCF calculations

Previous calculations have shown the need for a double zeta description of the valence orbitals, in order to obtain accurate ESCA shifts.¹⁴ We use a basis of this quality for calculations of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$.¹² We have used a molybdenum (17s11p8d) basis¹⁵ contracted to (5s3p3d) with an additional s function of exponent 0.32. For chromium a (12s6p4d) primitive basis¹⁶ was slightly modified. The diffuse functions representing the atomic 4s orbital were replaced by an s type Gaussian having exponent 0.32, and a p function having the same exponent was added to represent the 4p orbital. The basis was then contracted to (4s3p2d). The carbon and oxygen bases were (9s5p)¹⁷ contracted to (3s2p)¹⁸ and the hydrogen basis was (4s) contracted to (2s)¹⁸ with a scaling factor of 1.2. The calculations were carried out for both molecules assuming D_{4h} symmetry. The experimental structure¹⁹ was used for $\text{Mo}_2(\text{O}_2\text{CH})_4$ with a Mo–Mo bond length of 2.091 Å. Due to the sensitivity of the Cr–Cr bond length to environment, and the lack of a gas phase structure for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, we choose a Cr–Cr bond length of 2.2 Å,²⁰ and take other structural parameters from the crystal structure²¹ of the acetate complex, together with an assumed C–H bond length of 1.085 Å. These calculations, which used 176 and 162 contracted Gaussian functions for $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$, respectively, were carried out on the CRAY 1S computer of the SERC Daresbury Laboratory.

In both molecules, the four metal–metal bonding orbitals are of symmetry b_{2g} , e_u , and a_{1g} , and are constructed mainly from the d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$ atomic functions, respectively. We shall refer to these bonding MO's as δ , π , and σ . The corresponding antibonding orbitals are of symmetry b_{1u} , e_g , and a_{2u} , and are denoted as δ^* , π^* , and σ^* , respectively. SCF calculations of the $^1A_{1g}$ states having the occupancies $\delta^2\pi^4\sigma^2$ gave total molecular energies of -8700.3694 a.u. and -2834.4813 a.u., respectively, for $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$. An SCF calculation was also carried out on HCO_2H using the same atomic basis sets as used for the complexes in order to calculate the C1s and O1s shifts between formic acid and the two tetraformates.

B. Calculation of ligand core electron ionization energies

In Table II we compare the measured O1s and C1s I. E.'s of HCO_2H and $\text{Mo}_2(\text{O}_2\text{CH})_4$ with the corresponding calculated values. At the level of Koopmans' theorem, the calculations correctly predict the magnitude of the splitting between the two O1s I. E.'s of HCO_2H . However, within this frozen orbital approximation the O1s I. E. of $\text{Mo}_2(\text{O}_2\text{CH})_4$ is predicted to be greater than the 1s I. E. of the carbonyl oxygen of HCO_2H , whilst experimentally the reverse is found. Similarly, the C1s I. E. of HCO_2H is found to be greater than that of $\text{Mo}_2(\text{O}_2\text{CH})_4$ by 2.2 eV, whilst the separation calculated by Koopmans's theorem is only 0.6 eV. These observations suggest that there is greater orbital relaxation accompanying core electron ionization in $\text{Mo}_2(\text{O}_2\text{CH})_4$ than in HCO_2H . To investigate if this is so, SCF calculations were carried out on the three core hole states of HCO_2H , and upon the O1s and C1s core hole states of $\text{Mo}_2(\text{O}_2\text{CH})_4$. In the latter case, the two core holes were forced to be localized since it is established that such states have a lower energy than those in which the core holes are delocalized.²³ Thus, the O1s and C1s core hole wave functions were $^2A'$ and 2A_1 , respectively, in C_s and C_{2v} symmetry. From the results of Table II it can be seen that such ΔSCF calculations of the I. E.'s result in predictions of the shifts between HCO_2H and $\text{Mo}_2(\text{O}_2\text{CH})_4$ which are a substantial improvement over those given by Koopmans's theorem. This is due to the greater relaxation energy accompanying C1s (1.3 eV) and O1s (0.8 eV) ionization in the complex than in the ligand (Table II). The charge redistribution occurring upon core electron ionization is shown in Table III. The major part of such redistribution takes place within the formate ligand from which ionization has occurred, the Mo atoms donating a total of 0.1e and the remaining three ligands a total of $\sim 0.3e$ to this ligand. Upon C1s ionization, the electron density on the carbon atom actually increases (by 0.5e), due to a loss of density from the oxygen and hydrogen atoms to which it is bonded. Upon O1s ionization, a net loss of electron density occurs, but only of 0.3e, because the carbon and other oxygen atoms of the same ligand are the major source of electron donation.

