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Polyoxometalates and Vanadium Alkoxides: Electronic Structure and Properties

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Abstract: The HeI/HeII photoelectron spectra of oxovanadium triethoxide (**I**) and oxovanadium triisopropoxide (**II**) are reported for the first time. We have observed significant differences in the electronic structure of the title molecules compared to their titanium analogues. Metal alkoxides (containing Mo, W, V, Nb) are precursors of polyoxometalates which are capable of supporting reversible redox reactions in the solid state. Vanadium alkoxides contain high lying occupied valence orbitals with metal character which explains the ability of their derivative polyoxometalates to become involved in reversible redox reactions.

1. Introduction

Vanadium alkoxides are important precursors for many chemicals and as such have found numerous applications over the years. These applications include their use as precursors in sol-gel processing for manufacturing of metal oxide coatings [1], as catalysts for the polymerization and oxidation of unsubstituted olefins [2] and most recently, in the preparation of extended modular frameworks which incorporate inorganic building blocks [3]. Such frameworks may be used to conduct reversible redox reactions with high selectivity. Bioinorganic chemistry of vanadium was also investigated [4]. Vanadium alkoxides exhibit hydrolysis [5] and thermochromism [6]. In solid state they exist as polymers with vanadium coordination polyhedra sharing edges [7, 8].

The reaction mechanisms of processes which involve vanadium alkoxides are not well understood and in view of the importance of title compounds in material science we have performed an investigation of their electronic structures.

2. Results and Discussion

The HeI/HeII photoelectron spectra of oxovanadium triethoxide (**I**) and oxovanadium triisopropoxide (**II**) are shown in Figs. 1-2, respectively. The assignments of the spectra are summarized in Table 1 and were based on the considerations of relative band intensities, ionization energies obtained from OVGF calculations, HeI/HeII band intensity variations and comparison with the assigned spectra of related molecules, particularly ethanol, isopropanol, titanium(IV) tert-butoxide [9]. We have also compared the measured spectra with the spectra of VOF_3 and VOCl_3 [10] and with the spectra of bis(2,4-pentanedionato-*O,O*)oxovanadium(IV) [11].

Photoelectron Spectra

In each photoelectron spectrum (Figs. 1-2) the first manifold appears in the ionization energy region of 9-12 eV followed by the second featureless manifold at around 13.5 eV. The higher energy manifolds comprise unresolved bands corresponding to numerous ionizations. Since these are mostly σ -orbital ionizations belonging to alkyl group localized orbitals they have not been analyzed further. The total number of ionizations in the lower energy manifold of each spectrum is seven. Their assignments are given in Table 1. The corresponding molecular orbitals are either localized on the alkoxy group oxygens (n_O) or on the V=O group.

The first manifold shows considerable enhancement of its total intensity relative to the second manifold, on going from HeI to HeII radiation. The ratio of relative intensities of the first vs. second manifolds increases (in **II**) from 0.45 to 0.84 on going from HeI to HeII radiation. In the spectra of **I** the corresponding ratio increases from 0.57 to 0.89. The same effect was observed in the spectra of titanium(IV) tert-butoxide [9] where the manifold was tentatively attributed to the ionization of oxygen lone pairs i.e. no orbitals with metal character were detected in it. The interesting question which now arises is whether in the vanadium alkoxides the highest occupied orbitals have more metal character than in the titanium derivatives. The ratios of HeII/HeI atomic orbital photoionization cross-sections for C2p, O2p, V3d and V4s orbitals are: 0.31, 0.64, 1.02 and 0.78, respectively. How can we assess whether there is metal character present in these orbitals or not? Closely spaced bands in the manifold indicate the presence of ionic states of similar energies so the calculations alone may not be a reliable guide to the assignment. However, the HeI/HeII band intensity variations together with atomic photoionization cross-sections suggest that if the first manifold contains orbitals with metal character, in addition to oxygen lone pairs, the metal

