The Electronic Structure of the Carbonyl Dihalides, COF_2, $COCl_2$, $COBr_2$, COClF, COBrF and COBrCl: A Combined Computational and Experimental Study *

Paul Sherwood,[a] **Elaine A. Seddon,**[a] **Martyn F. Guest,**[b] **Michael J. Parkington,**[c]
T. Anthony Ryan[d] **and Kenneth R. Seddon**[e]
[a] *Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK*
[b] *Environmental and Molecular Science Laboratory, Pacific Northwest Laboratory, PO Box 999, Mail Stop K1-96, Richland, WA 99352, USA*
[c] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Sussex BN1 9QJ, UK*
[d] *ICI Chemicals and Polymers Ltd., PO Box 8, The Heath, Runcorn, Cheshire WA7 4QD, UK*
[e] *School of Chemistry, The Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, UK*

The He-I, -II photoelectron (PE) spectra of the carbonyl dihalides, COF_2, $COCl_2$ and $COBr_2$, and the He I spectra of the mixed carbonyl halides COClF, COBrF and COBrCl have been recorded. The assignments of the photoelectron peaks are discussed with reference to *ab initio* electronic structure calculations in the Hartree–Fock, configuration interaction (CI) and Green's function (OVGF and 2ph-TDA) formalisms and the preferred assignments tabulated. Koopmans' theorem results in a systematic overestimate of the ionisation energies whereas the two Green's function methods give ionisation energies in very good agreement with the spectra, with errors of as little as 0.3 eV for the outer valence orbitals. A long standing problem with the assignments of the photoelectron spectra of $COCl_2$ was resolved by the use of multi-reference CI calculations on the low-lying states of the ion. The trends in the halogen-dependent ionisation energies are discussed in terms of the halide inductive effects and the energies of the halogen lone-pair orbitals relative to the π-bonding orbital of CO.

The carbonyl dihalides, COF_2, $COCl_2$, $COBr_2$, COClF, COBrF and COBrCl have an appealing geometrical simplicity and yet a challenging electronic complexity that make them attractive subjects for detailed study. In recent years there has been a revival of interest in the electronic structure of COF_2, COClF and $COCl_2$ owing to their observation as photo-oxidation products in the upper atmosphere. The fluoro compounds are formed from chlorofluorocarbons (CFCs) in the stratosphere, while phosgene arises from oxidation of chloroalkanes and chloroalkenes in the troposphere.[1-4]

In this paper the He-I and -II photoelectron spectra of the carbonyl dihalides, COF_2, $COCl_2$ and $COBr_2$ are described, and the assignment of the observed peaks is discussed by reference to *ab initio* calculations. A number of theoretical techniques have been used, including Hartree–Fock SCF calculations with the application of Koopmans' approximation, Green's functions calculations using the Outer Valence Green's Function (OVGF) and extended two-particle-hole Tamm–Dancoff Approximation (2ph-TDA) methods. In the case of $COCl_2$, the results of multi-reference CI calculations designed to characterise the low-lying states of the $COCl_2$ cation are also reported.

The photoelectron spectra of the mixed carbonyl halides (COClF, COBrF and COBrCl) have been obtained using He I radiation, and interpreted using Koopmans' approximation and the OVGF approach.

Overview of the Computational Techniques

This section is a brief review of the computational techniques for the prediction of ionisation energies (i.e.s) used in this study. Specific details of the current work may be found in the section 'Computational Details' towards the end of the paper.

Koopmans' Approximation.—Within Hartree–Fock (HF) theory, and neglecting orbital relaxation effects, Koopmans[5] showed that the energy required for removal of an electron is given by the negative of the orbital eigenvalue corresponding to the orbital from which the electron had been removed. As it is based on the HF Hamiltonian, this procedure neglects all electron correlation effects. Since inclusion of correlation lowers the energy of the system, and there is more correlation in the neutral molecule than in the ion (due to the extra electron pair), the omission of correlation leads to i.e.s being underestimated. The omission of relaxation effects in the ion contributes an error of the opposite sense. On balance, the magnitude of the relaxation effects is larger, and the Koopmans' approximation i.e.s are too large, by around 1–3 eV.

Δ-SCF Calculations.—Where the cation state generated by an ionisation is the lowest of its symmetry, it is possible to perform a HF calculation on the ion. The Δ-SCF approximation to the i.e. is then defined as the difference in the SCF energies of the neutral molecule and the ion. The resulting i.e.s include the effects of relaxation, but not of electron correlation. As a result, they are typically underestimates.

CI Methods.—It is possible to improve on the Δ-SCF and Koopmans estimates of the i.e.s by explicit treatment of correlation by configuration interaction (CI).[6] The CI calculations are performed on the neutral molecule and on a series of low-lying ionic states, and the i.e.s are obtained by

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* *Non-SI units employed:* eV $\approx$ 1.602 $\times$ 10^{-19} J, a.u. = Hartree $\approx$ 4.360 $\times$ 10^{-18} J.

subtraction. In this study such calculations have been performed only for the five lowest states of $[COCl_2]^+$. The analysis presented is based on the character of the natural orbitals (NOs), which may be defined as the set of molecular orbitals (MOs) for which the CI electron density may be described by a set of (generally non-integral) occupation numbers.

Green's Function Methods.—In the Green's Function (GF) methods, the ionisation energy is calculated directly from the ground-state wavefunction, rather than as the difference between two independent calculations. Some of the effects of electron correlation and relaxation are included through many-body perturbation theory. Two such approaches have been employed, the Outer Valence Green's Function (OVGF) and extended two-particle-hole Tamm–Dancoff (extended 2ph-TDA) methods.

The OVGF procedure[7] is the computationally cheaper of the two approaches. It is, however, limited in applicability to ionisations which are well described by an orbital model, in which each ionisation may be viewed as removal of an electron from a single orbital in the HF wavefunction. This is usually the case for outer valence ionisations.

The OVGF method breaks down when electron correlation effects lead to the ionisation being accompanied by additional excitation, or shake-up processes. The simplest such process involves a second electron being excited to an unoccupied orbital, leading to a so-called two-hole particle (2hp) state. Such processes are included in the extended 2ph-TDA scheme,[8-11] which can therefore provide an indication that the OVGF procedure is no longer valid, as well as providing information for the assignment of shake-up ionisations.

