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THE INFRARED SPECTRA OF THE MoOCl, MoO_2Cl_2, WOCl, WO_2Cl_2, MoO_2, MoO_3 AND Mo_3O_9 GASEOUS MOLECULES

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ABSTRACT

The IR spectra of several gaseous molybdenum and tungsten oxides and oxychlorides which are thought to be transporting agents for these metals in halogen lamps have been obtained. MoO_2Cl_2 and WO_2Cl_2 were observed in absorption and emission by heating the solid compound; Mo_3O_9 was observed in absorption by heating the solid and by observing the products of the reaction between Mo and N_2O; MoO_2 and MoO_3 were observed as products from the reaction between Mo and N_2O; and MoOCl and WOCl were formed from the reaction between the metal and $POCl_3$. All spectra were obtained at a resolution of 0.5 cm^{-1} which permits the band shapes to be resolved and definite spectral assignments to be made.

INTRODUCTION

Molybdenum and tungsten are used extensively to make components of high performance lamps. The transport of these metals as volatile metal oxides, halides, or oxyhalides can lead to failure of the lamp. Thermodynamic calculations for possible reactions which can occur in the lamp indicate that the main species responsible for this transport changes as the conditions in the lamp change [1, 2]. While these calculations favor highly oxidized species like MoO_2Cl_2 or Mo_3O_9 as the principal transport species under all conditions, less stable molecules like MoOCl or WOCl are predicted to make significant contributions in the higher temperature regions.

Experimental spectroscopic data are available for only the more stable possible transport molecules. IR spectra have been reported in the gas phase and in rare gas matrices for MoO_2 [3, 4], MoO_3 [4], Mo_3O_9 [3-6], $MoOCl_4$ [6-8], MoO_2Cl_2 [6, 9-12], WO_2 [14-17], WO_3 [13-16], W_3O_9 [14, 16, 17], WO_2Cl_2 [9-12] and $WOCl_4$ [7, 10]. Raman spectra have been reported for MoO_2Cl_2 [17], $MoOCl_4$ [17], and $WOCl_4$ [17]. All of the reported frequencies are in good agreement for MoO_2Cl_2, $MoOCl_4$ and $WOCl_4$. However, there is disagreement in the frequencies reported for WO_2Cl_2 and Mo_3O_9 which appears to be outside the expected experimental error. For example, the ν_1 frequency of

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WO_2Cl_2 has been reported as being 984 cm^{-1} [9], 992 cm^{-1} [10] and 1014 cm^{-1} [12]. Similarly, the gas phase spectra reported for Mo_3O_9 are in good agreement (970, 815 cm^{-1} [3]; and 966, 815 cm^{-1} [6]) and the matrix isolation values are in good agreement (978, 840 cm^{-1} [4]; and 977, 837 cm^{-1} [5]) but they do not agree well with each other. Too few experiments have been done to assess the reliability of the frequencies reported for the other molecules.

Since further investigation of the molybdenum and tungsten oxides and oxyhalides is needed, the IR spectra of these molecules have been obtained in the gas phase. The spectra observed for the tungsten oxides have been published previously [15]. This paper discusses the IR spectra obtained for some molybdenum oxides, oxychlorides and tungsten oxychlorides. Most spectra have been scanned with sufficient resolution to resolve band shapes. This has permitted spectral assignments to be made and has resolved the uncertainties in the previous data.

EXPERIMENTAL

The stainless steel high temperature IR cell used to obtain the absorbance spectra has been described in detail previously [15, 18–21]. Briefly, the cell was constructed from an MDC 4-way cross stainless steel vacuum flange. KBr windows are attached to the cell with O-ring seals. The connection to the vacuum system is made through one of the remaining ends and the furnace assembly is attached to the fourth connection flange. The furnace assembly was constructed from a 15 cm long section of stainless steel vacuum tubing and a standard MDC electrical flange. A 10 cm piece of 0.5 mm Mo or W wire (Alfa) is wrapped into a coil, wired across the electrical leads, and placed inside the furnace. The walls of the cell are heated radiatively by passing a direct current provided by a Perkin Regulated d.c. power supply through the filament. By carefully wrapping the cell with several layers of aluminum foil, temperatures in excess of 700 K can be reached in the hottest section of the cell.

