by an average value m_{ij}, and we have integrated eq 2 over many such intervals to give

$$-\log (y^\infty - y)/y^\infty = a\sum m_{ij}I_0\int_{t_i}^{t_j} I\mathrm{d}_0 t$$

where the integrals are proportional to areas under the photomultiplier plots of the split beam. Then, a plot of $\log (y^\infty - y)$ *vs.* $\Sigma m_{ij}\int_{t_i}^{t_j} I_0 \mathrm{d}t$ gave straight lines. From the slopes, obtained by the method of least squares, Q_t is readily calculated.

Finally, Q_c is obtained from the photostationary state conditions

$$Q_c = \frac{\epsilon_t Q_t}{\epsilon_c}\frac{1 - y^\infty}{y^\infty} - \frac{kV}{I_0^\infty m^\infty E_0}$$

It should be noted that, in the calculation of Q_c, the thermal rate could not be neglected.

To calculate quantum yields in ethanol solution, the photochemical reaction was run starting with both pure isomers. Plots of concentration of product formed *vs.* time were prepared, and the slope at time zero was estimated and used to calculate the quantum yield.

Photoelectron Spectra of Osmium and Ruthenium Tetroxides

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Abstract: Photoelectron spectra of OsO_4 and RuO_4 have been obtained and the five highest energy filled MO's have been assigned. A Jahn–Teller splitting of the order of 10^2–10^3 cm^{-1} has been detected in the $^2T_2$ ground state of OsO_4^+.

Despite a considerable mass of computational results,[1] the nature and order of energies of the highest energy filled MO's of tetrahedral molecules which are isoelectronic with MnO_4^- remain obscure. It is generally agreed that the five highest energy MO's are $1t_1$, $3t_1$, $2a_1$, $2t_1$, and 1e, with the $1t_2$ and $1a_1$ MO's at considerably lower energies. Apart from this, virtually all possible permutations of the topmost filled five MO's have been suggested at one time or another. Indeed, apart from electronic spectroscopic considerations and inferences drawn therefrom, the only relevant experiment extant is the ESCA results[2] on crystalline $LiMnO_4$, $Mg(MnO_4)_2$, and Li_2CrO_4, which indicates the presence of two groups of ionization events, each group covering only a small energy spread (~3-5 eV).

This work represents an attempt to assign the ionic states of gaseous RuO_4 and OsO_4 and to deduce the nature and order of the highest energy filled MO's. The experimental technique used is photoelectron spectroscopy which, surprisingly enough in view of molecule weight and complexity, generates remarkably well-resolved spectra. Computations are also indulged but are used only in a qualitative vein.

Experimental Section

RuO_4 and OsO_4 (Alfa Inorganics) were repeatedly degassed at reduced temperatures immediately prior to study.

Photoelectron spectra were measured using a Perkin-Elmer Model 18 spectrometer. The resolution was better than 20 MeV. A volatile-probe ionization chamber, in which the tetroxides could be flowed, was used. No significant difficulty was experienced with OsO_4. However, the extreme reactivity of RuO_4, and its tendency to plate out, led to deterioration of instrument characteristics, including the resolution, and necessitated complete instrument overhaul between individual runs. The net result was poorly resolved photoelectron spectra for RuO_4 and a severely malfunctioning electron detector and cathode source which are presently being replaced.

Results

The photoelectron spectra of RuO_4 and OsO_4 are shown in Figure 1. Despite the poor resolution of the RuO_4 spectrum, it is clear that both spectra contain five band systems and that these systems can be correlated in the manner denoted by dashed lines in Figure 1. The correlation of Figure 1 is based on band shapes and relative intensities, as estimated by planimetry. Energies and intensities are given in Table I. An enlarged spectrum of band A of OsO_4 is shown in Figure 2.

Molecular orbital computations were carried out

Table I. Adiabatic Ionization Potentials, Band Areas, and Proposed Assignments[a]

Band	IP, eV	Relative area	Proposed assignment
	RuO_4		
A	12.09	5	$3t_2$
B	12.91	3	$1t_1$
D	13.78	1	$2a_1$
C	13.88	2	1e
E	16.03[b]	2	$2t_2$
	OsO_4		
A	12.32_0	5	$3t_2$
B	13.13_8	3	$1t_1$
C	13.50_2	2	1e
D	14.54_3	1	$2a_1$
E	16.31[b]	2	$2t_2$

[a] Band assignments are cited in terms of that MO from which an electron has been ionized. [b] Energies of band maxima.