C. Interpretation of ligand satellite peaks

The satellite peaks commonly observed to high I. E. of the main core ionization peak in molecules which do

TABLE III. Calculated atomic charges in $^1A_{1g}$ ground state and in C1s and O1s hole states of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CH})_4$.

Atom ^a	$^1A_{1g}$	C1s hole state	O1s hole state
Mo	+1.26	+1.31	+1.30
C	+0.08	-0.60	+0.27
O	-0.59	-0.18	-0.32 ^b , -0.43
H	+0.46	+0.91	+0.57
Ligand charge	-0.64	-0.05	+0.09
Cr	+1.58	+1.58	
C	+0.13	-0.47	
O	-0.65	-0.23	
H	+0.38	+0.85	
Ligand charge	-0.79	-0.08	

^aThe C, O, and H contributions are for the ligand from which ionization occurs.

^bAtomic charge on O atom from which ionization occurs.

not contain a transition metal atom are usually interpreted in terms of states in which valence electron excitation as well as core electron ionization has occurred. If we write the wave function (Ψ_0^*) for the primary core hole state in the restricted Hartree-Fock (RHF) approximation as

$$\Psi_0^* = |\phi_1\phi_2\bar{\phi}_2 \cdots \phi_n\bar{\phi}_n|, \quad (1)$$

then two possible doublet states may be constructed from the orbital excitation $i \rightarrow j$

$$(2)^{-1/2}(|\phi_1\phi_2\bar{\phi}_2 \cdots \phi_i\bar{\phi}_j \cdots \phi_n\bar{\phi}_n| - |\phi_1\phi_2\bar{\phi}_2 \cdots \bar{\phi}_i\phi_j \cdots \phi_n\bar{\phi}_n|) \quad (2)$$

and

$$(6)^{-1/2}(2|\bar{\phi}_1\phi_2\bar{\phi}_2 \cdots \phi_i\phi_j \cdots \phi_n\bar{\phi}_n| - |\phi_1\phi_2\bar{\phi}_2 \cdots \phi_i\bar{\phi}_j \cdots \phi_n\bar{\phi}_n| - |\phi_1\phi_2\bar{\phi}_2 \cdots \bar{\phi}_i\phi_j \cdots \phi_n\bar{\phi}_n|). \quad (3)$$

In (2), the unpaired valence electrons are singlet coupled and in (3), they are triplet coupled. Denoting such excited states as Ψ_i^* , the use of the sudden approximation²⁴ gives the relative intensity of a transition to ionic state Ψ_i^* compared with that to the primary ionic state Ψ_0^* as

$$I_i/I_0 = |\langle \bar{\alpha} \Psi_0 | \Psi_i^* \rangle|^2 / |\langle \bar{\alpha} \Psi_0 | \Psi_0^* \rangle|^2, \quad (4)$$

where Ψ_0 is the wave function for the ground state of the un-ionized molecule and $\bar{\alpha}$ annihilates the appropriate core electron from Ψ_0 . Equation (4) results in a greater intensity for the singlet coupled (2) than for the triplet coupled excitation (3).

1. C1s hole states of $\text{Mo}_2(\text{O}_2\text{CH})_4$

We first investigated whether the additional C1s peak observed for $\text{Mo}_2(\text{O}_2\text{CH})_4$ can be understood in terms of states generated by single valence excitations (2) and (3) from the RHF wave function for the primary C1s hole state of 2A_1 symmetry in C_{2v} . A CI calculation was carried out including the core hole RHF wave function and single excitations generated from it involving the five highest filled and four lowest virtual orbitals. The evaluation of I_i/I_0 [Eq. (4)] for the states resulting from this CI calculation showed that only one had an intensity

greater than 4% of the main peak, and for this state the dominant configuration was a singlet coupled single excitation from the highest filled to lowest virtual MO. These orbitals were both of b_1 symmetry (in C_{2v}) and were, respectively, the metal-metal bonding δ orbital (having 71% Mo d character, compared to 86% in the $^1A_{1g}$ ground state) and an MO whose single dominant component is a $2p\pi$ orbital on the carbon atom from which core ionization occurred. This latter orbital which we denote as $Lp\pi$ has the atomic character 35% C, 46% O, and 17% Mo. This state was calculated to give rise to a peak 4.6 eV from the main C1s line with a relative intensity of 15%, values in rather poor agreement with the experimental results (Table I).