The spectra of MoO_2Cl_2 and WO_2Cl_2 were obtained by vaporizing the solid dioxydichloride. After outgassing the cell, approximately one gram of the dioxydichloride (Alfa) was sprinkled into the bottom of the furnace assembly and a vacuum of at least 4×10^{-2} Pa was quickly established. The cell was heated enough to sublime the sample by passing current (10–20 A) through a Mo filament for MoO_2Cl_2 or through a W filament for WO_2Cl_2. Since it was possible that solid compound could deposit on the windows, several heating and cooling cycles were used to establish the bands which arose from the vapor phase molecules.

Emission spectra have also been obtained for MoO_2Cl_2 and WO_2Cl_2. The cell used for these experiments was made from a quartz tube. A T seal was made near one end of the tube to make the connection to vacuum. The KBr window was attached to this end past the vacuum connection with O-ring seals.

This part of the cell was not heated. The remaining end of the tube was sealed and heated with an externally wrapped nichrome wire. The temperature in the hot part of the cell could be measured with a chromel/alumel thermocouple. Difference spectra taken with sample and without sample were used to establish the sepctra of the molecules of interest.

The procedure used for the emission investigations was similar to that used for absorption. The cell was outgassed, charged, and quickly evacuated. Temperatures between 600 and 800 K were sufficient to observe the emission spectra of both compounds.

The procedure used to observe the molybdenum oxides was similar to that used previously to observe the tungsten oxides [15]. These experiments were done in the stainless steel IR cell. The furnace assembly was modified so that a reactive gas could enter the cell through a quartz tube and be passed over the filament heater. After the cell was evacuated, the filament was heated. Although the exact temperature of the filament could not be measured, approximate temperatures of the filament were established by monitoring the current and voltage being applied to the filament. Most experiments were between 1500 and 2500 K. After the spectrometer was started, N_2O (Matheson) was metered into the cell through a stainless steel needle valve (ca. 1–5 Pa total pressure). The products from the reaction were monitored as the reagents were pumped through the optical path just downstream from the filament. Since solid product tended to collect on the optical windows, difference spectra taken during and after the reaction were used to identify the bands arising from gaseous products.

If $POCl_3$ were used in place of N_2O, IR bands identified as MoOCl and WOCl were produced. The $POCl_3$ (Aldrich) was placed in a glass tube and entered the cell through a teflon needle valve. All other steps in the procedure were the same.

All spectra were obtained from 4800 to 400 cm^{-1} by using either a Nicolet 740 FTIR or a Nicolet 10DX FTIR spectrometer. These spectra represent 10, 15 or 32 scans for these instruments. The spectral resolution for the vaporization experiments was 0.5 cm^{-1}. The resolution of the chemical reaction experiments was ca. 1 cm^{-1}. All IR bands were measured with the peak locating program in the spectrometer. This program is calibrated with CO_2 and has an estimate absolute uncertainty equal to the resolution of the spectrometer.

RESULTS AND DISCUSSION

Vaporization experiments

The spectra observed for MoO_2Cl_2 in absorption and emission are shown in Figs. 1 and 2. The frequencies obtained from these spectra agree well with the frequencies reported previously (see Table 1). An expanded view of the metal oxygen stretching region (Fig. 3) clearly shows a B type band (symmetric