The Green's function calculations in this paper were all performed using codes developed by Cederbaum, von Niessen and co-workers,[7-11] and implemented in the GAMESS-UK package.[12,13]

Results, Assignment and Discussion

Carbonyl Difluoride (COF_2).—The He-I and -II photoelectron spectra of COF_2 are shown in Fig. 1. A total of eight bands are observed, five of which (A, B, D, E and F) show clear evidence of extensive vibrational structure.

There have been two previous reports of the photoelectron spectra; He I measurements were reported by Thomas and Thompson[14] and a He I/He II study was performed by Brundle *et al.*[15] Both of these studies assign the spectra by reference to the vibrational structure that is evident, and in the latter study, to *ab initio* calculations using a double-zeta basis and a scaled Koopmans' approach. As the resolution of the He I spectra in the current work is similar to that reported previously, we offer no further analysis or assignment of the vibrational structure, discussing the features only briefly in the context of our assignment based on the new computational results.

The experimental and computational results for COF_2 are summarised in Table 1. In this and all subsequent tables, each experimental value represents an estimate of the vertical ionisation energy, obtained from the position of the maximum of the peak profile. The theoretical results are ordered by the HF-SCF eigenvalue (*i.e.* the Koopmans' approximation to the ionisation energy) and include a qualitative description and Mulliken analysis of the SCF orbital character. The point group labels for the C_{2v} systems refer to an axis definition in which the molecule lies in the xz plane with the CO bond parallel to the z axis.

Band A in the He I spectrum is readily assigned to ionisation from the $5b_1$ orbital, which is predominantly oxygen lone pair in character. The band exhibits an extensive vibrational progression, with an interval of 1555 cm^{-1}, corresponding to excitation of the v'_1 mode (CO stretch) that occurs at 1928 cm^{-1} in the neutral molecule.[16,17] This is a somewhat surprising observation given the predominantly non-bonding character of the orbital. The most likely explanation, as advanced previously,[14,15] is that (despite the lone-pair nature of the orbital), ionisation leads to a substantial change in geometry. This may arise from some delocalisation of the orbitals; as noted by Brundle *et al.*,[15] the $5b_1$ orbital has some C–O bonding and O–F antibonding character. Thomas and Thompson[14] have also suggested other more indirect effects, such as the electrostatic effects of a positive charge centred on the oxygen atom on the other valence orbitals.

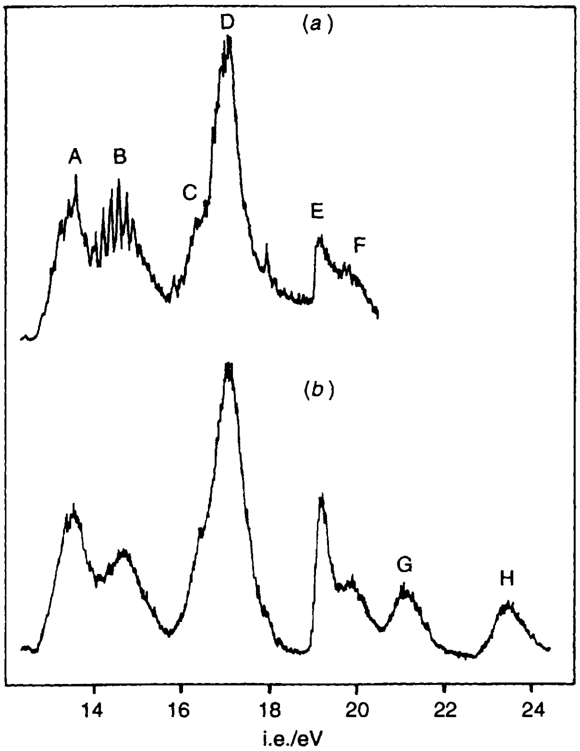

Fig. 1 The He I (*a*) and He II (*b*) photoelectron spectra of COF_2

To estimate the geometry changes involved, a geometry optimisation has been performed at the SCF level on the ground state of $[COF_2]^+$, in a double-zeta plus polarisation (DZP) basis. The structure remains planar, but undergoes significant geometrical changes. Relative to a corresponding calculation on COF_2, the ion structure exhibits a lengthening of the C–O bond by 0.1 Å, a shortening of the C–F bonds by 0.07 Å and an increase in the FCF angle by 12°, in agreement with the inferences made by Thomas and Thompson[14] from the Franck–Condon factors.

The assignment of band B to ionisation from the $2b_2$ orbital (π_{CO} bonding) is also straightforward, based on its energetic separation from other bands and its vibrational structure, an extensive progression from the C–O stretching mode [1430 cm^{-1} (ref. 14)] is observed.

The next group of three ionisations are computed to occur within a range of 0.6 eV, corresponding to peaks C and D of the spectrum. The same order of ionisation energies ($4b_1$, $8a_1$, $1a_2$) is predicted from Koopmans and Green's function calculations with a variety of basis sets. We tentatively assign the $4b_1$ ionisation to band C and the $8a_1$ and $1a_2$ ionisations to band D. It should be noted that the computed order of the $4b_1$ and $8a_1$ orbital energies is very sensitive to changes in the geometry, and that our ordering differs from that reported previously.[18-20] However it can be seen from Table 1 that the small energy difference between the $4b_1$ and $8a_1$ Koopmans i.e.s is reinforced by the Green's function calculations, giving some weight to the assignment suggested here.

