The polarized Raman band at 348 cm^{-1} may be assigned to the Cd–OH$_2$ stretch and is therefore characteristic of the solvated cadmium ion (Table I), as assigned previously.[19] The occurrence of a polarized Raman band at 1324 cm^{-1} suggests that the nitrate is coordinated in a monodentate manner.[20] This would suggest the formulation of a CdONO$_2^+$ species in which the normal D_{3h} symmetry of the nitrate ion is lowered to C_{2v}. The reduced representation for a nitrate ion of this symmetry is $3A_1$ (infrared, Raman) + $2B_1$ (infrared, Raman) + B_2 (infrared, Raman).[15] The observed spectra fit this assignment well (Table II). The absence of a Cd–O stretch in the Raman spectra may be interpreted in terms of a predominantly ionic Cd–O bond.

---

[19] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 768 (1964).

[20] H. Brintzinger and R. E. Hester, *ibid.*, **5**, 980 (1966).

Contribution from the Department of Chemistry and the Materials Research Center,
Northwestern University, Evanston, Illinois 60201

Synthesis and Structure of Four- and Five-Coordinated Gaseous Oxohalides of Molybdenum(VI) and Tungsten(VI)[1]

By Brian G. Ward and Fred E. Stafford

Received May 27, 1968

A method for generating molybdenum and tungsten oxohalides is described. New gas-phase infrared spectral data (400–4000 cm^{-1}, in emission and/or absorption) are given for the dioxodihalides and oxotetrahalides MoO_2F_2, MoO_2Cl_2, MoO_2Br_2, MoO_2I_2, WO_2Cl_2, WO_2Br_2, WO_2I_2, $MoOF_4$, $MoOBr_4$, WOF_4, $WOBr_4$, and WOI_4 and for $(MoO_3)_n$ vapor. The spectra of the dioxodihalides are compatible with the existence of monomeric species in the gas phase. Correlations are made among (1) the M–O double-bond stretching frequencies in the oxohalides and gaseous monoxides, dioxides, and trioxides, (2) the M–F and M–O–M stretching mode frequencies, and (3) the gas-phase and condensed-phase M–O frequencies.

Introduction

Structural information for the monomeric four- or five-coordinated oxohalides of chromium, molybdenum, and tungsten decreases in availability for the heavier metals. Chromium has been studied in detail in the normal highest oxidation state (VI) and structural parameters have been established for the known dioxodihalides CrO_2F_2 and CrO_2Cl_2[2–5] but not for the oxotetrafluoride. Molybdenum has been studied as the dioxodichloride[6–8] and more recently as the dioxodibromide, oxotetrachloride, and the gaseous polymeric trioxide,[9–11] the results being related to those for the corresponding chromium compounds. Tungsten compounds are poorly documented, tentative information for the dioxodichloride[10] being the only entry. The lack of structural information restricts reliable interpretation of kinetic and thermodynamic data for compounds of these important refractory metals. The main problem associated with such studies is the physical state of the compounds under investigation. For the molybdenum and tungsten oxohalides, the solid and liquid phases contain polymer species[10] with octahedrally coordinated metal atoms; the vapor phase, where observed,[10,11] contains predominantly monomeric species with features in common with the chromium analogs.[2–5]

The present paper describes a method of generating, observing, and identifying the vaporized oxohalides using an infrared spectrometer to record vibrational frequencies, both in emission and absorption, and offers a generally applicable synthetic method for similar studies. Results are given for the oxohalide species of molybdenum and tungsten.

Experimental Section

The molybdenum- and tungsten(VI) oxohalides were generated using a fused mixture of an alkali metal halide with the metal trioxide, as previously suggested[12,13] for the synthesis of WOF_4 and MoO_2Cl_2. The oxofluorides were prepared in a stainless steel cell 1 m in length, fitted with end windows. The fused reaction mixture was contained in a nickel boat placed in the hot central zone of the cell. The apparatus for the remaining oxohalides consisted of a 1 m long mullite ($2Al_2O_3 \cdot SiO_2$) cell with glass ends onto which the appropriate windows were sealed. The reaction mixture was located in the center of the cell in a quartz boat. The central 50 cm of the cells was heated using a Kanthal (Stamford, Conn.) wound mullite tube furnace. Steady

---

[1] Supported by the U. S. Advanced Research Projects Agency through the Materials Research Center. The infrared spectrometer was acquired in part through a National Science Foundation Institutional Facilities Grant.