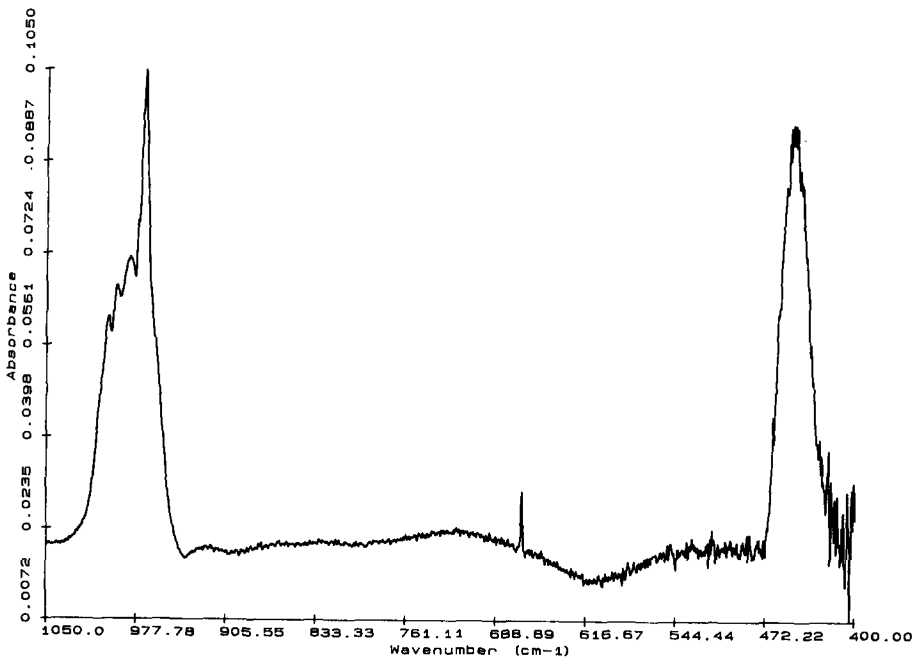

Fig. 1. The IR spectrum observed for MoO_2Cl_2 in absorption.

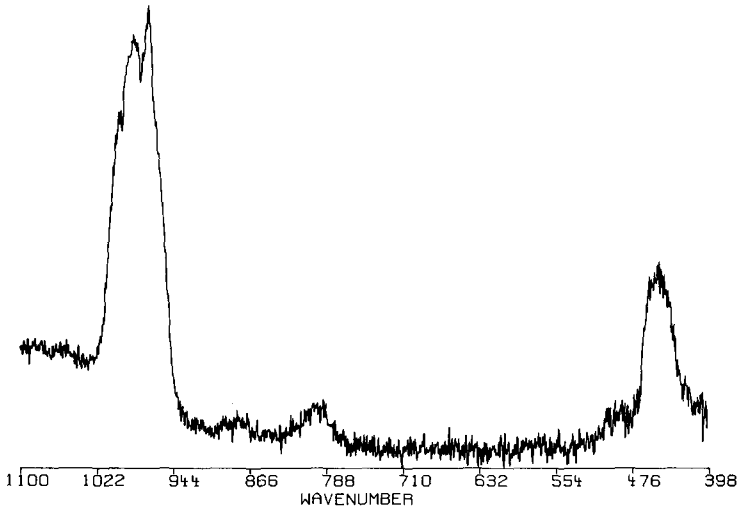

Fig. 2. The IR spectrum observed for MoO_2Cl_2 in emission.

stretch) and a C type band (asymmetric stretch) confirming the assignments made previously [9, 12]. In addition, there is clearly resolved structure on the *Q* subband of the C type band which has not been previously reported in the

TABLE 1

Comparison of the fundamental vibrations (cm^{-1}) observed for MoO_2Cl_2

Vibrational modes	Gas phase IR			Gas phase Raman		N_2 matrix [12]	This work
	[6]	[9]	[10]	[17]	[11]		
A_1 (Mo=O)		996	994	996	996	996	997.4
B_1 (Mo=O)	972	972	972	966	970	968	971.4
A_1 (Mo-Cl)		437	437	432	429	434	434.0
B_2 (Mo-Cl)	450	453	450	470	470	451	450.4
A_1 (MoO_2)				339	338	340	
A_1 ($MoCl_2$)				113	167		
B_1 (MoO_2)				211	202		
B_2 ($MoCl_2$)				267	180		
A_2 twisting				196	116		