The remaining four ionisations are energetically well

Table 1 Experimental and computational results for COF_2

		Mulliken population (%)				i.e./eV			
Orbital	Koopmans i.e./eV	C	O	F	Principal character[a]	OVGF	2ph-TDA	Assignment	Exptl. i.e./eV
$5b_1$	15.24	5	81	14	n(O), n(F)	13.74	13.89	A	13.62
$2b_2$	15.76	17	66	17	π_{CO}, n(F)	14.86	14.89	B	14.80
$4b_1$	19.12	1	1	98	n(F)	16.97	17.07	C	16.7 (sh)
$8a_1$	19.20	11	51	38	σ_{CO}, n(F), n(O)	17.30	17.60	D	17.27
$1a_2$	19.74	1	0	99	n(F)	17.54	17.62	D	
$7a_1$	21.88	8	30	62	n(F), n(O), σ_{CO}	19.56	19.80	E	19.40
$1b_2$	22.21	19	6	75	n(F), π_{CO}	20.15	20.37	F	19.99
$3b_1$	23.50	23	8	69	n(F), σ_{CF}, $\pi_{\parallel CO}$[b]	21.54	21.73	G	21.16
$6a_1$	26.02	22	6	72	n(F), σ_{CF}	23.92	24.04	H	23.51

[a] In this and subsequent tables the notation n(F) has been used to denote orbitals with fluorine lone-pair character. As noted in the text, there is sometimes a significant amount of mixing with the other (occupied) orbitals and the MOs individually show some bonding or antibonding character. However, no nett bonding arises from these interactions. [b] $\pi_{\parallel CO}$ denotes orbitals with CO π-bonding character in the plane of the molecule.

separated allowing their assignment as given in Table 1 with a high degree of confidence.

The TDA and OVGF calculations give qualitatively the same results for all ionisations in the region 10–25 eV, with no significant satellite structure. In contrast, ionisations in the range 30–50 eV (F 2s and a σ-bonding combination of O 2s and C 2s) are predicted to be poorly described by a one-electron orbital model of ionisation.

The overall quality of the GF results may be summarised by noting that all i.e.s have been overestimated (by up to 0.4 eV) and that the magnitude of the error is greatest for orbitals with a large fluorine character or large i.e. This systematic error probably arises from the failure of the GF based approaches to recover all of the relaxation energy associated with ionisation from the compact n(F) orbitals.

Carbonyl Dichloride ($COCl_2$).—Two independent research groups have reported the He I spectrum of $COCl_2$,[14,21] and although the reported spectra were similar, the proposed assignments differed in two respects.

(*a*) Chadwick[21] assigned the first peak (A) to ionisation from an oxygen lone pair and peaks B and C to ionisation from chlorine orbitals, whereas Thomas and Thompson[14] assumed that the first ionisation (A) was chlorine based and associated the oxygen ionisation to peak C.

(*b*) The σ_{CO} and π_{CO} levels were assigned to bands F and G respectively by Chadwick, and to G and F respectively by Thomas and Thompson.

The He-I and -II photoelectron spectra of $COCl_2$ are shown in Fig. 2.

From the computational results (Table 2), the first ionisation (peak A) is expected to arise from ionisation from an orbital of b_1 symmetry, this being the symmetry of both the highest (HOMO) and second highest (SHOMO) occupied MOs. Both orbitals have extensive n(Cl) character, the latter intermixed with significant n(O) character also.

The variation in relative peak intensity when switching between He I and He II radiation can provide an indication of the amount of oxygen character associated with the MO from which an electron is ejected, a greater oxygen character leading to a smaller relative intensity decrease. Unfortunately, a direct comparison between the He I/He II intensity variations of peaks A and B is not reliable as peak B is observed as a shoulder on peak C. However, of the five peaks observed below 14 eV, it is clear that peak A shows the smallest relative intensity decrease on changing from He I to He II radiation. This would appear to support the Chadwick assignment, in which peak A is associated with ionisation from the SHOMO, rather than the HOMO, in violation of the order expected from Koopmans' approximation. This assignment, however, is not supported by the Green's function calculations. The extended 2ph-TDA calculations indicate ionisation from the HOMO is expected at 11.92 eV, and that from the SHOMO at 12.52 eV, in excellent agreement with the observed ionisation potentials. Since the GF approaches incorporate some effects of relaxation in the ion, this Koopmans'-like assignment does not necessarily imply that the character of the cation states resulting from the first two ionisations can be predicted simply from the character of the HF orbitals. To investigate the possibility that relaxation effects may be responsible for the observed intensity variation of Peak A a CI study on the $[COCl_2]^+$ cation states has been performed and is reported in the next Section.

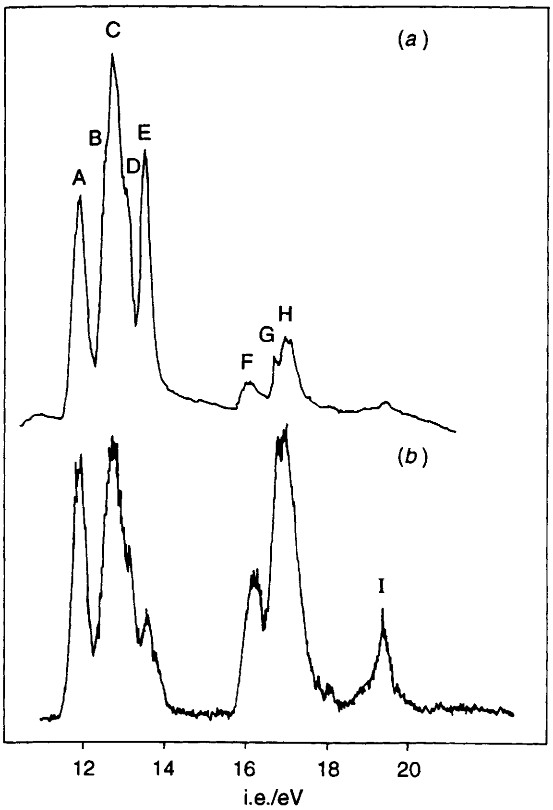

Fig. 2 The He I (*a*) and He II (*b*) photoelectron spectra of $COCl_2$

The third and fourth peaks (C and D) of the photoelectron spectrum are assigned to the $3b_2$ and $2a_2$ ionisations. They are predicted to be close in energy, with an energy ordering that depends on the particular method used. The $2a_2$ i.e. is greater