We have previously shown²⁵ that for a satellite peak described by a singlet coupled single excitation $i \rightarrow j$, from the RHF core hole state configuration, its intensity may be estimated as $2|\langle i' | j \rangle|^2$, where i' is the corresponding MO in the molecular ground state. This approximation gives the intensity of the satellite peak arising from the $\delta \rightarrow Lp\pi$ transition to be 24% in semi-quantitative agreement with the value calculated using a CI wave function and Eq. (4). In addition to this state, three further states with a relative intensity of greater than 1% of the main peak are calculated to be within 5 eV of the main peak. These are the two doublet states arising from excitation from the $\pi(b_1)$ metal-metal bonding orbital to $Lp\pi$, and the state arising from the $\delta \rightarrow Lp\pi$ transition in which the unpaired valence electrons are triplet coupled. The first two states being close in energy to the $\delta \rightarrow Lp\pi$ singlet coupled transition may contribute to the satellite peak. This single excitation CI calculation has probably correctly identified the origin of the intense satellite peak, although the calculated intensity and position remain seriously in error.

The ground states of the molecules investigated here are known to be poorly described by a single determinant owing to the substantial correlation effects associated with the metal-metal quadruple bond, particularly in $\text{Cr}_2(\text{O}_2\text{CH})_4$. In view of this the possibility that the poor prediction of the satellite position and intensity was due to such correlation effects was investigated. A CI calculation was carried out using the RHF MOs of the primary C1s hole state with single and double excitations from two root configurations, the C1s hole state, and the $\delta \rightarrow Lp\pi$ excitation from it. The active space consisted of 9 MOs, the metal-metal bonding and antibonding orbitals, and $Lp\pi$. We denote this expansion CII. The lowest root from this calculation corresponded to the primary ionic state, with the triplet and singlet coupled $\delta \rightarrow Lp\pi$ satellite states being to 2.0 and 3.3 eV higher energy. A substantial improvement in the calculated position of the satellite peak has occurred, the error being reduced from 2.3–1.0 eV.

To include correlation effects in the calculation of the satellite intensity, Ψ_0 , Ψ_0^* , and Ψ_i^* [Eq. (4)] must be represented by multideterminantal wave functions. To simplify this computation, and to allow an understanding of the origin of any intensity changes, these three states were described by small CI expansions consisting of the

TABLE IV. CI calculation of C1s satellite of Mo₂(O₂CH)₄.

Ground state (Ψ_0)		Ionic states		
Excitation from $\sigma^2 \pi^4 \delta^2$ configuration	Contribution (%)	Excitation from $\sigma^2 \pi^4 \delta^2$ configuration	Contribution (%)	
			Primary hole state (Ψ_0^*)	Satellite state
...	86	...	84	1
$\pi\pi \rightarrow \pi^*\pi^*$	3	$\delta^2 \rightarrow Lp\pi^2$	3	16
$\delta^2 \rightarrow \delta^{*2}$	6	$\delta\pi \rightarrow \delta^*\pi^*$	4	5
$\pi\delta \rightarrow \pi^*\delta^*$	5	$\delta^2 \rightarrow \delta^{*2}$	2	10
		$\delta \rightarrow Lp\pi$	5	66
		$\pi\delta^2 \rightarrow \pi^*\delta^*Lp\pi$	2	2
		Relative energy (eV)	0	3.0
		Relative Intensity (%)	100	41

dominant configurations derived from the larger expansions: CI1 for the ion states, and for Ψ_0 , single plus double excitations from the quadruple bond configuration to the four virtual metal orbitals (CI2). The configurations used together with their contributions to the various states are shown in Table IV, together with the relative energy and intensity of the satellite state. The relative energy (3.0 eV) is close to that given by the larger CI expansions (3.3 eV), and the relative intensity (41%) is considerably greater than the value (15%) obtained from the single excitation CI expansion. The reasons for the substantial improvement in both the position and intensity of the satellite peak upon the inclusion of correlation effects follow from the characters of the individual states shown in Table IV. The dominant configurations in the satellite state involve the $\delta \rightarrow Lp\pi$ excitation, as in the single excitation CI calculation. However, its contribution is only 66%, the remaining terms in the CI expansion being multiple excitations involving the δ , δ^* , and $Lp\pi$ orbitals. These additional excitations are more important in the satellite than in the primary hole state due to their closeness in energy to the $\delta \rightarrow Lp\pi$ configuration. The admixture of these additional configurations results in the relative lowering of the satellite state energy compared to that of the primary hole state to yield much better agreement with the observed position of the satellite peak.