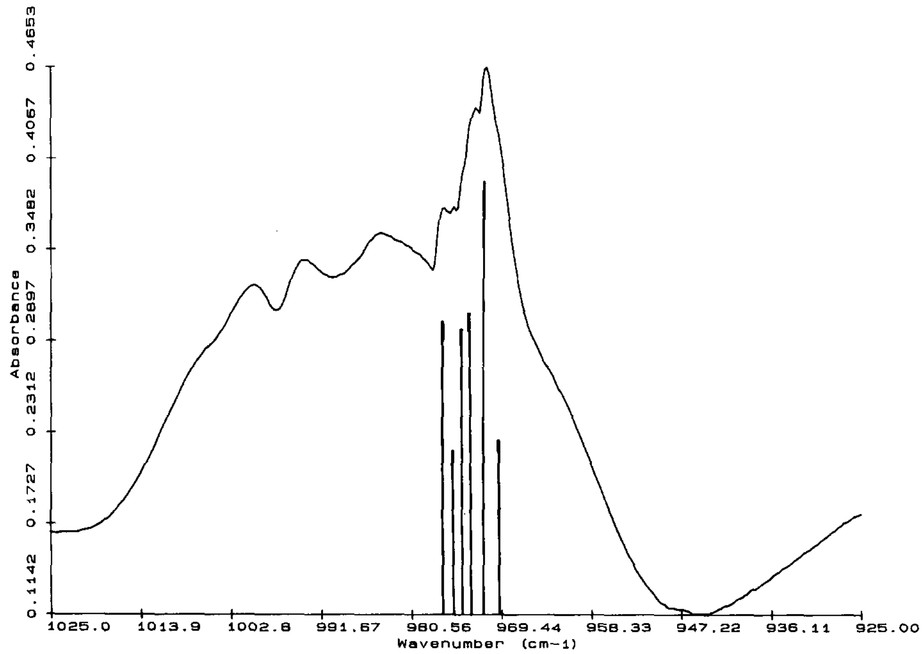

Fig. 3. An expanded view of the Mo-O stretching region in absorption; the lines mark the Mo isotope positions.

gas phase. This structure is readily assigned as Mo isotopic structure. As can be seen from Table 2 a comparison of the isotopomer frequencies observed here to those observed in N_2 matrices indicates a constant matrix shift of ca. 5.1 cm^{-1}.

TABLE 2

Comparison of the isotope frequencies observed in N_2 matrices [12] and those observed in this work

Isotope	N_2 matrix	Gas phase	Matrix shift[a]
92	972.1	977.3	5.2
94	970.2	975.1	5.1
95	969.2	974.3	5.1
96	968.2	973.2	5.0
97	967.4		
98	966.5	971.5	5.0
100	964.7	969.6	4.9

[a] Matrix shift is $\omega_g - \omega_{mat}$.

Levason et al. [2] have shown that the MoO_2 bond angle (2θ) can be estimated using

$$\sin^2\theta = \mathrm{Mo}'\mathrm{Mo}''[(\omega')^2 - (\omega'')^2]/32[\mathrm{Mo}''(\omega'')^2 - \mathrm{Mo}'(\omega')^2]$$

where ω' and ω'' are the zero-order frequencies corresponding to molybdenum isotopes Mo′ and Mo″ respectively. These frequencies should be corrected for anharmonicity, but uncorrected frequencies often give satisfactory agreement with other data [12]. The bond angle calculated using this assumption produced a bond angle of 112 ± 6°. This agrees well with the matrix isolation value of 109 ± 3° and is within experimental uncertainty of the electron diffraction value of 104 ± 2° [22].

Force constants for the M–O bonds were computed using the Wilson FG formalism and the uncoupled oscillator (high energy) approximation [23]. This procedure gave $f_r = 785(1)$ N m^{-1} and $f_{rr} = 46(2)$ N m^{-1} for the data reported here.

The IR spectrum observed for WO_2Cl_2 is presented in absorption and emission in Figs. 4 and 5. An expanded view of the tungsten oxygen stretching region (Fig. 6) clearly shows a B type band centered at 1014.9 cm^{-1} and a C-type band with Q head at 977.8 cm^{-1}. Assuming a small matrix red shift, these frequencies are in excellent agreement with those reported by Levason et al. [12] in N_2 matrices (see Table 3). However, they do not agree well with either of the earlier gas phase values [9, 10]. Since neither of the earlier papers presented representations of their spectra, it is not possible to determine whether or not some features in the earlier work were mistaken for the A_1 mode or whether the A_1 mode was assigned as an impurity. However, given the clarity of the sub-band structure in both absorption and emission and the close similarity of the matrix shifts observed for WO_2Cl_2 and MoO_2Cl_2, the assignments reported here are thought to be correct.