Table 2 Experimental and computational results for $COCl_2$

		Mulliken population (%)				i.e/eV				
Orbital	Koopmans i.e./eV	C	O	Cl	Principal character	OVGF	2ph-TDA	CI	Assignment	Exptl. i.e./eV
$8b_1$	12.92	0	11	89	n(Cl)	11.72	11.92	11.54	A	11.90
$7b_1$	13.48	7	43	50	n(O), n(Cl)	12.26	12.52	12.17	B	12.5 (sh)
$3b_2$	13.54	2	28	70	n(Cl), n(O)	12.56	12.75	12.38	C	12.70
$2a_2$	13.60	0	0	100	n(Cl)	12.43	12.71	12.52	D	13.1 (sh)
$11a_1$	14.42	2	2	96	n(Cl)	13.17	13.49	13.05	E	13.51
$2b_2$	17.74	36	41	23	π_{CO}	16.40	16.54		F	16.09
$10a_1$	19.15	23	48	29	σ_{CO}	17.25	17.51		G	16.72
$6b_1$	19.35	27	35	38	σ_{CCl}, $\pi_{\|CO}$	17.37	17.62		H	16.99
$9a_1$	22.10	24	33	43	σ_{CCl}	19.91	19.91		I	19.40
							20.18*			

* Shake up ionisation.

than the $3b_2$ i.e. when estimated by Koopmans' approximation or by CI, while the Green's function results give the reverse ordering. It is thus not possible to assign C and D unequivocally.

Peak E is energetically well separated and can be assigned to ionisation from the $11a_1$ orbital. The pronounced intensity decrease on changing from He I to He II radiation suggests it has very low oxygen character, in agreement with the Mulliken analysis of $11a_1$ which is almost pure Cl.

The next group of three peaks are labelled F, G and H. Koopmans and Green's function calculations indicate that the first of these should be assigned to ionisation from the π_{CO} orbital. Peaks G and H are very close in energy and are tentatively assigned to the σ_{CO} and antisymmetric σ_{CCl} orbitals respectively by reference to the ordering of computed ionisation energies. We note here that our computational results confirm the chemically logical σ_{CO} and π_{CO} ordering proposed by Thomas and Thompson.[14]

Peak I is energetically isolated and is assigned to the symmetric σ_{CCl} ionisation ($9a_1$). The extended 2ph-TDA calculations suggest that some breakdown of the orbital picture of ionisation is expected here. The ionisation is split between two components separated by 0.3 eV, with the stronger of the two (by *ca.* a factor of 2 on pole strength[11]) at lower ionisation energy. However, in view of the fact that all of the computed ionisations at energies > 16 eV have errors of 0.2 to 0.5 eV, it is unlikely that this feature should be regarded as reliable.

Overall, the valence i.e.s of $COCl_2$ are well reproduced by the Greeen's function calculations, remarkably so for four of the five ionisations below 14 eV, where the discrepancies are of the order of 0.1 eV or less. The remaining peak (D) is not reproduced clearly by any of the calculations. It is predicted to occur within 0.1 eV of peak C but is observed as a shoulder of the latter peak, shifted about 0.4 eV to higher energy. The inner valence i.e.s are all overestimated (typically by 0.4–0.5 eV) probably because of the increasing importance of relaxation effects.

One further aspect of the assignment given here is worthy of note as it differs from that suggested in previous work. Examination of the HF orbital characters indicates that $2a_2$ and $11a_1$ are both almost pure chlorine orbitals, but only in the former case is this expected from the orbital symmetry (a_2). Such symmetry considerations led Frost and co-workers[22] to assign band E (which almost completely disappears in the He II PE spectrum) to ionisation from the $2a_2$ orbital. In contrast to the assignment presented here, this assignment led to an unexplained discrepancy between the ordering of the $2a_2$ and $11a_1$ levels when compared with the corresponding orbitals of $F_2C{=}CCl_2$.

Calculations on the $[COCl_2]^+$ *Cation*.—It was noted above that there is an apparent discrepancy between the character of the first two ionisations suggested by the character of the corresponding HF orbitals and by the He I/He II relative intensity variations of the peaks. We have therefore sought to corroborate the Green's function results by characterising the cation states.

It has been known for some time that STO-3G and 4-31G SCF calculations on the ground state of the $[COCl_2]^+$ ion predict that the singly occupied molecular orbital (SOMO) has substantial oxygen character,[23] and we have established that a similar result is obtained using a DZP basis set. We note here that it is also possible to converge to a second SCF solution, for which the singly occupied orbital is of Cl character; this may be regarded as an approximation to the first excited state of the cation. However, this is higher in energy than the ground state by 1.3 eV and is probably rather poorly described.

At first glance the presence of substantial oxygen character in the SOMO of the ground state of $[COCl_2]^+$ suggests that correlating the high lying MOs with the first three ionisations by orbital eigenvalue is incorrect. In particular, that for the b_1 symmetry orbitals, $8b_1$ gives rise to an ionisation at higher energy than $7b_1$. However, as noted above, this result is not supported by the results of the Green's function calculations. Compared with the Koopmans based predictions, the energy ordering of the two b_1 ionisations is unchanged, in fact the energy separation between the predicted ionisations is maintained. Furthermore, the extended 2ph-TDA procedure allows analysis of the contribution of each simple 'Koopmans-like' orbital ionisation to the predicted ionisation process for each band. From this analysis, it is found that there is some mixing of both $7b_1$ and $8b_1$ into the ionisations correlating with bands A and B, but the predominant character is consistent with the Koopmans assignment.

In considering the apparent discrepancy between the Green's function and ion-state SCF results, the shortcomings of each of the approaches must be considered. The SCF calculation on $[COCl_2]^+$ allows for full relaxation of the ion wavefunction but omits electron correlation, while the Green's function methods include correlation effects on the ionisation energy but would be expected to provide a more limited (non-self-consistent) treatment of relaxation.

One approach that should be capable of including both effects is configuration interaction (CI). We have performed a series of multi-reference CI (MRCI) calculations on the $COCl_2$ cation to establish the energies of the five states below 14 eV, including both states of b_1 symmetry.

The ionisation energies are given in Table 2. Clearly the assignment of state symmetries follows that of the Koopmans results. Comparison of the energy range spanned by the five states with the experimental result suggests an underestimation of the i.e.s by about 0.4 eV. This is probably due to the fact that more correlation energy is associated with the neutral molecule than the ion due to the extra electron pair. In a small basis set like the one (DZP) used here this will be incompletely recovered by the CI leading to a larger correlation error for the neutral species.