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(1) For reference see J. P. Dahl and C. J. Ballhausen, *Advan. Quantum Chem.*, **4**, 170 (1967); H. Johansen, *Chem. Phys. Lett.*, **17**, 569 (1972); K. H. Johnson and F. C. Smith, Jr., *ibid.*, **10**, 219 (1971); I. H. Hillier and V. R. Saunders, *ibid.*, **9**, 219 (1971), and references contained therein.

(2) R. Prins and T. Novakov, *Chem. Phys. Lett.*, **16**, 86 (1972).

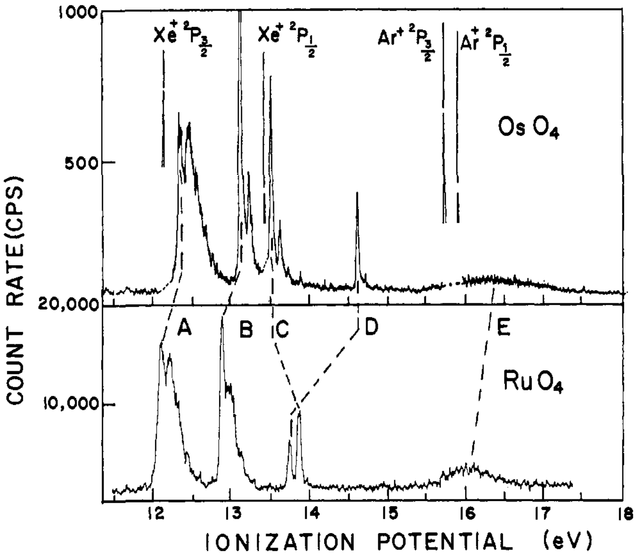

Figure 1. Photoelectron spectra of gaseous RuO_4 and OsO_4.

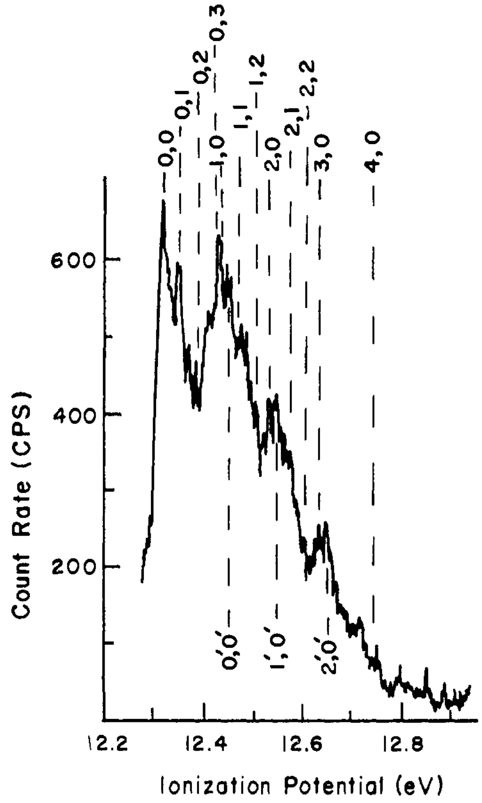

Figure 2. Expanded photoelectron spectrum of band A of OsO_4.

using an approach (ARCANA) described elsewhere.[3] The atomic data used in these computations are collected in Table II. The Ru–O bond length was taken as 1.706 Å and that of Os–O as 1.711 Å. The computations were iterated to charge self-consistency. The results are given in Table III and Figure 3 and are quite similar for both molecules. RuO_4, for example, is computed to have a charge of $-0.45|e|$ on each oxygen whereas OsO_4 has $-0.53|e|$, both at charge self-consistency. The dominant conclusions of the computational work are that both molecules should possess five accessible

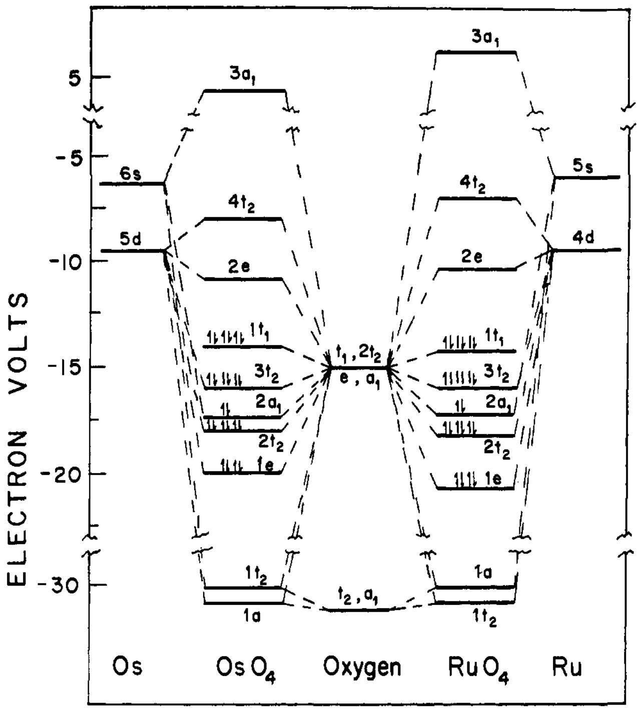

Figure 3. Molecular orbital energy diagram for RuO_4 and OsO_4.