character orbitals should exhibit considerable HeII/HeI relative intensity enhancement compared to the rest. On the other hand, if all the bands in the first manifold show uniform intensity enhancement they would correspond to oxygen lone pair types only. Our spectra show variable increase in relative band intensity with bands at 9.85 and 9.65 eV in **I** and **II** being enhanced more than others within the same manifold. This observation suggests that, unlike titanium alkoxide, vanadium molecules have upper lying orbitals with V 3d metal character. The V 4s cross-section is comparable to O 2p so we could not draw any firm conclusions regarding V 4s character in the outer valence orbitals. The measured values of V3d and V4s orbital energies in atomic vanadium which are 9.71 and 7.42 eV, respectively [13] also support our assignment. (V3d and V4s orbital energies were calculated as weighted averages of ionization energies for the set of electronic states corresponding to a particular orbital). V3d energy is close to the ionization energy of 9.85 eV band while V4s is not. Two other characteristics of the spectra of **I** and **II** should be mentioned. Firstly, the ionization energies in the spectrum of **II** are reduced by 0.2 eV compared to energies in **I**. This is due to the well established inductive effect which reduces ionization energy and which increases with the size of alkyl substituent. Secondly, the bands in the spectrum of titanium alkoxide [9] are narrower than in **I** and **II**. This can be explained by greater conformational flexibility in the latter molecules compared to the Ti derivative. The presence of bulky t-butyl groups hinders rotation around Ti-O bonds, reduces the number of accessible conformations and subsequently the bandwidth. Alkyl groups present in **I** and **II** (ethyl, isopropyl) are smaller which leads to larger number of accessible conformations that can be reached by rotation around V-O bonds and hence to the greater bandwidth. We have performed OVGf calculations on different rotamers of **I** and **II** and found that the largest calculated changes in

ionization energies within the sets of rotamers **I** and **II** amounted to 0.1 eV. The FWHM of bands in the 9-12 eV region which are assigned to single ionizations are approximately 0.4 eV which is consistent with our suggestion that existence of rotamer population leads to the broadening of bands.

3. Conclusion

We have determined the electronic structure of vanadium alkoxides and found that it reveals metal character in some of its highest lying valence orbitals. This metal character provides explanation for the catalytic activity of vanadium based polyoxometalate frameworks in the solid state. Such frameworks were found to be capable of supporting reversible redox reactions in the solid state involving ascorbic acid and metal centres in the solid framework. The presence of high lying occupied orbitals possessing transition metal atom character can be expected to facilitate such redox reactions which involve electron transfer to and from partially filled metal d shells. For the metalloorganic frameworks to be effective in catalysis and to participate in redox reactions they should possess partly filled metal based orbitals with low ionization energy i.e. good electron transfer ability. The presence of metal atom alone does not guarantee this property as our results have shown. Why are there different contributions of 3d orbitals in titanium vs. vanadium alkoxides even though both complexes are formally of d^0 type? We have performed natural atomic orbital and natural bond orbital analysis [16] for **I** and **II** and established that four orbitals in 9-12 eV range have significant (up to 100%) V 3d character. The calculated AO character depends of course on the formalism employed to perform the population analysis, but nonetheless our calculations confirm the presence of ionizations from orbitals with vanadium character. The reason for the difference between titanium and vanadium alkoxides can be attributed to the presence of V=O bond in the latter as was

established by X-ray diffraction [8]. The double bonds allow $O2p\pi \rightarrow V3d\pi$ dative bonding which transfers some electron density from the oxygen ligand to the metal [17]. Further study of the electronic structures various metal alkoxides would be beneficial in predicting their usefulness as precursors for the preparation of polyoxometalates and metalloorganic frameworks.

4. Experimental and Computational methods

The sample compounds were purchased from Aldrich and used without further purification after checking their identity and purity by NMR spectroscopy.

The HeI/HeII photoelectron spectra (UPS) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 meV and 70 meV, respectively when measured as FWHM of the $3p^{-1} \ ^2P_{3/2} \ Ar^+ \leftarrow Ar \ (^1S_0)$ line. The spectra were recorded down to ionization energy of 7 eV, but no bands were observed in 7-9 eV region. The spectra obtained were reproducible and showed no signs of decomposition.

