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The HeI and HeII Photoelectron Spectra of VOF_3 and $VOCl_3$

E. PELLACH

Solid State Institute, Technion, Haifa 32000, Israel

G. M. BANCROFT

Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7, Canada

and J. S. TSE[†]*

Division of Chemistry, National Research Council of Canada, Ottawa, Ont. K1A 0R9, Canada

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Photoelectron spectra in the gas phase using HeI and HeII radiation are reported for the oxyhalides VOF_3 and $VOCl_3$. The nature of the metal–ligand bonding in these molecules as inferred from the experimental and theoretical results is discussed. Assignment of the spectra is made with the aid of theoretical molecular orbital calculations and relative intensity changes between the HeI and HeII spectra.

Introduction

The HeI photoelectron spectrum of $VOCl_3$ has been reported by Orchard and co-workers [1]. Owing to the rather low molecular symmetry and the strong overlapping of the photoelectron peaks, their assignments were mainly based on the relative intensities arguments and guided by simple Extended-Hückel calculations.

It is well known today that an empirical rule for predicting relative intensities of photoelectron peaks according to degeneracy or electron occupancy is not appropriate in many cases [2, 3]. In particular, for the metal–ligand orbitals in transition metal compounds, the photoionization cross-section of these orbitals can be very different due to differences in orbital characters and accordingly different localization properties. On the other hand, the use of photoelectron spectra taken with more than one photon energy [4, 5] can greatly facilitate the interpretation, especially for transition metal compounds where the metal d orbitals are strongly involved in the bonding.

In this paper, we report the results of a study on the valence photoelectron spectra of VOF_3 and $VOCl_3$ in the gas phase using both HeI and HeII radiation. We assign the spectra with the aid of the relative intensity changes between HeI and HeII spectra and theoretical molecular orbital (MO) calculations using SCF-Xα-SW and Green's Function methods.

The experimental setup and the theoretical details are described in the next section. In Section III, we suggest an alternative assignment for the $VOCl_3$ and propose an assignment for VOF_3.

Experimental

The compounds used in the present study were purchased commercially from Alfa Co. (minimum purity of 99.8%). The samples were loaded on the sample probe in a dry nitrogen glove box and transferred to the spectrometer in a locked dry N_2 system to avoid hydrolysis. The photoelectron spectra were measured with a McPherson ESCA-36 spectrometer. The hollow cathode lamp described previously [6] was used as the light source. VOF_3 being a solid, was heated to 270 °C in order to achieve a reasonable count rate. The spectra were calibrated by reference to Ar 3p lines which was introduced through an external leak valve into the probe simultaneously with the sample. The spectra have been recorded at a medium resolution (35 meV for HeI and 40 meV for HeII) except for the HeI spectrum of VOF_3 which was taken at high resolution of 20 meV (full width at half height of the Ar $3p_{3/2}$ line). The HeII spectra were obtained by multiscanning the region of

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[†]NRCC No. 20392.

*Author to whom correspondence should be addressed.

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TABLE I. Parameters Used in the Xα-SW Calculation (a.u.).[a,b]

	Region	X	Y	Z	R	α
$VOCl_3$	Outer	0.0	0.0	−0.4875	6.2608	0.72601
	V	0.0	0.0	0.0	1.8155	0.71556
	O	0.0	0.0	2.9686	1.1531	0.74447
	Cl	3.8428	0.0	−1.2409	2.2226	0.72323
	Cl	−1.9214	3.3278	−1.2409	2.2226	0.72323
	Cl	−1.9214	−3.3278	−1.2409	2.2226	0.72323
VOF_3	Outer	0.0	0.0	−0.6883	4.8277	0.73526
	V	0.0	0.0	0.0	1.7066	0.71556
	O	0.0	0.0	2.9667	1.2601	0.74447
	F	3.1160	0.0	−0.9824	1.5606	0.73732
	F	−1.5580	2.6986	−0.9824	1.5606	0.73732
	F	−1.5580	−2.6986	−0.9824	1.5606	0.73732

[a] α_{HF} were taken from K. Schwarz, *Phys. Rev. B.*, *5*, 2466 (1972). [b] The coordinates were calculated using bond lengths from Ref. 11.