Table II. Atomic Orbital Parameters

Atom	Orbital	n[a]	Z[b]	A[c]	B[d]	RI[e]
Ru	5s	2	0.754	−5.81	4.47	2.96
	4d	1	0.913	−9.66	10.33	1.28
Os	6s	3	0.798	−6.02	4.44	2.99
	5d	1	0.995	−9.42	9.21	1.44
O	2s	2	2.190	−32.00	16.78	0.79
	2p	1	1.220	−15.30	14.67	0.90

[a] The effective principal quantum number in a single Slater-type orbital (STO) representation, $r^{n-1}\exp(-Zr)$. [b] As defined in the above STO. [c] Valence orbital ionization energy (VOIE) of a doubly occupied atomic orbital of a neutral free atom. [d] Change in VOIE with unit change in the net charge on the atom on which it is located. [e] $1/\mathrm{RI} \equiv \langle 1/r \rangle$.

Table III. Molecular Orbital Characteristics

MO	% O[a]	Occupation	Energy, eV
		RuO_4	
$4t_2$	22	0	−7.16
$2e$	48	0	−10.16
$1t_1$	100	6	−14.11
$3t_2$	99	6	−15.86
$2a_1$	99	2	−17.18
$2t_2$	64	6	−18.17
$1e$	41	4	−20.69
$1a_1$	99	2	−31.59
$1t_2$	95	6	−31.77
		OsO_4	
$4t_2$	23	0	−8.12
$2e$	48	0	−10.81
$1t_1$	100	6	−14.09
$3t_2$	99	6	−15.94
$2a_1$	99	2	−17.36
$2t_2$	65	6	−17.86
$1e$	44	4	−19.72
$1t_2$	79	6	−31.44
$1a_1$	100	2	−31.48

[a] The percentage of electron density on the oxygen centers for an electron in the orbital in question.

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(3) J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, **94**, 3040 (1972).

ionizations covering an energy range of ~5.5 eV, that one of these ($1t_1$) should involve removal of an electron of complete oxygen 2p character, and that two of them ($2t_2$ and 1e) should be heavily MO bonding and of approximately equal metal and oxygen parentage.

Discussion

Given the assertion that band area should be roughly proportional to orbital degeneracy,[4] it follows that we must assign the two lowest energy ionizations to removal of t electrons. By the same token, band D must be associated with removal of an a_1 electron. Bands C and E, to the extent that we vest any trust in the computational results of Table III, must then be assigned, by default argument, to ionization of t or e electrons.

The correlation of relative band areas with orbital degeneracies can be used faithfully only when the AO composition of the MO's are similar. Thus, for all MO's composed of *only* oxygen 2p AO's, the cross sections will stand in the ratios of their degeneracies, while for those MO's having large metal contributions, no such relationship is expected. Hence, the use of relative band areas, as above, is a dangerous procedure.

In terms of the MO calculations, we note the prediction of five low-energy ionizations and the concordance of this prediction with experiment with regard to number (*i.e.*, five), to energy spread (*i.e.*, approximately 6 eV predicted *vs.* 4 eV observed), and to absolute energy (*i.e.*, lowest energy computed ionization approximately equal to 14 eV *vs.* 12 eV observed). We also note the dominance of the photoelectron spectrum by ionizations which are not overly perturbative of the ground state geometry and the concordance of this result with prediction (see Table III, where three of the MO's are seen to have very small amplitude on the metal, M).

We now discuss the individual band systems.