The quantum chemical calculations performed with Gaussian 03 program [14] included full geometry optimization of the neutral molecule (using Stuttgart effective core potential basis set [15b] for all elements) as the first step. The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT geometry was used as the input into the single point calculation using the outer-valence Green's function (OVGF) method at the same set level [15] i.e. DFT formalism was used in the OVGF calculations. This method obviates the need for using Koopmans approximation and provides vertical ionization energies with typical deviation of 0.3-0.5 eV (depending on the size of the basis set) from the experimental values. The basis set used was selected with regard to

computational efficiency. The optimized bond lengths agree well with the available X-ray diffraction data e.g. calculated and the measured V-O bond lengths are consistent to within 0.02 Å [7,8].

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References

- [1] L.L. Hench, J.K. West, *Chem.Rev.* 90 (1990) 33.
- [2] E.C. Rosenthal, H. Cui, J. Koch, *Coordination chemistry and applications of vanadium alkoxides in catalysis*. ACS Symposium Series No. 974 (Vanadium), American Chemical Society, Washington, 2007, p.70.
- [3] C. Ritchie, C. Streb, J. Thiel, S.G. Mitchell, H.N.Miras, D.-L. Long, T. Boyd, R.D. Peacock, T. McGlone, L. Cronin, *Angew.Chem.Int.Ed.Engl.*, 47 (2008) 6881.
- [4] D.C. Crans, H. Chen, O.P. Anderson, M.M. Miller, *J.Am.Chem.Soc.* 115 (1993) 6769.
- [5] V.G. Kessler, G.A. Seisenbaeva, *Inorg.Chem.Commun.* 3 (2000) 204.
- [6] G.G. Nunes, G.R. Friedermann, J.L.B. dos Santos, M.H. Herbst, N.V. Vugman, P.B. Hitchcock, G.J. Leigh, E.L. Sa, C.J. da Cunha, J.F. Soares, *Inorg.Chem.Commun.* 8 (2005) 83.
- [7] W. Pribsch, D. Rehder, *Inorg.Chem.* 29 (1990) 3014.
- [8] C.N. Caughlan, H.M. Smith, K. Watenpau, *Inorg.Chem.* 5 (1966) 2131.
- [9] I. Novak, B. Kovač, *Chem.Phys.Lett.* 427 (2006) 47.
- [10] E. Pellach, G.M. Bancroft, J.S. Tse, *Inorg.Chim.Acta* 83 (1984) 93.
- [11] S. Di Bella, G. Lanza, A. Gulino, I. Fragala, *Inorg.Chem.* 35 (1996) 3885.
- [12] J.J. Yeh, *Atomic Calculation of Photoionization Cross-sections and Asymmetry Parameters*, Gordon and Breach: Langhorne, 1993.
- [13] J.M. Dyke, B.W.J. Gravenor, M.P. Hastings, G.D. Josland, A. Morris, *J.Electron Spectrosc.Relat.Phenom.* 35 (1985) 65.
- [14] Gaussian 03, Revision E1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam,

A.D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi,
V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo,
S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui,
K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari,
J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu,
A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin,
D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara,
C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen,
M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon,
E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2007.

[15] (a) W. Von Niessen, J. Schirmer, L.S. Cederbaum, *Comp.Phys.Rep.* 1 (1984) 57.

(b) U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Mol.Phys.*78 (1993) 1211.

[16] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem.Rev.* 88 (1988) 899.

[17] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley: New York, 1999, p.720.

Table 1. Experimental (E_i /eV) and calculated (OVGF/eV) vertical ionization energies, orbital assignments and relative band intensities in I and II^a and related compounds

Compound	Band	E_i	OVGF	Assignment
I	<i>X</i>	9.45	9.00	n_O
	<i>A-B</i>	9.85	9.62, 9.94	V3d, n_O
	<i>C</i>	10.45	10.25	n_O
	<i>D-E</i>	10.95	10.52, 10.69	n_O , π_O (V=O)
	<i>F</i>	11.65	12.12	π_{VO}
	II	<i>X</i>	9.25	8.82
<i>A-B</i>		9.65	9.50, 9.72	V3d, n_O
<i>C</i>		10.25	10.10	n_O
<i>D-E</i>		10.75	10.45, 10.46	n_O , π_O (V=O)
EtOH		10.64		n_O
i-PrOH		10.36		n_O