[2] J. K. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

[3] W. E. Hobbs, *J. Chem. Phys.*, **28**, 1220 (1958).

[4] H. Stammreich, K. Kawai, and Y. Tavares, *Spectrochim. Acta*, **15**, 438 (1959).

[5] F. A. Miller, G. L. Carlson, and W. B. White, *ibid.*, **15**, 709 (1959).

[6] H. A. Skinner, Thesis, Oxford University, 1941, unpublished; cited in "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[7] H. G. J. Dehmelt, *J. Chem. Phys.*, **21**, 380 (1953).

[8] E. M. Shustorovich and L. O. Atovnyan, *Zh. Strukt. Khim.*, **4**, 273 (1963).

[9] G. A. Kokovin and N. K. Toropova, *Zh. Neorgan. Khim.*, **10**, 560 (1965).

[10] C. G. Barraclough and J. Stals, *Australian J. Chem.*, **19**, 741 (1966).

[11] T. V. Iorns and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 4819 (1966).

[12] O. Scmitz-Dumont, I. Bruns, and I. Heckmann, *Z. Anorg. Allgem. Chem.*, **271**, 347 (1953).

[13] A. N. Zelikman and N. N. Gorovits, *Zh. Obshch. Khim.*, **24**, 1916 (1954).

temperatures (±1°) were achieved in the hot zone through the use of a Thermac proportional temperature controller (R.I. Inc., Minneapolis, Minn.), the control thermocouple being situated at the center of the furnace between the cell and the furnace lining.

Before running an experiment, the lithium halide–metal trioxide mixtures were heated in the cell for 12 hr in air at the highest temperature possible before sublimation or decomposition occurred (usually 250–300°). The cell was evacuated and the mixture was heated for a further period to remove all traces of water, carbon dioxide, and other volatile impurities. It was then filled with a buffer gas (such as argon or oxygen) at 1 atm to act as a diffusion barrier, an aid in the synthesis, or both. During the experiment, traces of impurities were removed by evacuating the cell and refilling with the buffer gas.

The infrared spectra were recorded over the range 400–4000 cm^{-1} using a Beckman IR-9 spectrometer suitably modified[14] to allow an external light source to be focused through the cell and onto the spectrometer entrance slit. The optical path has been modified further to allow the high-temperature cell assembly to be located above the spectrometer source compartment. The instrument was run in the single-beam mode throughout. The external chopper and source were used to observe absorption spectra, and the internal chopper with no light source except the hot sample and cell was used to observe emission spectra. Potassium bromide windows were normally used, but silver chloride and polyethylene windows were used when attempting to resolve metal–halogen absorption bands. The 400–500-cm^{-1} region is a relatively insensitive range for this apparatus. This was partially overcome by monitoring and recording emission spectra. It was thus possible to observe metal–chlorine stretching frequencies as full-scale emission bands against a low background, with improved resolution.

Molecules normally volatile at temperatures as low as room temperature were synthesized at temperatures in excess of 300°. The vapor migrated to the cooler zones of the cell and resulted in the self-absorption of emission bands. This was eliminated for all but the oxofluorides by causing a slow flow of buffer gas along the cell toward the light-source end. The temperature-gradient zone at the ends of the cells resulted in fractional sublimation of the volatile species and aided in the identification of the band carriers.

Only those bands showing the proper temperature dependence during repeated cycling were assigned to high-temperature species.[11] Where vapor pressures were known or could be estimated, the temperature at which bands were first observed agreed within experimental error with those predicted from the vapor pressure curves.

Impurity bands due to condensed species on the windows and as a result of window attack (observed in the fluoride experiments) were characterized by their presence at ambient temperature after evacuation of the cell.

The only volatile decomposition products were the hydrogen halides, produced by reaction of the oxohalides with traces of water vapor in the cell.

Data and Results

The observed bands (Tables I–III) were often superimposable on those for the compounds which had been reported previously.[10,11] Representative spectra in absorption and emission are presented for MO_2X_2 vapor species (Figure 1a and b) and a spectrum in absorption is shown for the MOX_4 vapor species (Figure 1c).