Turning now to a discussion of the relative intensity of the satellite peak, we first note that the total probability for shake-up and shake-off processes

$$1 - |\langle \tilde{a} \Psi_0 | \Psi_0^* \rangle|^2 \quad (5)$$

is considerably greater when Ψ_0 and Ψ_0^* are described by the CI expansions given in Table IV, this value being increased from the single determinantal value of 0.39 to 0.53. Such a change may be attributed to the contribution of excitations to the primary hole state involving the $Lp\pi$ orbital, for which there are no corresponding excitations in the CI expansion of Ψ_0 . Similarly, the occurrence of configurations in the CI expansion of the satellite state involving the δ^* orbital which do correspond to configurations in Ψ_0 will lead to an increase in the intensity of the satellite state. It is this intensity borrowing mechanism which leads to a decrease in the

intensity of the primary ionization peak and an increase in that of the satellite peak upon the inclusion of correlation effects. In addition to the 2A_1 state, whose major component is the $\delta \rightarrow Lp\pi$ singlet coupled excitation, the CI calculation described in Table IV also yields a state, whose major component is the $\delta \rightarrow Lp\pi$ triplet coupled excitation, with relative intensity 10% that of the main peak. In addition to those states arising from the excitation $\delta \rightarrow Lp\pi$, we expect significant intensity from those arising from $\pi(b_1) \rightarrow Lp\pi$ excitations, which we have identified in the single excitation CI calculation. We thus assign four states to the intense C1s satellite peak.

2. C1s hole states of Cr₂(O₂CCH₃)₄

The C1s XPES of Cr₂(O₂CCH₃)₄, in contrast to that of Mo₂(O₂CCH₃)₄ has only two peaks, with the one due to $-\text{CO}_2$ C1s ionization being only slightly less intense than that due to $-\text{CH}_3$ C1s ionization. Although no intense satellite peak is found, there are indications of a shoulder to high I.E. of the $-\text{CO}_2$ C1s ionization peak.

We have carried out calculations on Cr₂(O₂CH)₄ similar to those described previously for Mo₂(O₂CH)₄ in an attempt to understand these observed differences. An RHF calculation on the 2A_1 C1s hole state of Cr₂(O₂CH)₄ yielded slightly less relaxation energy than in the case of Mo₂(O₂CH)₄ (Table II). From a comparison of the charge distributions for the molybdenum and chromium species (Table III), it can be seen that less charge redistribution occurs upon C1s ionization of the chromium complex; in particular, the formal charge on the chromium atoms remains unaltered. This is reflected in the value of $|\langle \tilde{a} \Psi_0 | \Psi_0^* \rangle|^2$, which is increased from 0.61 for Mo₂(O₂CH)₄ to 0.68 for Cr₂(O₂CH)₄. To investigate the effect of correlation on the intensity of the primary ionic state both Ψ_0 and Ψ_0^* were represented by CI expansions. From the expansion CI2 for Ψ_0 and from the expansion CI1 for Ψ_0^* , the ten dominant configurations were selected for the small CI calculations used in the calculation of the photoionization intensity. All these configurations involved excitations from the metal-metal bonding to antibonding MO's and none involved $Lp\pi$, unlike the situation found for Mo₂(O₂CH)₄. For this reason, the intensity ($|\langle \tilde{a} \Psi_0 | \Psi_0^* \rangle|^2$) calculated us-

ing these small CI expansions (0.69) is essentially unchanged from the SCF value (0.68). The interaction matrix elements connecting the core hole RHF configuration to excitations involving δ and $Lp\pi$ will depend upon the overlap charge density $\langle\delta|Lp\pi\rangle$, which will be smaller for the chromium than for the molybdenum complex. Furthermore, the population of the δ MO is less in the chromium than in the molybdenum complex due to the greater participation in the former of configurations involving the δ^* MO. For these two reasons, the configurations involving $Lp\pi$ are less important in the C1s hole state of $\text{Cr}_2(\text{O}_2\text{CH})_4$ than of $\text{Mo}_2(\text{O}_2\text{CH})_4$.