We have computed natural orbitals (NOs)[6] from the CI wavefunctions for the two b_1 states. In each case a single natural orbital has approximately unit occupancy, we will refer to this orbital as the singly occupied natural orbital (SONO) for brevity, and use the character of this orbital to describe the nature of the cation state. These SONOs are plotted in Fig. 3 together with the $8b_1$ and $7b_1$ Hartree–Fock orbitals of $COCl_2$ for comparison.

Examination of these orbital plots suggests an explanation for the apparent discrepancy between the Green's function and ion state results discussed above. In the correlated treatment of the b_1 ionic states there is more oxygen character in the SONO for the ground state [Fig. 3(*a*)], indicating that the inclusion of correlation has not extensively affected the conclusions from the SCF calculations on the ion. A Mulliken analysis of the SONO of the ground state shows it to have 51% oxygen character, while the corresponding figure for the SONO of the first excited state is 16%. In this sense both the theoretical and experimental results indicate that Chadwick[21] was correct to assign the oxygen lone pair character to the first ionisation rather than the second.

However, if the nodal properties of the orbitals (rather than the atomic characters) [Fig. 3(*a*)–(*d*)] are taken into account, it is clear that the most reasonable correlation between the character of the ionic states and the MOs of the SCF calculation would associate the ground state of the ion [Fig. 3(*a*)] with ionisation principally from the HOMO of $COCl_2$ [Fig. 3(*c*)], and the first excited state [Fig. 3(*b*)] with ionisation from the SHOMO [Fig. 3(*d*)]. This explains why the Green's function calculations indicate an essentially 'Koopmans-like' correlation.

The confusion is seen to have arisen from a mixing of the Cl and O lone-pair orbitals in the ion states when compared with the orbitals of neutral $COCl_2$. While not amounting to an interconversion of the states, this mixing transfers a substantial amount of oxygen character from one to another.

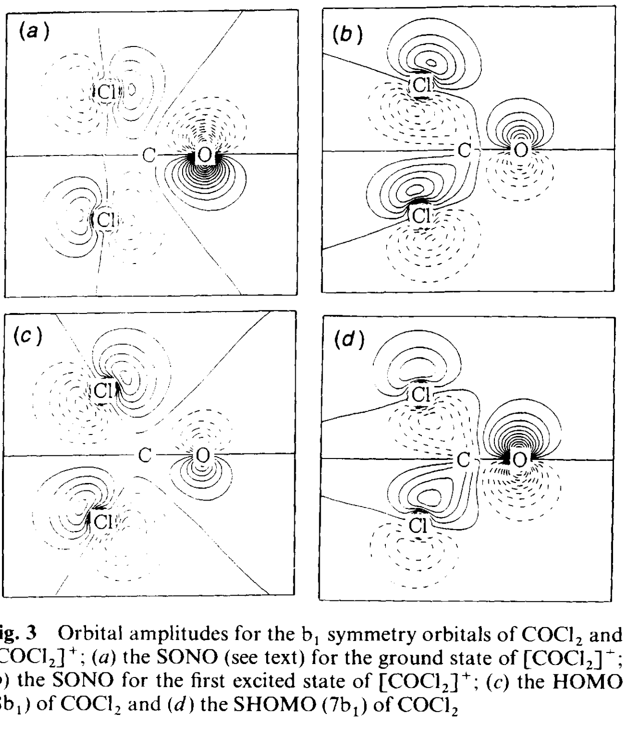

Fig. 3 Orbital amplitudes for the b_1 symmetry orbitals of $COCl_2$ and $[COCl_2]^+$; (*a*) the SONO (see text) for the ground state of $[COCl_2]^+$; (*b*) the SONO for the first excited state of $[COCl_2]^+$; (*c*) the HOMO ($8b_1$) of $COCl_2$ and (*d*) the SHOMO ($7b_1$) of $COCl_2$

Carbonyl Dibromide ($COBr_2$).—The He-I and -II photoelectron spectra of $COBr_2$ (Fig. 4) show many similarities with those of phosgene. The experimental and theoretical results are summarised in Table 3. We note that these assignments are in agreement with those originally suggested by Thomas and Thompson.[14]

The first five peaks in the spectrum of $COBr_2$ occur over a narrow energy range. The computed ionisation energies fit closely to the observed values, and assignment of peaks A, D and E (to $14b_1$, $6b_2$ and $17a_1$ respectively) can be made with reasonable confidence. A speculative assignment of B and C based on the order of the theoretical ionisation energies (Koopmans' and Green's function methods give the same ordering) ascribes B to $5a_2$ (a Br based orbital), and C to $13b_1$ (mainly O character). This assignment is strongly supported by the He I/He II intensity variation of the peaks. Peaks F and G are assigned to ionisations from the $5b_2$, $16a_1$ and $12b_1$ orbitals. The most probable assignment, based on the pattern of computed energies, ascribes peak F to the $5b_2$ ionisation and peak G to the superposition of $16a_1$ and $12b_1$. Peaks H and I may be ascribed to ionisation from the $15a_1$ orbital, the latter being a shake-up state.

Of the seven bands in the He I spectrum of $COBr_2$, only one (F) exhibits any vibrational structure. The period of this vibrational structure [1690 cm^{-1} (ref. 14)] indicates that it is associated with stretching of the carbonyl group, additional support for the assignment of band F to ionisation from an orbital with π_{CO} character.

The Mixed Carbonyl Halides.—The He I spectra for the mixed carbonyl halides COClF, COBrF and COBrCl are presented in Fig. 5. The results of computations using Koopmans' Approximation and the Outer Valence Green's Function method are tabulated, together with the measured i.e.s, in Tables 4, 5 and 6. Owing to the lack of experimental