Molybdenum Oxofluorides.—The only absorption band observed with argon in the cell, at >300°, was a sharp, intense band at 1030 cm^{-1} (Figure 1c) for which the band shape was identical with that due to the Mo=O stretching frequency of $MoOCl_4$(g).[11] This

TABLE I

COMPARISON OF THE M=O VIBRATIONAL FREQUENCIES (CM^{-1}) OF GASEOUS MO_2X_2 AND MO_2 SPECIES OF THE GROUP VIa METALS[a–c]

M	MO_2F_2	MO_2Cl_2	MO_2Br_2	MO_2I_2	MO_2
Cr	1016[d] as	994[e] as			
	1006 s	984 s			
Mo	1009[f]	994[f–h] s	991[f–h] s	(972)[i]	969[f,g,j]
	987	972 as	969 as	(950)	
W		992[f,h] s	985[f]	(980)[i]	982[k]
		978 as	973	(960)	928

[a] s, symmetric; as, antisymmetric. [b] The values quoted above are the averages of results from the sources indicated. In no case does the range of reported values exceed 8 cm^{-1}. [c] Emission values were obtained for all of the molybdenum and tungsten dioxodihalides and molybdenum trioxide and agree within 2 cm^{-1} of the absorption values at the maxima. [d] Hobbs.[3] [e] Stammreich, *et al.*[4] [f] Present work. [g] Iorns, *et al.*[11] [h] For MoO_2Cl_2 and MoO_2Br_2, Barraclough, *et al.*,[10] report the M–X stretching frequencies within ±2 cm^{-1} of the values listed and within ±7 cm^{-1} for WO_2Br_2. [i] Only tentative data are available for these molecules; see text. [j] Stretching frequency observed for $(O–MoO_2–)_n$ vapor species. [k] Weltner, *et al.*;[19] these frequencies are for WO_2 molecules isolated in rare gas matrices.

TABLE II

CORRELATION OF THE M=O VIBRATIONAL FREQUENCIES (CM^{-1}) OF GASEOUS MOX_4 AND MO SPECIES OF THE GROUP VIa METALS[a,b]

M	MOF_4	$MOCl_4$	$MOBr_4$	MOI_4	MO
Mo	1030	1015[c]	998		
W	1030	1032	1015 sh	(1032)[d]	1056[e]
			1004		

[a] sh, shoulder. [b] Emission values were obtained for all of the oxotetrahalides listed and agree within 2 cm^{-1} of the absorption values at the maxima. [c] Iorns, *et al.*[11] [d] Only tentative data are available for this molecule; see text. [e] For the diatomic species in inert gas matrices two bands each were observed in neon (1047 and 1064 cm^{-1}) and argon (1050 and 1062 cm^{-1}) matrices. Matrix shifts are possible; see Weltner, *et al.*[19]

TABLE III

COMPARISON OF THE METAL–HALOGEN VIBRATIONAL FREQUENCIES (CM^{-1}) OF GASEOUS MO_2X_2 AND MOX_4 SPECIES OF THE GROUP VIa METALS[a,b]

Species	M–F	M–Cl
CrO_2X_2	789[c] as	499[d] as
	727 s	475 s
MoO_2X_2	710	453[e,f] as
	692	437 s
WO_2X_2		437
		430
$MoOX_4$	553	<400
	539	
	527	
	516	
WOX_4	554	<400
	539	
	533	
	523	
	516	

[a] s, symmetric; as, antisymmetric. [b] The M–Br vibrational frequencies lie below the range of the instrument (<400 cm^{-1}). [c] Hobbs.[3] [d] Stammreich, *et al.*[4] [e] Iorns, *et al.*,[11] and the present work. [f] Barraclough, *et al.*[10]

---

[14] S. M. Chackalackal and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 723 (1966).