Figure captions

Fig. 1 HeI and HeII photoelectron spectra of oxovanadium triethoxide **I**

Fig. 2 HeI and HeII photoelectron spectra of oxovanadium triisopropoxide **II**

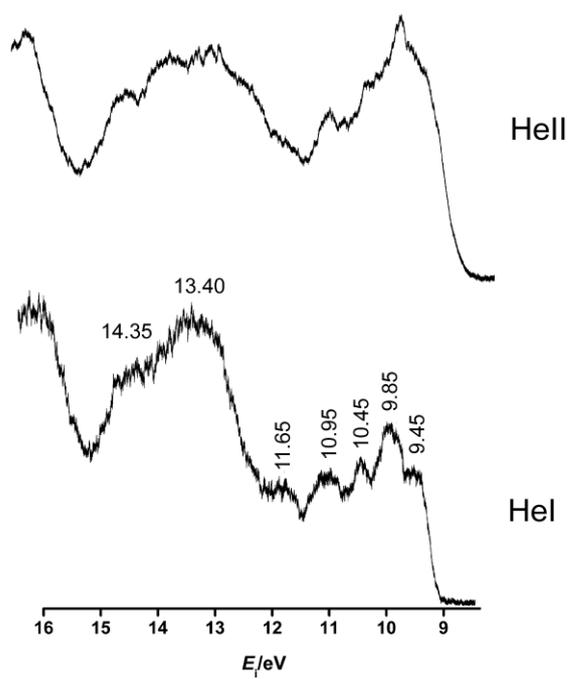
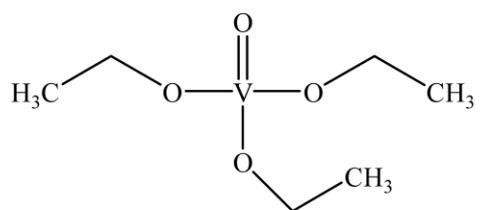


Fig.1

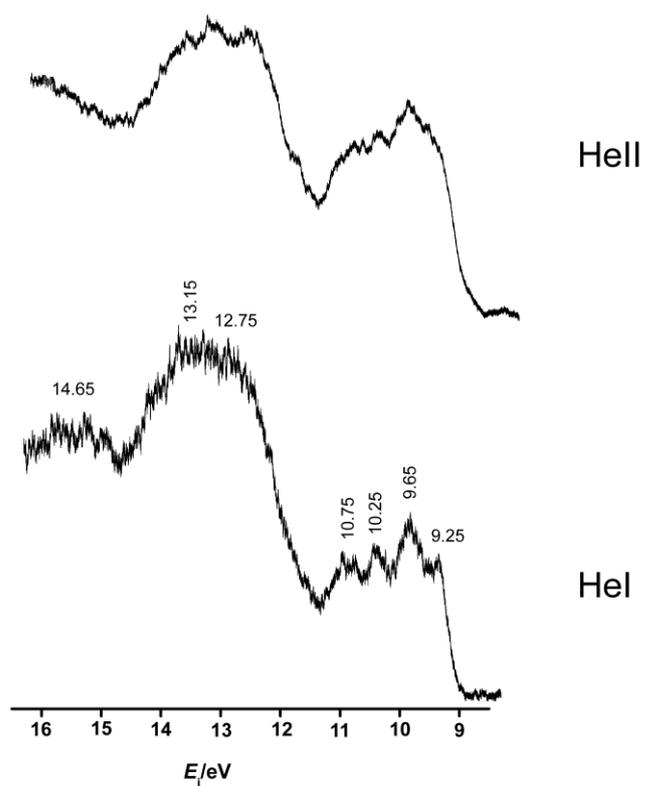
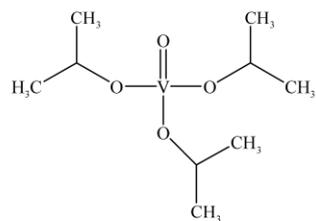


Fig.2