Band A. The ionic state is either $^2T_2$ or $^2T_1$. The vibronic details of this band, for OsO_4, are shown in Figure 2 and analyzed in Table IV. The details of the corresponding RuO_4 band appear to be identical. The analysis given is not unique. Nonetheless, a number of conclusions are clearcut. First, the spectrum contains reasonably long progressions in a frequency interval of 806 cm^{-1}, which we take to be the $\nu_1(a_1)$ stretching mode which occurs[5] at 965.2 cm^{-1} in the ground state, $^1A_1$, of OsO_4. Second, the spectrum contains considerable vibrational activity of a nontotally symmetric nature. This nontotally symmetric vibration has a frequency of 280 cm^{-1} in the ionic state and probably corresponds to the 333.1 cm^{-1} e vibration of the molecular ground state.[5] Third, the e progression based on the 12.32-eV origin exhibits a splitting of the individual progression members. The first member (*i.e.*, 0,1 peak) appears to consist of two subbands, the second consists of a least two, and the third member contains at least three subbands. Fourth, a second origin for an a_1 progression is required at 12.44_8 eV. It is not possible that the $12.44_8 - 12.32_0 = 0.12_8$ eV = 1024 cm^{-1} interval represents one quantum of a $\nu_3(t_2)$ vibration since this mode has a 960.1 cm^{-1} frequency in the ground state and would be expected to decrease in the ionic state.

Table IV. Analysis of Band A of OsO_4

Energy, eV	Assignment ν_1, ν_2	Assignment ν_1', ν_2'
12.32_0	0,0	
12.35_6	0,1	
12.39_2	0,2	
12.41_6	0,3	
12.42_2	1,0	
12.44_8		0′,0′
12.45_8	1,1	
12.49_4	1,2	
12.53_2	2,0	
12.54_8		1′,0′
12.56_8	2,1	
12.60_8	2,2	
12.62_8	3,0	
12.64_4		2′,0′
12.70_4	??	??
12.73	4,0	
Av ν_1 = 806 cm^{-1}		
Av ν_2 = 280 cm^{-1}		
Av ν_1' = 806 cm^{-1}		

The presence of an e progression indicates that the ionic state is not tetrahedral. The substructure of individual members of the e progression is in accord with Jahn–Teller considerations for a distorted (and split) ^2T state. Thus, $T \times e = T_1 + T_2$, $T \times e \times e = T_1 + 2T_2$, $T \times e \times e \times e = 2T_1 + 2T_2$ and one would expect a doublet for the first e member, a triplet for the second e member, etc. The observed substructure corresponds to a Jahn–Teller splitting of the e vibration of ~50 cm^{-1}. The 12.44_8 eV origin is now taken to be the second component of the split ^2T state, the third component being obscured by the dense vibrational structure.

The Jahn–Teller splitting in the A band of OsO_4^+ appears to be identical with that of the $^2T_2$ state[6] of CH_4^+, with the following exceptions.

(i) The splitting in OsO_4^+ is an order of magnitude less than that in CH_4^+. This fact is associable with the heavily bonding nature of the t_2 MO of CH_4, the almost nonbonding nature of $1t_1$ and $3t_2$ MO's of OsO_4, and the larger vibrational frequencies of CH_4.

(ii) The origin band is missing in the CH_4^+ spectrum.[6] This fact is attributable to the 44% reduction of the $\nu_1(a_1)$ frequency which occurs in the $^2T_2$ state of CH_4^+ and the unfavorable Franck–Condon factors which such a large frequency decrement necessitates. The frequency decrement in OsO_4, on the other hand, is only 14% and favorable Franck–Condon factors obtain; hence, the intense origin band.

(iii) The t_2 MO of CH_4 is C–H σ bonding, whereas $3t_2$ of OsO_4 or RuO_4 is of oxygen $2p_\pi$ nature. A better comparison might be found in CF_4 in which the upper MO is of fluorine $2p_\pi$ nature; unfortunately, this MO is of t_1 symmetry, it is C–F nonbonding, and, additionally, the $CF_4(^1A_1) \rightarrow CF_4^+(^2T_1)$ ionization exhibits no vibronic structure.

In view of the similarities to CH_4^+ and the arguments adduced above, we tentatively assign the A band to the

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(4) C. R. Brundle and M. B. Robin, "Determination of Organic Structures by Physical Methods," Vol. 3, Academic Press, New York, N. Y., 1971.

(5) (a) For OsO_4, the ground-state frequencies are $\nu_1(a_1)$ = 965.2 cm^{-1}, $\nu_2(e)$ = 333.1 cm^{-1}, $\nu_3(t_2)$ = 960.1 cm^{-1}, $\nu_4(t_2)$ = 322.7 cm^{-1}: R. McDowell and M. Goldblatt, *Inorg. Chem.*, **10**, 625 (1971). (b) For RuO_4, the ground-state frequencies are $\nu_1(a_1)$ = 885.3 cm^{-1}, $\nu_2(e)$ = 319 cm^{-1}, $\nu_3(t_2)$ = 921.0 cm^{-1}, $\nu_4(t_2)$ = 336.0 cm^{-1}: R. S. McDowell, L. B. Asprey, and L. C. Hoskins, *J. Chem. Phys.*, **56**, 5712 (1972).