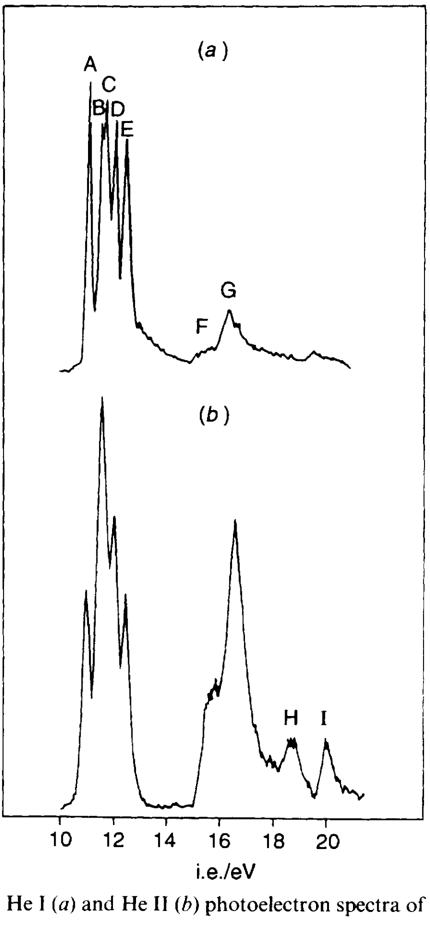

Fig. 4 The He I (*a*) and He II (*b*) photoelectron spectra of $COBr_2$

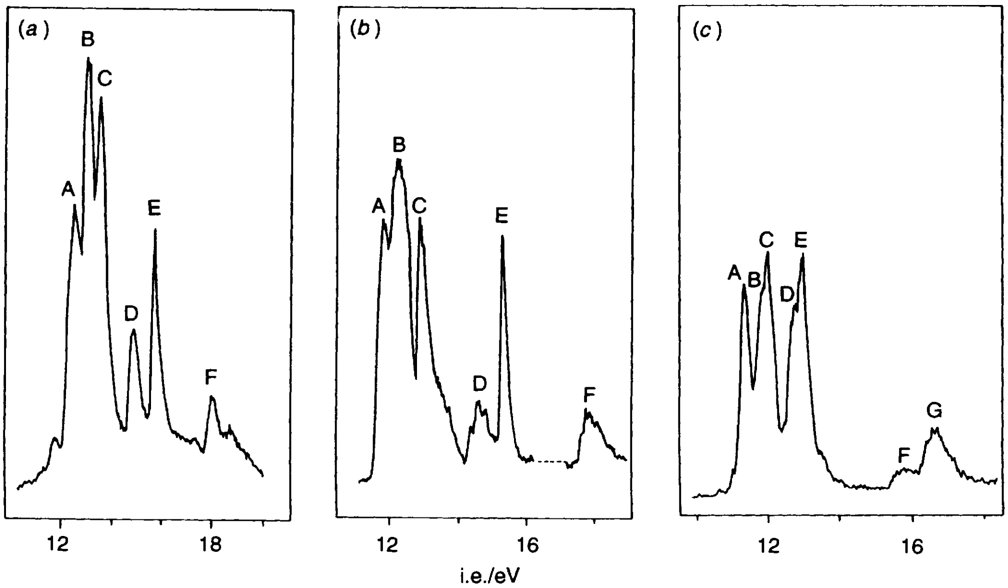

Fig. 5 The He I photoelectron spectra of (*a*) COClF, (*b*) COBrF and (*c*) COBrCl

Table 3 Experimental and computational results for $COBr_2$

Orbital	Koopmans i.e./eV	Mulliken population (%) C	O	Br	Principal character	i.e./eV OVGF	2ph-TDA	Assignment	Exptl. i.e./eV
$14b_1$	11.73	1	1	98	n(Br)	10.85	11.04	A	10.98
$5a_2$	12.26	0	0	100	n(Br)	11.36	11.56	B	11.45
$13b_1$	12.53	7	39	54	n(O), n(Br)	11.55	11.62	C	11.61
$6b_2$	12.58	1	15	84	n(Br)	11.73	11.97	D	11.92
$17a_1$	13.04	2	1	97	n(Br)	12.05	12.28	E	12.36
$5b_2$	17.32	36	54	10	π_{CO}	15.92	15.86	F	15.56
$16a_1$	18.54	29	33	38	σ_{CO}	16.72	16.62	G	16.12
$12b_1$	18.76	26	48	26	σ_{CBr}, $\pi_{\parallel CO}$	16.64	16.69	G	
$15a_1$	21.70	25	48	27	n(O), σ_{CO}, σ_{CBr}	19.37	19.02	H	19.0
							20.15*	I	20.1

* Shake up ionisation.

Table 4 Experimental and computational results for COClF

Orbital	Koopmans i.e./eV	Mulliken population (%) C	O	F	Cl	Principal character	OVGF i.e./eV	Assignment	Exptl. i.e./eV
16a′	13.71	1	22	2	75	n(Cl), n(O)	12.50	A	12.58
4a″	13.82	2	18	0	80	n(Cl), n(O)	12.83	B	13.10
15a′	14.79	7	45	9	39	n(O), n(Cl)	13.47	C	13.63
3a″	16.39	19	45	21	15	π_{CO}, n(F)	15.10	D	14.87
14a′	17.85	14	28	37	21	n(F), σ_{CO}	15.97	E	15.64
13a′	20.60	18	60	15	7	n(O), σ_{CO}	18.51	F	18.07
2a″	20.86	16	7	75	2	n(F), π_{CO}	18.70	F	
12a′	21.33	16	10	54	20	n(F), $\pi_{\parallel CO}$	19.08		
11a′	24.43	22	9	58	11	σ_{CF}	22.26		

structural data, the calculations on COBrF and COBrCl were performed using estimated geometries derived as described in the Computational Details section.

The assignments of these three photoelectron spectra are based on the comparison of the experimental peaks with the OVGF values. The agreement appears reasonably good and it is therefore suggested that the correct assignment is that suggested by the order of the predicted bands. In general, the predicted i.e.s are underestimated for those bands in the region below about 14 eV, and overestimated elsewhere, similar behaviour to that seen using the OVGF method for the symmetric carbonyl halides.

Summary of the Computational Results.—In this section the results of the SCF and Green's Function calculations will be considered, with a view to assessing the relative accuracy of the methods and any trends in the discrepancies observed.