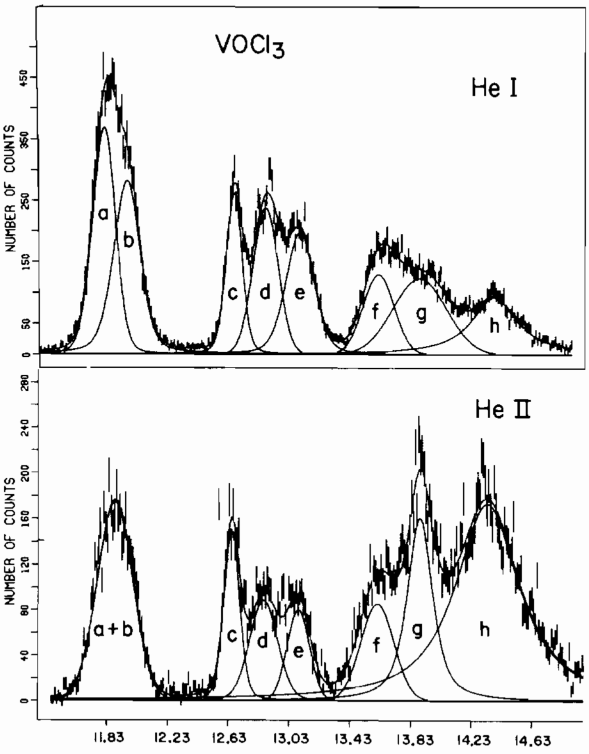

Fig. 1. HeI (top) and HeII (bottom) Photoelectron Spectra for $VOCl_3$.

interest. Unfortunately the resolution was degraded after running spectra of these compounds for a relatively short time. From our experience we recognize, in general, the more volatile the compound is, the faster the degradation in the resolution and also the count rate [7]. The photoelectron peaks were convoluted with a Voigt function simulated by a linear combination of Gaussian-Lorentzian line shapes [8].

Computational Details

SCF-Xα-SW calculations were carried out on the ground state geometry of both molecules employing the touching sphere model [9]. Ionization energies were estimated by using Slater's 'transition state' approximation [10]. A C_{3v} molecular symmetry was assumed in the calculations [11]. The geometries, spheres sizes and exchange parameters employed in the calculations are summarized in Table I. The highest l values used in the basis function expansions are 4 for the outer, 3 for V and 2 for O, F and Cl spheres. Core levels were never frozen during the self-consistent field iterations.

It is well known that the electron correlation effect is the most important relaxation mechanism in the ionization of valence electrons in transition metal compounds [12]. We adopted the diagonal 2ph-TDA (two-particle-hole Tamm-Dancoff approximation) to estimate this multi-electron contribution [13]. All relevant coulomb and exchange integrals were evaluated within the INDO approximation [14]. Previous applications of this method to transition metal compounds have met with considerable success [15].

Results and Discussion

The HeI and HeII photoelectron spectra of $VOCl_3$ and VOF_3 are shown in Figs. 1 and 2, respectively. Our HeI spectrum of $VOCl_3$ agrees with that previously reported [1]. Orbital binding energies

TABLE II. Valence Band Parameters of $VOCl_3$ (in eV).[a]

Band	B.E.[d]	Experimental				Calculated		SCF-Xα % charge distribution					Assignment
		HeI		HeII		XαSW[c]	2ph-TDA[e]	V-3s	V-3d	O-2p	Cl-3p	Intersphere	
–		FWHM	AREA[b]	FWHM	AREA[b]								
a	11.82	0.18(1)	7.60(1.1)			13.47	12.30(0.8)				78	20	$1a_2$
				0.28(1)	5.37(0.2)								
b	11.97	0.20(2)	7.35(1.2)			13.48	12.09(0.8)			12	63	23	5e
c	12.68	0.12(1)	4.29(0.2)	0.12(1)	1.99(0.2)	13.93	13.28(0.8)		4	5	65	24	4e
d	12.89	0.19(2)	5.69(0.5)	0.21(4)	3.69(0.6)	13.90	13.53(0.8)	3		6	67	22	$5a_1$
e	13.11	0.22(2)	6.18(0.5)	0.18(2)	1.60(0.2)	13.95	14.43(0.5)				71	26	$4a_1$
f	13.63	0.24(2)	4.19(1.3)	0.25(3)	2.90(0.4)	14.51	13.95(0.7)		23		54	21	3e
g	13.90	0.41(7)	7.13(1.6)	0.20(2)	5.71(1.2)	15.03	14.45(0.5)		24	33	14	29	2e
h	14.40	0.36(4)	7.37(1.0)	0.51(10)	19.90(0.8)	15.92	15.51(0.8)		33	40	4	22	$3a_1$