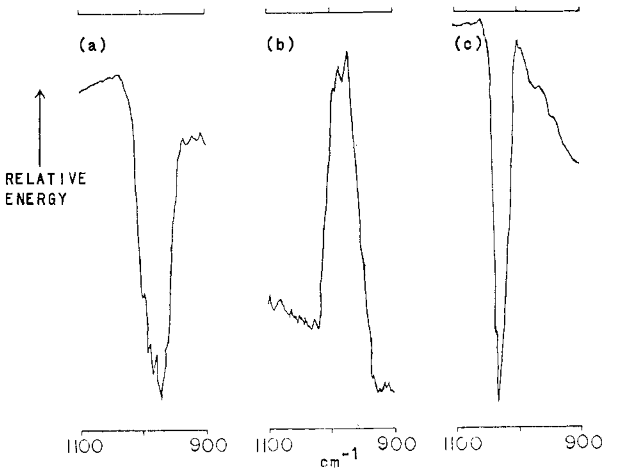

Figure 1.—Representative infrared band profiles, relative energy *vs.* wave number: (a) absorption spectrum of MoO_2Cl_2 vapor; (b) emission spectrum of MoO_2Cl_2 vapor; (c) absorption spectrum of $MoOF_4$ vapor.

band was observed also as an absorption band in the emission spectrum; in addition, weaker bands were observed at 553, 539, 527, and 516 cm^{-1} in emission and could be traced as weak bands in absorption. These bands are assigned to $MoOF_4(g)$ species. The bands in the region 516–533 cm^{-1} are at low frequency compared with the Mo–F stretching frequency observed for MoF_6.[15,16]

With oxygen in the cell the same bands were observed, but in addition a new series of bands appeared above 500° at 987 and 1009 cm^{-1} in the Mo=O stretching region and at 692 and 710 cm^{-1}. The frequency of the Mo=O vibrations correspond closely with those attributed to symmetric and antisymmetric modes of CrO_2F_2,[3] MoO_2Cl_2, and MoO_2Br_2[10,11] both in frequency and splitting. The bands at 692 and 710 cm^{-1} correlate with the independently observed Mo—F stretching frequencies of MoF_6 at 742 (ir),[15] 736 (Raman), and 641 cm^{-1} (Raman).[16] Formation of MoO_2F_2 in an oxygen atmosphere above 500° explains the observed results.

Molybdenum Oxochlorides.—This experiment was carried out to test the fused-salt synthetic method and to obtain emission spectra for comparison with the absorption spectra reported for $MoO_2Cl_2(g)$ and $MoOCl_4(g)$.[10,11] Only those bands previously observed for MoO_2Cl_2 were noted during the experiment.

Molybdenum Oxobromides.—Bands which appeared at 250° correspond closely with those of $MoO_2Br_2(g)$ reported by other workers;[10,11] the color of the sublimate in the cold zone was identical with that of MoO_2Br_2 prepared by other methods. Appearance of a higher temperature band at 998 cm^{-1} coincided with the formation of a dark brown sublimate. When the brown sublimate was isolated and reexamined, the 998-cm^{-1} band was stronger in the vapor over this material confirming that it was not due to $MoO_2Br_2(g)$. Its envelope is sensibly identical with those of $MoOCl_4$ and $MoOF_4$ and is assigned to the oxotetrabromide.

Molybdenum Oxoiodides.—The frequencies of weak transitory bands (900–1000 cm^{-1}) observed between 400 and 900° and the appearance of a sublimate (which proved to be moisture sensitive leaving a yellow film on hydrolysis) suggest the formation of molybdenum oxoiodide species. Recent work by Tillack, Eckerlin, and Dettingmeijer[17] has shown that analytically pure WO_2I_2 may be both prepared and sublimed by heating a mixture of tungsten metal, tungsten trioxide, and iodine, in a sealed quartz tube. These conditions are similar to those used in our experiment.

The absorption and emission spectra of $(MoO_3)_n$ were observed for the vapor over this reaction mixture at temperatures above 900°.

Tungsten Oxofluorides.—The position and shape of the observed absorption band is almost completely superimposable on the $MoOF_4$ spectrum (in the absence of MoO_2F_2) and is a good indication for the presence of WOF_4 vapor-phase species. The metal–fluorine stretching frequencies are much lower than those observed in the hexafluoride WF_6,[15,16] for which bands occur at 769, 712, 670, and 322 cm^{-1}. No evidence was obtained for WO_2F_2.

Tungsten Oxochlorides.—Unambiguous spectra of $WO_2Cl_2(g)$ and $WOCl_4(g)$ were observed in the mullite cell using pure samples prepared by the reaction

$$WO_2 + Cl_2 \xrightarrow{\text{heat}} WO_2Cl_2 + WOCl_4$$

The products were purified by fractional sublimation.