In the discussion given below, use will be made of the assignments given above, assignments that were chosen to

Table 5 Experimental and computational results for COBrF

Orbital	Koopmans i.e./eV	Mulliken population (%)				Principal character	OVGF i.e./eV	Assignment	Exptl. i.e./eV
		C	O	F	Br				
22a′	12.50	1	6	1	92	n(Br)	11.64	A	11.87
7a″	12.61	0	8	0	92	n(Br)	11.84	B	12.27
21a′	14.10	10	48	8	34	n(O), n(Br)	12.91	C	12.89
6a″	16.16	21	56	18	5	π_{CO}, n(F)	15.06	D	14.57
20a′	17.38	16	36	29	19	n(O), n(F)	15.50	E	15.32
19a′	20.49	21	64	8	7	n(O), σ_{CO}	18.38	F	17.78
5a″	21.02	15	6	78	1	n(F), π_{CO}	18.75		
18a′	21.29	12	10	66	12	n(F)	18.88		
17a′	24.51	22	9	60	9	n(F), σ_{CF}	22.23		

Table 6 Experimental and computational results for COBrCl

Orbital	Koopmans i.e./eV	Mulliken population (%)				Principal character	OVGF i.e./eV	Assignment	Exptl. i.e./eV
		C	O	Cl	Br				
25a′	12.12	1	4	14	81	n(Br)	11.19	A	11.30
8a″	12.41	0	6	1	93	n(Br)	11.58	B	11.83
24a′	12.98	7	40	22	31	n(O), σ_{CCl}, σ_{CBr}	11.90	C	11.98
7a″	13.59	2	16	82	0	n(Cl), π_{CO}	12.49	D	12.73
23a′	13.95	2	5	77	16	n(Cl)	12.71	E	12.95
6a″	17.53	36	46	13	5	π_{CO}, n(Cl)	16.15	F	15.75
22a′	18.77	27	39	8	26	σ_{CO}, n(Br)	16.87	G	16.52
21a′	19.17	25	43	28	4	n(O), $\pi_{\parallel CO}$, σ_{CCl}	17.14		
20a′	21.91	26	40	21	13	n(O), σ_{CO}, σ_{CCl}, σ_{CBr}	19.64		

Table 7 Root mean square errors for computed i.e.s

Calculation	Intercept (eV)	Slope	r.m.s. error (eV)	Notes
Koopmans	0.0	1.0	1.73	As computed
Koopmans	0.0	0.92	0.56	Conventional scale factor
Koopmans	1.61	0.81	0.30	Optimal linear transformation
OVGF	0.0	1.0	0.33	As computed
OVGF	1.06	0.92	0.20	Optimal linear transformation
Extended 2ph-TDA	0.0	1.0	0.37	As computed
Extended 2ph-TDA	0.62	0.95	0.19	Optimal linear transformation

provide an optimal fit between theory and experiment. As such, there is a risk of using circular logic as these assignments are now used to judge the quality of the theoretical methods. However, we feel that when this and previous work is considered very few of the assignments are in doubt, and where they are, the small energy differences in the experimental i.e.s would suggest that the following discussion is worthwhile.

Koopmans' approximation. Overall, Koopmans' approximation, and the one-electron picture of ionisation on which it is based, appears to hold reasonably well for the interpretation of the PE spectra under study here.

The Koopmans i.e.s are, in all cases, greater than the observed values. The magnitude of the Koopmans error varies from around 0.5 eV for orbitals strongly localised on Cl and Br, to around 2.5 eV for orbitals associated with C, O and F. The error is also found to be systematically greater for energetically lower-lying orbitals, a fact that has led to the use of 'scaled Koopmans' i.e.s. Typically, the scale factor chosen is 0.92.[24] We have computed the root mean square (r.m.s.) error in the i.e.s computed using Koopmans' theorem, and by scaling the Koopmans values by 0.92 (see Table 7). In addition, by linear regression we have derived the linear transformation of the Koopmans values that gives the best fit to the experimental values. Although we do not recommend this as an alternative scaling procedure, the result suggests that a better empirical relationship for general use may be obtained by incorporating a constant and using a scale factor considerably smaller than 0.92.

OVGF and extended 2ph-TDA results. For comparison, we have computed the r.m.s. error in the computed i.e.s from the Green's function calculations, with and without a linear transformation derived from a regression analysis of the computed and experimental results. We are not suggesting here the use of 'Scaled Green's function' calculations, but merely using the transformation parameters derived from the regression calculation to give some measure of the nature of any i.e. dependent systematic errors.

Clearly, the two GF methods are approximately comparable in their ability to predict the i.e.s. The fact that 2ph-TDA results are similar to those from the OVGF method, with a small number of predicted satellites is an indication that the one-electron model of ionisation is generally appropriate. Both approaches yield substantially better results than the Koopmans or scaled Koopmans calculations. Interestingly, the r.m.s. error for the GF results is slightly larger than that derived from the Koopmans values after the latter have been subjected to the optimum linear transformation. Applying a similar scaling transformation to the two sets of GF data reduces the r.m.s. errors further, as expected. The results are given in Table 7. The slope of the regression lines is again below 1.0, indicating (as noted previously) that the GF methods tend systematically to overestimate the i.e.s of the inner valence orbitals. It appears that the Green's function results still display some of the systematic errors of the Koopmans' result, a not unsurprising result given that method is based on the SCF wavefunction and can only treat the ion-state relaxation effects approximately.

Electronic Structure Trends in the Carbonyl Halides.—In this section the effects of halogen substitution on the electronic structure of the carbonyl halides are discussed, with particular emphasis on the trends exhibited by the i.e.s reported in the previous section. It is useful to consider the consequences of both inductive effects, acting through the σ framework, and conjugative effects, arising from the participation of halide orbitals with π symmetry.