Since isotopic structure was not resolved, the isotopomer frequencies could

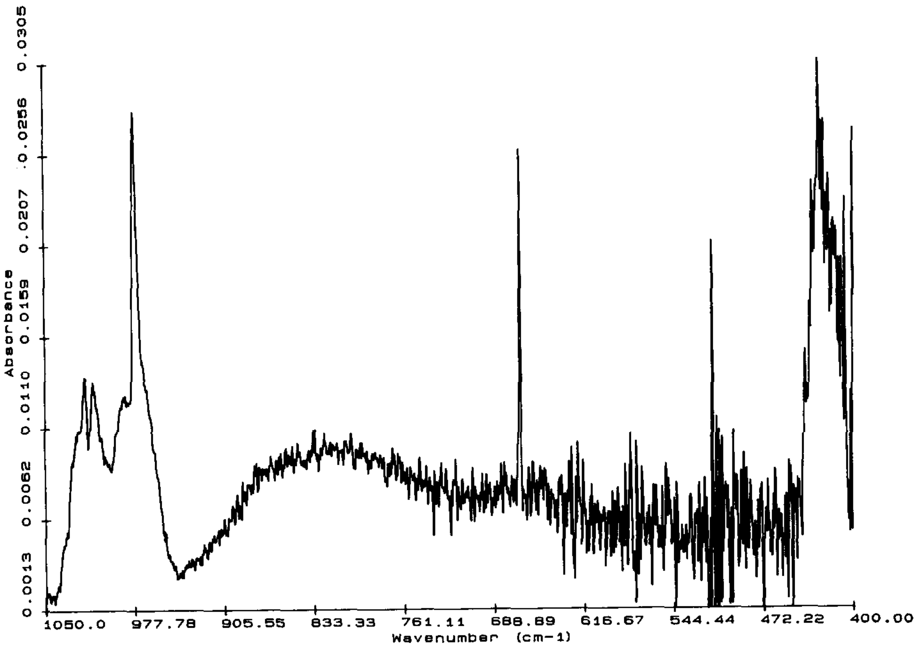

Fig. 4. The IR spectrum observed for WO_2Cl_2 in absorption.

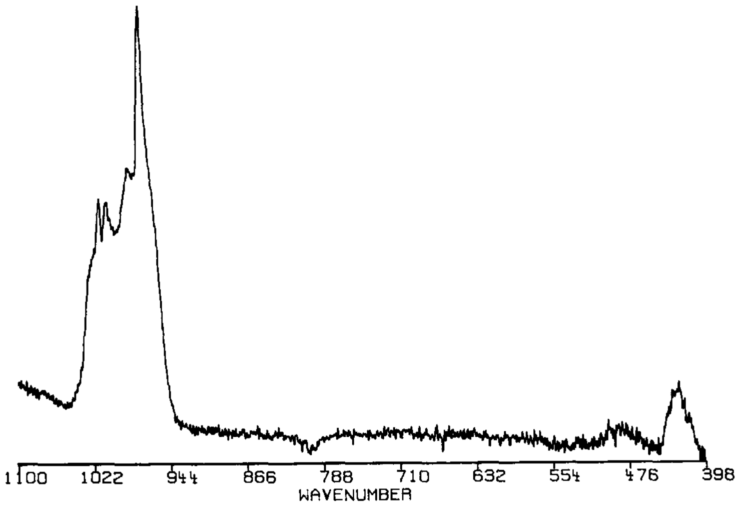

Fig. 5. The IR spectrum observed for WO_2Cl_2 in emission.

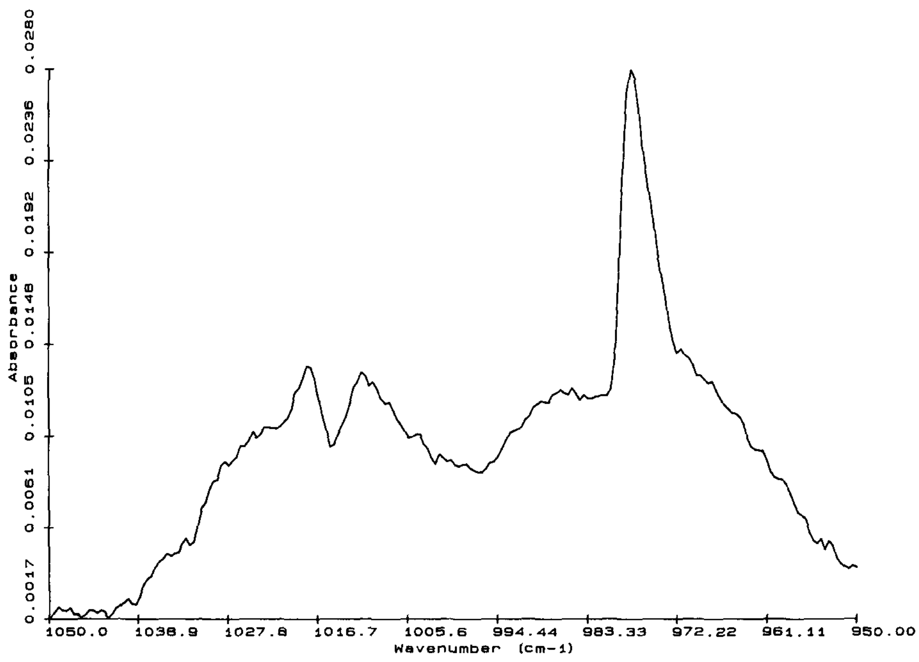

Fig. 6. An expanded view of the W-O stretching region in absorption.