$WO_2Cl_2(g)$ was observed at temperatures between 110 and 140° displaying well-defined bands at 992 and 978 cm^{-1} and a poorly defined band at 435 cm^{-1} in absorption. These frequencies are identical with those obtained in the fused-salt experiment but differ slightly from the results of previous workers.[10]

$WOCl_4$ was observed above 70° giving a single, well-defined, sharp band at 1032 cm^{-1}. During the fused-salt experiment, however, the presence of $WOCl_4$ was neither observed by spectroscopic methods nor as a sublimate.

Tungsten Oxobromides.—The first appearance of bands occurred at 400°; bands were observed at 969 and 991 cm^{-1} in absorption and emission, coincident with the formation of an orange-brown sublimate in the cold zone. Above 500°, a new band appeared at 998 cm^{-1}, which varied in intensity independently of the original lower temperature bands. As the 998-cm^{-1} band appeared, a pale brown sublimate began to collect in the cold zone of the cell. Usable amounts of the two sublimates were not readily obtained owing to overlap of the sublimation zones. These observations are readily explained by the formation of $WO_2Br_2(g)$ at 400° and formation of $WOBr_4(g)$ at 500°, analogous to the results of the molybdenum oxobromide synthesis.

Tungsten Oxoiodides.—The spectra were not suffi-

---

[15] J. Gaunt, *Trans. Faraday Soc.*, **49**, 1122 (1953).

[16] K. N. Duncan and A. B. F. Tanner, *J. Am. Chem. Soc.*, **73**, 1164 (1951).

[17] J. Tillack, P. Eckerlin, and J. H. Dettingmeijer, *Angew. Chem.*, **5**, 421 (1966).

ciently detailed for any firm conclusion to be drawn regarding the identity of the vapor-phase species, but the position of the band center, the formation of sublimate, and the absence of bands over the trioxide in the absence of lithium iodide suggest the formation of a volatile oxoiodide of tungsten. Evidence for formation of WO_2I_2 has been given previously.[17]

The reaction mixtures, conditions, and observed gaseous products are listed below. With the exception of reaction 2 which occurred only in an oxygen atmosphere, the observed products were independent of the atmosphere used (oxygen or argon). The mole ratio of intimately mixed LiX–MO_3 was always greater than 5:1 with an added covering layer of lithium halide.

$$MoO_3 + LiF \xrightarrow{>300°} MoOF_4 \quad (1)$$

$$MoO_3 + LiF \xrightarrow{O_2\ atm} MoOF_4\ (>300°) + MoO_2F_2\ (>500°) \quad (2)$$

$$MoO_3 + LiCl \xrightarrow{>350°} MoO_2Cl_2 \quad (3)$$

$$MoO_3 + LiBr \longrightarrow MoOBr_4\ (>200°) + MoO_2Br_2\ (>300°) \quad (4)$$

$$MoO_3 + LiI \longrightarrow MoO_2I_2\ (>400°) + (MoO_3)_n\ (>900°) \quad (5)$$

$$WO_3 + LiF \xrightarrow{>500°} WOF_4 \quad (6)$$

$$WO_3 + LiCl \xrightarrow{>500°} WO_2Cl_2 \quad (7)$$

$$WO_3 + LiBr \longrightarrow WO_2Br_2\ (>400°) + WOBr_4\ (>500°) \quad (8)$$

$$WO_3 + LiI \longrightarrow WOI_4 \text{ or } WO_2I_2 \quad (9)$$

Discussion

The fused-salt synthesis provides a source of molybdenum(VI) and tungsten(VI) oxohalides in the vapor and condensed phases without the use of the halogen gases. Synthesis of most of the known, as well as hitherto unknown, oxohalides was accomplished, and their infrared spectra were observed, in some cases for the first time for any physical state of the compound. The ease with which the formation of the oxofluorides and oxochlorides may be controlled suggests this method for the generation of pure vapor-phase species for structural analysis by electron diffraction, microwave, and/or far-infrared techniques.

The high-temperature nature of the synthesis permitted accurate recording of the emission spectra. Emission bands showed clearer detail than the normal absorption bands for which the background and/or a sloping base line obscures significant details of the spectra. They provide evidence also that the band progenitors are high-temperature species in the hot zone of the cell.