[a] Errors given in parentheses. [b] Arbitrary units divided by kinetic energy for normalization. [c] Calculated from Transition State Procedure. [d] Binding Energy. [e] Pole strength in parenthesis.

TABLE III. Valence Band Parameters of VOF_3 (in eV).[a]

Band	B.E.[d]	Experimental				Calculated		SCF-Xα % charge distribution				Assignment
		HeI		HeII		XαSW[c]	2ph-TDA[e]	V-3d	O-2p	F-2p	Intersphere	Assignment
		FWHM	AREA[b]	FWHM	AREA[b]							
a	14.04	0.48(2)	18.52(1.1)	0.51(4)	7.83(0.8)	16.07	12.14(0.8)			82	16	$1a_2$
						16.23	12.73(0.7)	3		78	17	4e
						16.27	13.00(0.7)	4		76	16	$4a_1$
b	14.62	0.27(3)	10.47(2.9)									
				0.79(5)	13.61(1.1)	15.24	12.10(0.7)	6	48	16	28	5e
c	14.98	0.34(3)	8.44(1.3)			15.59	12.77(0.7)	15	41	22	20	$5a_1$
d	15.46	0.22(1)	10.26(0.5)	0.22(1)	9.58(0.8)							
e	15.75	0.17(2)	8.09(0.7)	0.34(4)	8.00(1.1)	16.95	14.30(0.7)	13		60	20	3e
	16.09	0.20(4)	3.23(0.3)									
	16.28	0.19(2)	8.29(1.0)									
						17.13	15.34(0.7)	15	8	56	19	$3a_1$
f	16.45	0.12(3)	4.38(1.2)									
				0.87(5)	25.46(1.7)							
	16.60	0.17(4)	2.25(0.6)			17.09	15.63(0.7)	13		67	18	2e
	16.80	0.20(4)	2.47(1.0)									

[a] Errors given in parenthesis. [b] Arbitrary units divided by kinetic energy for normalization. [c] Calculated from Transition State Procedure. [d] Binding Energy. [e] Pole strength in parenthesis.

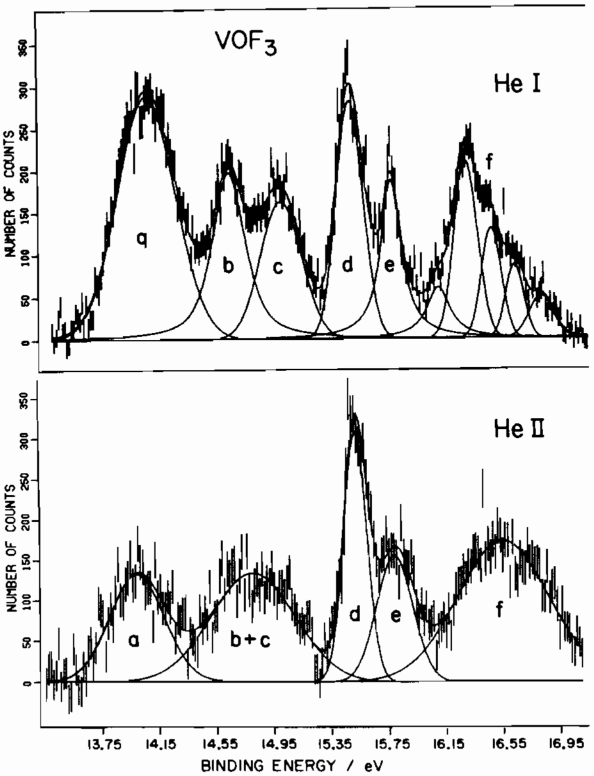

Fig. 2. HeI (top) and HeII (bottom) Photoelectron Spectra for VOF_3.

along with the theoretical results are given in Tables II and III.