The halides act as σ acceptors and withdraw charge density from the CO group, raising the energy required to induce ionisation from many sigma-bonding and lone-pair orbitals. As an example, consider the ionisation from the in-plane oxygen lone-pair orbital (b_1 symmetry in the symmetric halides). In COH_2, this ionisation occurs at 10.88 eV.[25] All the carbonyl halides studied in the current work show larger i.e.s, ranging from 11.61 in $COBr_2$ to 13.62 eV for COF_2. This inductive effect would also be expected, through an electrostatic mechanism, to increase the ionisation energy of the π-symmetry orbitals of the CO group. However, the filled halogen p orbitals are capable of acting as π donors to CO. In the fluoride case, the F p orbitals lie at lower energy than the CO π orbitals with which they interact, compare the F-based ionisations observed in this study (generally at or below 16.7 eV) with the π_{CO} ionisation in formaldehyde at 14.5 eV.[25] The MO with the most π_{CO} character will thus be the antibonding combination, and will be raised in energy. The π_{CO} ionisation is thus observed at 14.80 eV in COF_2, 14.87 eV in COClF and 14.57 eV in COBrF, and is in each case antibonding with respect to the F character. From the similarity between these values and that for H_2CO given above it can be seen that the inductive and conjugative effects largely cancel out in the case of fluoro substitution. The mixed halides containing F also show similar π_{CO} i.e.s. In contrast, both Cl and Br possess p orbitals which give rise to ionisations in the range 11–13 eV, and thus lie energetically above the H_2CO π_{CO} orbital, which gives rise to an ionisation at 14.5 eV. As a result, the orbital most easily identified as π_{CO} has the halogen p-orbital contributions and π_{CO} character in phase. The inductive and conjugative effects thus combine to lower the π_{CO} i.e., leading to values of 16.09 eV in $COCl_2$, 15.56 eV in $COBr_2$, and an intermediate value of 15.75 eV for COBrCl.

The differential effect of fluorine substitution on the ionisation energies of σ and π orbitals has been exploited in the assignment of photoelectron spectroscopic results by comparison of perhydro and perfluoro analogues. In general, the larger stabilising effect on the σ MOs, compared to the π MOs enables the systems to be discriminated. When used in this way, it is referred to as the perfluoro effect.[15,26–30]

Experimental

Samples of COF_2, $COCl_2$ and COClF were obtained commercially from Fluorochem, BDH and Ozark-Mahoning respectively. Samples of $COBr_2$, COBrCl and COBrF were prepared by standard routes or slight modifications of them.[31] All of the samples were purified by vacuum distillation prior to use.

The photoelectron spectra were obtained on a Perkin-Elmer PS16 spectrometer (modified to enable He II spectra to be obtained) or on a higher resolution 'fast-flow' photoelectron spectrometer originally designed and built at Southampton University.*[,32] The spectra were calibrated by simultaneous admission of xenon (12.130 eV) and by reference to the helium self ionisation peak (4.991 eV).

Computational Details

All calculations were performed using the GAMESS-UK suite of programs.[12] Orbital plots were generated using a modified version of the program MOPLOT.[33]

Geometries.—The geometries used in the calculations are given in Table 8. Those for COF_2, $COCl_2$ and $COBr_2$ were taken from microwave studies[34–36] and that of COClF from an electron diffraction study.[37]

The bond angles for the bromohalides COBrF and COBrCl were taken from SCF geometry optimisations with the basis sets indicated below. However, because of systematic errors expected in the bond distances at this level of calculation (particularly for multiply bonded systems), the distances were taken from those of the dihalides. The C–X bond lengths for COBrF and COBrCl were estimated from those of COF_2, $COCl_2$ and $COBr_2$. The average C–O distance was used in each case.

Basis Sets.—Carbon, O and F were treated by the double-zeta plus polarisation (DZP) basis of Dunning.[38] The Cl basis set is of DZP quality[39] based on the (11s7p) primitive basis of Huzinaga *et al.*[40] contracted to (6s4p), with the addition of a single d polarisation function with an exponent of 0.6. Bromine was treated by the first-order polarised basis of Sadlej.[41]

Details of the CI Calculations on $COCl_2$.—The Dunning DZP basis set was used throughout these calculations, and the active space for the CI excluded the 12 lowest and 6 highest energy orbitals. In the case of a_1, a_2 and b_2 symmetries the CI calculations were performed by starting with a single reference configuration, using the orbitals derived from an SCF calculation on the cation of the appropriate symmetry. All single and double excitations from this reference were included. Any configurations appearing in the CI wavefunction with absolute value of the CI coefficient >0.03 were then added to the reference space and the calculation repeated. This was continued until no new reference configurations were generated.

Each CI calculation was performed with a reference state described by orbitals from an SCF calculation on the ion with appropriate symmetry. The reference configurations for both b_1 states were described by the orbitals resulting from an SCF calculation in which the two highest orbitals had occupancies of 1.5, *i.e.* an average of the occupancies expected in the SCF description of the two states of interest. This allows two orthogonal b_1 cation states to be generated, as the first two roots of the CI calculation, while minimising the bias arising from the choice of reference. The reference space was augmented as above, configurations being included if they had an absolute value of CI coefficient >0.03 in *either* root. The sizes of the reference spaces used in the final calculations are given in Table 9.

Details of the Green's Function Calculations.—The low-lying occupied orbitals were frozen in all Green's function calculations, only the 12 highest valence orbitals being included. In the OVGF studies of COF_2, $COBr_2$ and COBrF a corresponding number of high-lying (core-complement) virtual orbitals were excluded from the computation. For reasons of computational cost, extended 2ph-TDA Green's function calculations have been performed only for the symmetrical carbonyl dihalides. In these calculations a limitation on the number of 2h-1p or 2p-1h states of a given symmetry (to 3000) restricted the number of active orbitals to 42 (12 occupied and 30 virtual) in each case.

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* The spectrometer is a single detector version of the instrument described in ref. 32.

Table 8 Geometries used in the calculations for the COXY systems

X	Y	C–O/Å	C–X/Å	C–Y/Å	X–C–O/°	Y–C–O/°	Source	Ref.
F	F	1.170	1.317		126.2		Microwave	34
Cl	Cl	1.176	1.738		124.1		Microwave	35
Br	Br	1.172	1.917		123.9		Microwave	36
F	Cl	1.173	1.334	1.725	123.7	127.5	Electron diffraction	37
F	Br	1.171	1.317	1.917	125.7	124.0	Estimated	
Cl	Br	1.174	1.738	1.917	123.5	123.0	Estimated	

Table 9 Size of reference spaces for the CI calculations on $COCl_2$

System	State symmetry	Number of reference configurations	Number of states	Total energy (a.u.)
Neutral	$^1A_1$	7	845 488	−1 032.224 437
Cation	1^2B_1	14	2 332 336	−1 031.777 995
	2^2B_1	14	2 332 336	−1 031.801 687
	$^2B_2$	11	2 212 952	−1 031.769 270
	$^2A_2$	8	1 414 156	−1 031.764 195
	$^2A_1$	11	3 050 057	−1 031.744 529

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