Dioxodihalide Species.—In the 950–1020-cm^{-1} region, absorption bands are observed for the group VI transition metal MO_2X_2 species (Table I). These correspond in frequency with the established symmetric and antisymmetric metal–oxygen stretching modes of chromium dioxodichloride.[2–5] In general, the splitting between the two bands for a given compound is small (<25 cm^{-1}) although the bands due to the symmetric and antisymmetric stretching modes are inverted in frequency in going from chromium to molybdenum.[10,11] For all of the molecules, the shapes of the band envelopes are similar, as typified by Figure 1a and b. For the dioxodichlorides and dioxodibromides, the means of the symmetric and antisymmetric mode frequencies are sensibly constant. The frequencies of the MO_2 group in the fluorides are slightly higher.

The last column of Table I shows data for the binary gaseous oxides MO_2 and $(MO_3)_n$. Spoliti, *et al.*,[18] have shown that the stretching and bending frequencies of gaseous SO_2 can be correlated with the frequencies for the sulfuryl halides. Only one observation is available for these transition element species, namely, the frequencies for WO_2 in a neon matrix[19] (Table I). These frequencies are seen to correspond closely to those of the dioxodihalides, the possibility of matrix shifts notwithstanding. The only observation available for a trioxide vapor is for $(MoO_3)_n$,[11] which is believed to be cyclic, with MoO_2 groups linked through oxygen bridges. The observed frequency of the $(MoO_3)_n$ terminal metal–oxygen stretching mode does lie among those of the dioxodihalides. This is expected since a halogen and oxygen, each singly bonded to the metal, are similar in electron-withdrawing power. In emission, molybdenum and tungsten dioxodichloride vapors displayed two distinct bands in the region 400–500 cm^{-1} (Table III). The separation of these bands for WO_2Cl_2 is only 7 cm^{-1}, corresponding closely to the expected shift between ^{35}Cl and ^{37}Cl isotopic species. The relative intensities of the bands, however, were incompatible with those expected of normal isotopic abundance. Accordingly, we assign them to the symmetric and antisymmetric metal–chlorine stretching modes.

The symmetric and antisymmetric metal–fluorine stretching modes of CrO_2F_2 and MoO_2F_2 have mean frequencies of 758 and 701 cm^{-1}, with splitting of 62 and 18 cm^{-1}, respectively. For the three dioxodichlorides, the general pattern is similar with decreases in the mean stretching frequencies and in the splitting, with increasing atomic weight of the metal atom. By analogy with the S–OH and the S–F frequencies, Iorns and Stafford[11] predicted that the Mo–O–Mo stretching mode frequencies in the gaseous trioxide should be centered roughly 10% higher than those of the MoF_2 group. The presently observed average frequency for the fluoride is at 701 cm^{-1}, which leads to a prediction of 770 cm^{-1} for the M–O–M, compared to 815 cm^{-1} observed. Either the prediction is in error or another M–O–M stretching mode, probably with low infrared transition probability, lies at about 725 cm^{-1}.

Structural arguments for the dioxodihalides are based, by analogy, on the tetrahedrally coordinated structures deduced from electron diffraction[2] and vibrational spectra[3–5] data for chromium dioxodihalides and from unpublished electron diffraction data[6] for molybdenum dioxodichloride. From mass spectrometric data and from the location of the metal

---

[18] M. Spoliti, S. M. Chackalackal, and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1092 (1967).

[19] W. Weltner, Jr., and D. M. McLeod, Jr., *J. Mol. Spectry.*, **17**, 276 (1965).

oxygen frequencies, Barraclough and Stals[10] deduced that MoO_2Cl_2, MoO_2Br_2, and WO_2Cl_2 are predominantly monomeric. Using infrared and Raman data, other workers concluded that the vapor-phase species CrO_2F_2,[3] MoO_2Cl_2,[10,11] MoO_2Br_2,[10,11] WO_2Cl_2,[10] and $(MoO_3)_n$[11] possess distorted tetrahedral geometry around the metal atom by reason of the similarity of their spectra to that of CrO_2Cl_2. Because of the similarity of all of these spectra to one another, we propose further that the newly observed monomeric vapor-phase species MoO_2F_2 and WO_2Br_2 also possess this distorted tetrahedral geometry.