We begin our discussion with the photoelectron spectra of $VOCl_3$. Owing to the higher resolution of our HeI spectrum, we observed a distinct shoulder at the higher binding energy side of the first band. Spectral deconvolution of this band gave two peaks (a and b) separated by *ca.* 0.15 eV. Even without resolving these two peaks, Orchard *et al.* [1] assigned this band to ionization arising from the chlorine lone pair $1a_2$ and 5e molecular orbitals. Their assignment was based on extended-Hückel molecular orbital calculations on a series of pseudo-tetrahedral transition metal compounds which showed the t_1 orbital in T_d symmetry splits only slightly (*ca.* 0.2 eV) when the symmetry is lowered to C_{3v}. Our experimental and theoretical results substantiate their assignment. The small splittings of the lone pair orbitals have also been observed in the analogous MnO_3Cl molecule [16].

Guided by the relative intensities of the overlapping bands (f, g and h) in the HeI spectrum, Orchard *et al.* assigned them to the 2e and $3a_1$ + $4a_1$, orbitals respectively, leaving the central bands c, d and e to the remaining 3e, $5a_1$ and 4e orbitals without specifying the order. As we have commented earlier it is not very reliable to use the simple intensity argument alone without a prior knowledge of the cross-section of these molecular orbitals in the HeI region [4, 5]. However, the observation of the relative intensity changes of the spectrum with HeI and HeII radiation can be very useful in assisting the interpretation. In the HeII spectrum, we observed bands, a, b, d and e decrease in intensity relative to bands c and f while band g and h increase sharply. It is common to assume that the cross-section of p-type orbitals will decrease as the energy of the incident radiation increases. On the contrary, the more diffuse metal d-orbital cross-section will increase [17]. Following this empirical rule we would then expect bands a, b, d and e are primarily Cl-3p and O 2p in character and bands f, g and h are associated mostly with the V 3d orbitals. Furthermore, the relative intensities suggest the metal contribution increases in the order $f < g < h$.

The orbital characters calculated by both the INDO/2 and SCF-Xα-SW method agree very well with this prediction. The Xα-SW and 2ph-TDA calculations uniformly overestimated the binding energies by *ca.* 1.5 eV and 0.5 eV, respectively. The large Cl 3p character of orbitals $1a_2$ and 5e confirm the assignment of bands a and b. According to the increasing contribution of the 3d orbital, bands f, g and h are assigned to the V–O and V–Cl bonding 3e, 2e and $3a_1$ orbitals respectively. We suggest band c to be assigned to the 4e orbital. The apparent increase of intensity relative to the lone pair Cl orbitals in the HeII spectrum may be attributed to a small metal contribution and the slower decrease of O2p cross-section as compared to the Cl3p in this energy range. A similar intensity variation has been reported in the $TiCl_4$ and $SnCl_4$ photoelectron spectra [3]. Bands d and e are assigned to the remaining $5a_1$ and $4a_1$ orbitals. These orbitals are mainly Cl 3p σ bonding and should decrease in intensities in the HeII spectra.

Inspecting the profile of bands f, g and h indicates strong bonding character. This observation is also supported by the theoretical calculations. The broadening and, in particular, the asymmetry of band h is mainly due to unresolved vibrational progressions, though we do not preclude other possible causes such as Jahn-Teller splittings [18]. Governed by the molecular symmetry, the oxygen p_z orbital in $VOCl_3$ can be involved in bonding with orbitals of a_1 symmetry and the p_x, p_y orbitals only with e symmetry. It is clear from the orbital character established by the theoretical calculations that the V–O bond is stabilized by d_σ–p_σ ($3a_1$) and d_π–p_π (2e) interactions. These V–O bonding orbitals are also the most stable valence orbitals. The stronger σ metal–oxygen bonding relative to metal halide bond also explains the interchanging of the position of the last two orbitals ($3a_1$ and 2e) compared to the order suggested for MnO_3Cl [16]. The pole strength obtained from the Green's function calculations indicates most orbital ionizations retain the single particle character with the exception of the $4a_1$ and 2e orbitals.