TABLE 3

Comparison of the fundamental frequencies (cm^{-1}) reported for WO_2Cl_2

Vibrational modes	Gas phase IR			N_2 matrix IR	This work
	[9]	[10]	[11]	[12]	
A_1 (W=O)	984	992		1014	1014.9
B_1 (W=O)	972	978		974	977.8
A_1 (W-Cl)			431	425	426.0
A_1 (WO_2)			340		

not be used to estimate the WO_2 bond angle [20]. However, if the bond dipole model for IR intensities is assumed, it is easily shown that for WO_2Cl_2 [12]

$$\frac{I_B}{I_A}=\frac{\tan^2\theta\,(M_w+32\sin^2\theta)}{M_w+32\cos^2\theta}$$

where I_B, is the intensity of the B_1 mode, I_A is the intensity of the A_1 mode, and M_w is the atomic mass of tungsten. Since the bands were overlapped, peak heights were used to estimate the intensity ratio. The value of the WO_2 bond angle was 108 ± 2° based upon the intensity ratio of 1.95 determined from the peak intensities. In order to determine the reliability of this method, it was also used to estimate the bond angle for MoO_2Cl_2. The calculated intensity ratio of 2.2 gave an estimated bond angle of $110 \pm 2°$. This agrees well with the value of $112 \pm 6°$ obtained for the isotopic frequencies.

The W–O force constants were calculated using the same approximations as were used for MoO_2Cl_2. The values determined, $f_r = 862$ N m^{-1}, $f_{rr} = 53$ N m^{-1} indicate that the W–O bonds are stronger than the Mo–O bonds in these compounds.

Many spectra also showed that HCl was present in the cell. HCl most probably resulted from the reaction between the metal dioxydichloride and water

$$MO_2Cl_2 + H_2O \rightarrow MO_3 + 2HCl$$

In one of the MoO_2Cl_2 experiments, the spectrum shown in Fig. 7 was observed after several heatings. Temperature ramping experiments clearly showed that this spectrum was due to a gas phase molecule. A dark blue residue was observed in the cell at the conclusion of these experiments. Since this residue closely resembled the residue observed from the Mo + N_2O experiments and MoO_3 is expected to be present as an impurity in the cell, this molecule has been assigned as Mo_3O_9, the molybdenum oxide with the highest vapor pressure [24, 25]. The Mo + N_2O reaction experiments strongly support this assignment.

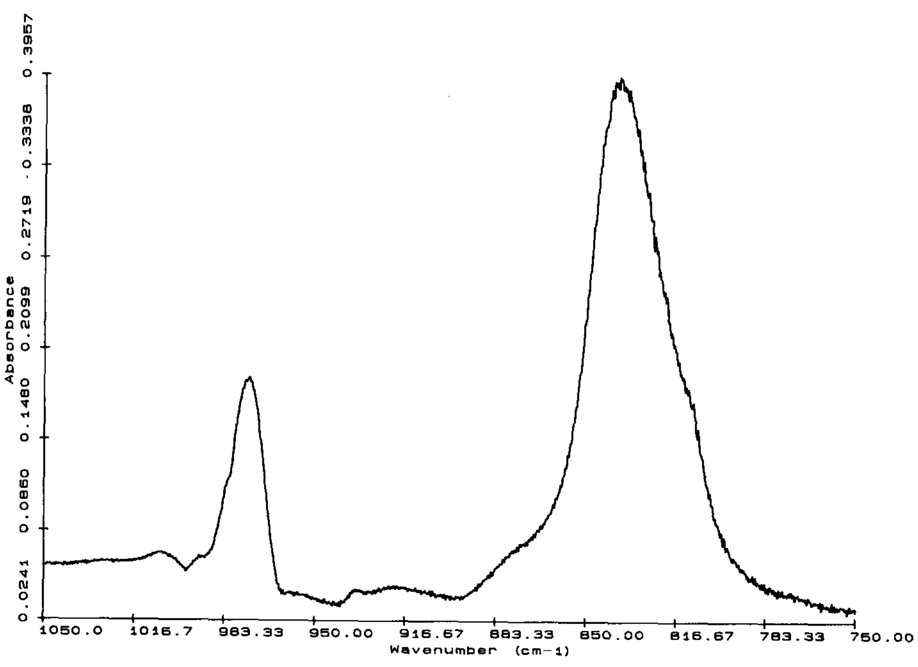

Fig. 7. The IR absorption spectrum of Mo_3O_9 observed by vaporizing MoO_3 (s).