Oxotetrahalide Species.—Previous infrared studies of the group VIa oxotetrahalides have been confined to molybdenum oxotetrachloride. A single, relatively sharp band due to the metal–oxygen stretching mode was observed for both the vapor produced by direct synthesis[11] (1015 cm^{-1}) and the solid film[20] (1010 cm^{-1}). No metal–halogen stretching modes were reported. All of these compounds which we observed showed a single, well-defined band (Figure 1c) in the 995–1035-cm^{-1} region (Table II) in both absorption and emission. This is assigned to the metal–oxygen stretching mode.

The frequencies for the phosphorus and vanadium oxotrihalides have been shown to correlate well with those of the corresponding diatomic gaseous oxides.[21] Only matrix-isolation data for WO are available for comparison with the presently observed species (Table II). The possibility of matrix-induced shifts in frequency notwithstanding, the correlation again is seen to be good. For certain purposes it may thus be useful to consider the gaseous monoxides and dioxides, respectively, as parents of the corresponding transition metal oxohalide series.

The metal–halogen stretching bands of the fluoro and chloro compounds were singularly difficult to detect. In the emission spectra, bands were observed in the region 510–560 cm^{-1} (Table III) for the fluoro compounds. These bands are complex and occur at frequencies which are notably low compared to those of the dioxodifluoride and the hexafluoride; the chloro compounds did not display metal–chlorine bands above 400 cm^{-1}.

The high frequency of the metal–oxygen vibration band for all of the oxotetrahalides (*ca.* 1030 cm^{-1}) immediately suggests the absence of polymer species with bonding through a metal–oxygen bridge system. The low frequency of the metal–fluorine stretching band suggests metal–fluorine bridging, but one would also expect to see some higher frequency metal–fluorine bands due to terminal fluorine groups. Further work is required.

Comparison with Condensed-Phase Species.—The physical state of the oxohalides affects the observed metal–oxygen vibration bands markedly. Possible causes are (1) the degree of association or polymerization of the molecules, (2) changes in coordination about the metal atom, and (3) solution or lattice effects. The vapor-phase spectra of the monomeric oxohalides represent the least externally influenced molecules, the spectra of matrix-isolated monoxide and dioxide being subject to matrix effects only. The matrix-isolated tungsten monoxide[19] may be considered to be the only example of an isolated, doubly bonded tungsten–oxygen group. Its stretching frequency of 1056 cm^{-1} is the highest frequency observed for any molecule containing discrete W=O groups. The gaseous dioxodihalides (Table I) and oxotetrahalides (Table II) exhibit infrared absorption bands due to metal–oxygen stretching vibrations at lower frequency, displaying two characteristic frequency ranges for the two classes of compounds. Molybdenum trioxide vapor represents the closest approximation to the least externally influenced metal–oxygen vibration due to the singly bonded M–O group.[11] This is the only vapor-phase specimen so far observed which is predicted to possess Mo–O single bonds, albeit as part of a cyclic structure $(-(MO_2)-O-)_n$. This establishes the bridging Mo–O stretching frequency[11] at a value of approximately 800 cm^{-1} as discussed above. The solution- and solid-phase spectra of the oxohalides and their coordination compounds[10,20,22] show terminal M–O vibrations at lower frequencies (890–970 cm^{-1}) than is observed for the vapor-phase species, but not approaching the M–O single-bond frequency observed for $(MoO_3)_n$. The present results support the conclusions of Barraclough and Stals[10] that metal–oxygen bridging does not contribute to the formation of dioxodihalide dimer in solution or to higher polymer formation in the solid phase.

Despite the differences observed between the solid-, solution-, and vapor-phase spectra of the oxohalides, the metal–oxygen stretching frequencies are all within the region 900–1100 cm^{-1}, the range proposed originally by Barraclough, Lewis, and Nyholm[23] as indicative but not conclusive of the presence of a terminal doubly bonded metal–oxygen group in oxo species of the transition metals.

Gaseous molecules such as those discussed here are shown to be important in the transport of tungsten even at temperatures as high as 1500°K.[24]

---

[20] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **5**, 805 (1966).

[21] S. M. Chackalackal and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 4823 (1966).

[22] B. J. Brisdon, *Inorg. Chem.*, **6**, 1791 (1967).

[23] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[24] D. E. Rosner and H. D. Allendorf, *Am. Inst. Aeronautics Astronautics*, **5**, 1489 (1967).