Despite the similarity between the molecular structure of VOF_3 and $VOCl_3$, the assignment of the VOF_3 photoelectron spectrum is more complicated. There are two major reasons for this difficulty: a) There are fewer distinct peaks observed in the VOF_3 spectrum than the number of occupied valence molecular orbitals. This suggests the molecular orbitals in VOF_3 are closely packed together and strongly overlapping; b) The relative intensity changes between the HeI and HeII spectra are not as profound as in $VOCl_3$. Only band a shows a drastic reduction in intensity relative to the other bands in the HeII spectrum (Fig. 2). Theoretical calculations showed that unlike the oxychloride, all the molecular orbitals in VOF_3 possesses some V-3d character except the $1a_2$ which is forbidden by symmetry. It is interesting to note that similar differences in the degree of metal d orbital participation in bonding have also been reported in MnO_3X (X = F, Cl) compounds [16]. This mixing of the metal and ligand orbitals may minimize any drastic and distinct variation in spectral intensities on going from HeI to HeII.

The lowest energy photoelectron peak in VOF_3 is located at 14.04 eV. The large width of this band suggests it may arise from more than a single ionization. The more electronegative fluorine atoms will increase the binding energy of the lone pair electrons. Resorting to previous experiments, we find that [19] most fluorine lone pair ionizations in transition metal complexes occur at the 14–16 eV region. On the other hand, the first ionization in VOF_3 also compares very well with the V–O π orbital in $VOCl_3$ (13.90 eV). Furthermore, both SCF-Xα-SW and Green's function calculations indicate that the highest occupied molecular orbital possesses fairly strong metal–oxygen character. It is tempting to assign the first band to the V–O bonding $5a_1$ and 5e ionizations. However, the observed intensity reduction in the HeII spectrum does not support such an assignment. It is more reasonable to assign the band to fluorine lone-pair ionizations ($1a_2$, 4e). Bands b, c and d can be assigned to nonbonding fluorine lone pair $4a_1$ and V–O bonding $5a_1$ and 5e orbitals respectively. The justification for this assignment is partly dictated by correlating the relative intensities with orbital degeneracies. The band shape of peaks e and f are more complicated. They resemble a collection of closely packed vibrational structures. We were able to fit five peaks into band f. The resulting peak separations however, are not evenly spaced. The average separation is about 0.18 eV (1450 cm^{-1}) which is even larger than the fundamental vibration of 1058 cm^{-1} [20]. We anticipate band e and f must be composed of several bonding orbitals. Following the theoretical calculations, we assigned the V–F bonding, 3e, 2e and $3a_1$ orbitals to this region.

Our 2ph-TDA calculation also showed the pole strength of the ionizations are generally smaller than in $VOCl_3$. This tends to suggest that the final ionic states are more correlated. As a result, the mixing of different particle-hole states will alter the pattern of cross-section anticipated for 'atomic-like' orbitals. This factor may contribute to the anomalous intensity variation observed in the HeI/II spectra.

Conforming to the above assignments for $VOCl_3$ and VOF_3, we observed that substituting fluorine by chlorine atoms increases the binding energy of the vanadium-halide orbitals by *ca.* 2 eV. The higher ionization energy of the F2p electrons relative to Cl2p and O-2p causes the V–F bond to be more stabilized than the V–O bond [21, 22]. Once again, this phenomenon is also observed in the MnO_3X spectra.

Conclusion

Using HeII and HeI spectra of the oxytrihalides and Xα calculations, we complete the assignment of $VOCl_3$ and suggest an assignment for the valence band orbitals of VOF_3. The proposed order for $VOCl_3$ orbitals is consistent with our new assignment of $TiCl_4$ [3]. However, even with the experimental and theoretical evidence that have been shown, further studies using high resolution and synchrotron radiation along with cross section and vibrational calculations can add to a further chemical understanding of the photoelectron spectra, particularly in the case of VOF_3.

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