Two bands at 974.7 and 838.0 cm^{-1} were clearly observed in the spectrum. As shown in Table 4, these frequencies agree well with the frequencies found in rare gas matrices for this molecule, but are 5–10 cm^{-1} and 23 cm^{-1} to the blue of the previous gas phase results. The previous spectra were taken at low resolution at ca. 1300 K. The published spectra show broad bands and there is a significant background absorption. This poor background, together with unresolved hot bands probably accounts for the lower frequencies observed previously. If these spectra are assumed to be shifted by hot bands, then estimates for the anharmonicity constants can be made. The three frequencies for the high energy bands are 4–5 cm^{-1} apart. This suggests that the anharmonicity constant for this band may be ca. 2 cm^{-1}. The observed spectrum shows slight tailing to lower frequencies and slight breaking at ca. 971 and ca. 967 cm^{-1}, which may indicate hot bands. The previous results suggest that the anharmonicity for the 838 cm^{-1} band is larger. Again, the spectrum observed here clearly tails to the blue and a definite shoulder at ca. 815 cm^{-1} is clearly seen. There may be a second shoulder at ca. 826 cm^{-1}, but it is less definite. These would indicate an anharmonicity of ca. 6 cm^{-1} for this band. Both seem reasonable and would help to explain the previous data. However, it will be necessary to obtain spectra at still higher resolution before this question can be answered with certainty.

TABLE 4

Observed IR product bands for the oxidation of Mo by N_2O

Molecule	Ar matrix		Gas phase		This work
	[4]	[5]	[3]	[6]	
MoO_2	899				905
	948		950		947
MoO_3	922				920
	976				—
$(MoO_3)_2$	350				
	694				
	976				
$(MoO_3)_3$	840	837	815	816	838.0
	858				
	978	977	970	966	974.7
$(MoO_3)_x$	514	856			851 (?)
$x=4,5$	865	865			870
	884				
	896				

The structure of Mo_3O_9 is expected to be similar to the structure observed for W_3O_9 [26]. W_3O_9 is formed from doubly bridged nearly tetrahedrally bonded WO_3 units. The tungsten and 3 oxygens form a 6 membered ring. The remaining oxygens are terminally bonded (2/W). The ring is slightly puckered, so that the unit has C_{3v} symmetry. The 974 cm^{-1} band is clearly a terminal Mo–O stretch and the 838 cm^{-1} band is probably a Mo–O ring stretching frequency. While this supports the proposed structure, too few frequencies are available to further establish the structure or to calculate force constants.

Chemical reaction experiments

It was difficult to obtain spectra of the gaseous molecules formed during the reaction between Mo and N_2O. A fine powder formed on the IR windows during the experiment. At the lower filament temperatures, the IR spectra of these window deposits were nearly identical to the spectra obtained as the "vapor" was transported through the cell. This indicated that most of the IR bands came from aerosols of this powder being transported through the cell. Some differences in the spectra of the transported material and the window deposits were observed at the higher filament temperatures. These difference bands were assigned as molecular species.

The IR spectra of the window deposits and a visual inspection of the residue scraped from the bottom of the cell indicated that at least three different solid phases were formed. The most commonly formed compound was a blue-black solid. Combustion analysis indicated that it had an average composition of Mo_4O_{11}. The IR spectra also clearly showed that MoO_3 was present. The composition of the remaining solid phases and a correlation of the IR bands to the solid phases will be the subject of future research.

The limited analysis of the solid phases formed suggested that it should be possible to observe IR bands arising from MoO_2 and $(MoO_3)_x$ ($x=1$–3) vapor molecules in the transported vapor. A comparison of the IR bands observed during the reaction to the spectrum of the solid deposits on the window led to the identification of several IR bands (see Fig. 8). Since difference spectra were used (Fig. 9), it is likely that some distortion in band shapes, relative intensities, and peak positions has occurred. Because of this, the frequencies are only expected to be good to ± 5 cm^{-1}.