For similar reasons, the relative intensity associated with the $\delta-Lp\pi$ singlet coupled configuration is found to be smaller for $\text{Cr}_2(\text{O}_2\text{CH})_4$ (8%) than for $\text{Mo}_2(\text{O}_2\text{CH})_4$ (25%). This is associated with a reduction in the overlap integral $\langle\delta|Lp\pi\rangle$ (where δ is the metal-metal bonding orbital in the ground state), from 0.35 in $\text{Mo}_2(\text{O}_2\text{CH})_4$ to 0.21 in $\text{Cr}_2(\text{O}_2\text{CH})_4$. To further investigate the position and intensity of the satellite peak, a CI calculation (CII) was carried out. The lowest root corresponded to the primary hole state. A further 19 roots occurred 2.5–4.2 eV higher in energy. In none of these was the singlet coupled $\delta-Lp\pi$ excitation dominant, although in a number of roots it contributed ~10%. Thus, in $\text{Cr}_2(\text{O}_2\text{CH})_4$, satellite intensity associated with the $\delta-Lp\pi$ excitation is considerably weaker than in $\text{Mo}_2(\text{O}_2\text{CH})_4$, and is spread out over a number of states.

3. O1s ionization in $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$

The O1s region of the XPES of the three molecules studied herein show a single sharp line with only a weak satellite peak at ~10 eV higher I.E. For $\text{Mo}_2(\text{O}_2\text{CH})_4$, the total relative intensity arising from all shake-up and shake-off states was estimated using RHF wave functions in Eq. (5) to be 0.35, close to the value found for C1s ionization (0.39). It thus appears that in the case of C1s ionization the majority of the total satellite intensity is concentrated in one or more transitions near to the main peak; whereas for O1s ionization, a similar satellite intensity is distributed amongst a number of weak peaks. For none of the configurations generated by single excitations from the five highest filled to the three lowest virtual orbitals of the O1s core-hole RHF wave function was the relative intensity found to be greater than 1% in agreement with the experimental observation of the lack of any intense satellite peak. We now estimate the positions of the $\delta-Lp\pi$ shake-up transitions, relative to the main ionization peaks, which we define as Δ_0 and Δ_c for oxygen and carbon 1s ionization, respectively. Ignoring differences in relaxation and correlation energy amongst the ion states, we have, approximately,

$$\Delta_0 - \Delta_c = \langle Lp\pi | 1/r_c - 1/r_o | Lp\pi \rangle - \langle \delta | 1/r_c - 1/r_o | \delta \rangle,$$

leading to an estimate for Δ_0 of 10.1 eV given the calculated value of Δ_c of 3.0 eV (Table IV). The major effect is the difference in nuclear attraction integrals for the $Lp\pi$ MO. At such an energy, extensive configurational mixing with numerous transitions to Rydberg-type orbitals is expected, leading to the total satellite

intensity being distributed amongst a number of states in line with our experimental observation of the lack of a single intense satellite peak in the O1s XPES of all three molecules.

IV. CONCLUSIONS

The intense satellite peak observed close to the primary C1s line in $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is due mainly to a metal (δ)–ligand ($Lp\pi$) transition. Its proximity to the main C1s line is due to the stabilization of the $Lp\pi$ MO by the C1s hole. In the O1s XPES the absence of an intense satellite peak is caused by the inability of the oxygen 1s hole to sufficiently stabilize the $Lp\pi$ MO. At the SCF level of approximation, this satellite peak acquires intensity due to the electron reorganization accompanying 1s ionization which is greater in the molybdenum than in the chromium complex. In $\text{Mo}_2(\text{O}_2\text{CH})_4$ further intensity is borrowed from the primary C1s line by the satellite state when correlation is included in the ground and ionic states, leading to an intense satellite peak. In $\text{Cr}_2(\text{O}_2\text{CH})_4$ this additional mechanism of intensity borrowing does not take place due in part to the increased correlation effects in the ground state of $\text{Cr}_2(\text{O}_2\text{CH})_4$, resulting in the lack of an intense satellite in the C1s XPES of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

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