(6) J. W. Rabalais, T. Bergmark, L. O. Werme, L. Karlsson, and K. Siegbahn, *Phys. Scr.*, 3, 13 (1971).

$^2T_2$ ionic state. The 12.320-eV origin probably corresponds to a $^2B_2$ or $^2A_1$ state produced by distortion to D_{2d} or C_{3v} symmetries, respectively. The 12.448-eV origin then corresponds to some one of the split E components of either D_{2d} or C_{3v} produced by further distortion to lower symmetry.

In sum, the $^2T_2$ assignment is preferred because the $3t_2$ MO has a capacity for M–O bonding which the $1t_1$ MO does not and because of analogy to the case of CH_4.

Band B. The relative intensity of this band suggests that it is also a ^2T ionic state. Three vibrational peaks are observed in OsO_4 at 13.138, 13.238, and 13.342 eV. The average separation is 820 cm^{-1}, indicating that $\nu_1(a_1)$ has a somewhat larger frequency than it does in the $^2T_2$ ionic state. In view of the fact that the band envelope indicates only a negligible change in the M–O bond distance and that no discernible vibrational activity other than $\nu_1(a_1)$ is detectable, it seems reasonable to associate this ionization with removal of a nonbonding electron. The only such triply degenerate filled orbital is $1t_1$ and, hence, we assign the ionic state as $^2T_1$.

Bands C and D. Based on the relative intensities of the observed bands, as shown in Table I, it appears clear that bands C and D interchange relative energies in going from OsO_4 to RuO_4. Such an interchange is indicated in Figure 1 and Table I. Vibrational analyses are given in Table V.

Table V. Analysis of Bands C and D of OsO_4

Energy, eV	Assignment ν_1
Band C	
13.502	0
13.602	1
13.734	2
13.866	?[a]
Av ν_1 = 840 cm^{-1}	
Band D	
14.543	0
14.643	1
Av ν_1 = 810 cm^{-1}	

[a] The 13.866 − 13.734 eV = 1070 cm^{-1} separation is too large to be associable with any vibrational mode of OsO_4. It may refer to impurity; however, our purification studies indicate otherwise.

Band D is the least intense band observed in either spectrum. Based on degeneracy arguments, the corresponding ionic state must be assigned, therefore, as $^2A_1$. In agreement with this, we note that the a_1 MO is almost wholly of ligand nature (~99% oxygen in Table III). Thus, the direction of shift of bands A, B, and D should be the same and of comparable magnitude in proceeding from OsO_4 to RuO_4, as is the case experimentally. In addition, one would expect the origin band to be intense, the vibrational frequency decrement to be small, and no vibronic activity other than $\nu_1(a_1)$, all of which are observed.

Band C is of small or moderate intensity, it shifts to higher energies on going from OsO_4 to RuO_4, and it may not exhibit vibronic characteristics typical of Jahn–Teller effects (see footnote to Table V). The VOIE data of Table II for the neutral metal predict a shift of 0.24 eV to higher energies in RuO_4; the observed shift is 0.38 eV. Molecular orbital calculations pertinent to a charge self-consistent configuration (see Table III) indicate a shift which is much too large (*i.e.*, 0.97 eV) for 1e and of the correct magnitude (*i.e.*, 0.31 eV) for $2t_2$, and which is in the right direction in both instances. It is rather difficult, therefore, to assign band C, that is, to choose between $2t_2$ and 1e MO ionizations. The ^2E assignment for the ionic state (*vide infra*) is the choice here.

Band E. This band is broad and structureless and is consistent with ionization of a bonding electron. The intensity also suggests that the degeneracy of the initial MO is greater than unity. The direction and magnitude of shift in going from OsO_4 to RuO_4 is reminiscent of bands A and B and, for that resaon, we assign this ionic state as $^2T_2$. The reasons for this assignment are weak and are inherent in the computational prediction that the $2t_2$ electron should be strongly bonding and yet have a large (~65%) 2p oxygen character.

Reservations

The assignments made here are based on a number of crucial assumptions. These are: (i) that the ionization cross sections for metal 5s,4d and 6s,5d electrons are not very different from those for 2s,2p oxygen electrons; (ii) that the O–O bonding in the $1t_1$ MO is too weak to induce a detectable Jahn–Teller splitting of a $^2T_1$ ionic state; and (iii) that the qualitative correctness of the MO computational results. To the extent that any of these assumptions are wrong, so also will the assignments we have made.

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