As shown in Fig. 8, bands at ca. 970 and ca. 820 cm^{-1} are observed from this procedure. These bands are readily assigned as Mo_3O_9. There also appear to be gas phase bands at 907, 927 and 947 cm^{-1}. The identification of these bands is less certain, since the blue-black molybdenum oxides have IR bands in this region. However, they were observed in several spectra and are tentatively assigned as arising from gas phase molecules. A comparison of these frequencies with those reported for MoO_2 and MoO_3 in argon matrices [4, 5] indicates that

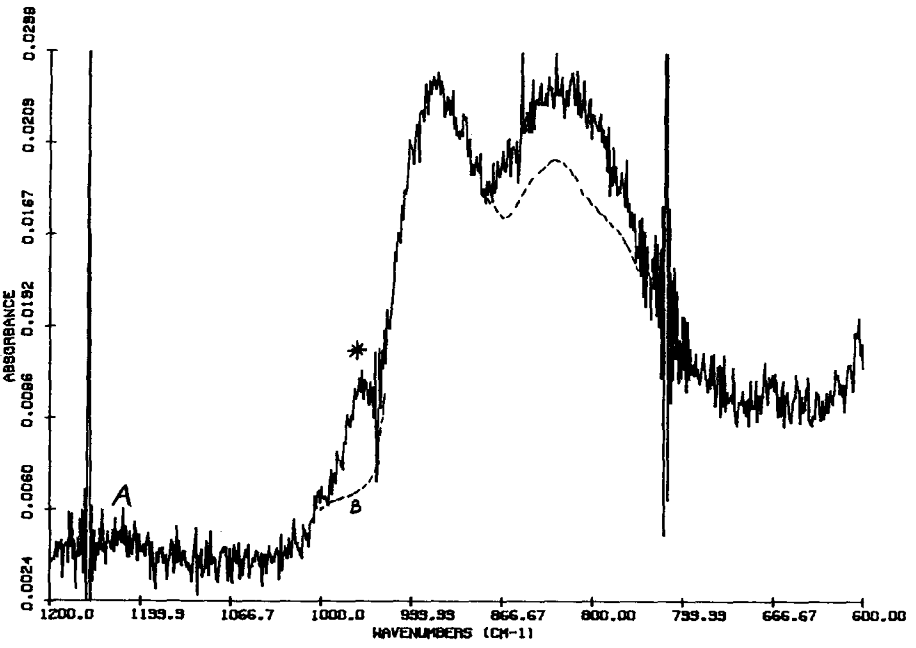

Fig. 8. Typical IR absorption spectra observed from the transport material produced by the reaction between Mo and N_2O. Trace A is the spectrum during transport. Trace B is the spectrum of the solid bands deposited on the windows. The asterisk marks bands arising from Mo_3O_9.

the 927 cm^{-1} band is from MoO_3 while the 907 and 947 cm^{-1} bands are from MoO_2.

Since MoO_2 has two IR active bands, it has a non-linear structure (C_{2v}). The 947 cm^{-1} band is assigned as the A_1 mode and the 907 cm^{-1} band is assigned as the B_2 mode. Unfortunately, it was not possible to accurately determine the relative intensities of these bands, so the bond angle could not be determined. Approximate force constants calculated by assuming a bond angle of 110° gave $f_r = 692$ N m^{-1} and $f_{rr} = 65$ N m^{-1}. This is ca. 90 N m^{-1} less than the force constant calculated for MoO_2Cl_2 using the same approximations.

Only one frequency was definitely observed for MoO_3. This result is consistent with the spectrum observed for WO_3, which is known to be planar. However, Hewett et al. [4] reported two frequencies for this molecule in rare gas matrices. Since one of their bands has nearly the same frequency as the high frequency band of Mo_3O_9, it would not be resolved here. Consequently, the symmetry of MoO_3 could not be determined.

The spectrum observed from the reaction between Mo and $POCl_3$ is presented in Fig. 10 and Table 5. In addition to unreacted $POCl_3$, IR bands were observed at 506, 535, 625 and 975 cm^{-1}. The bands at 506, 535 and 625 cm^{-1} can readily be assigned as a fundamental and two combination bands of

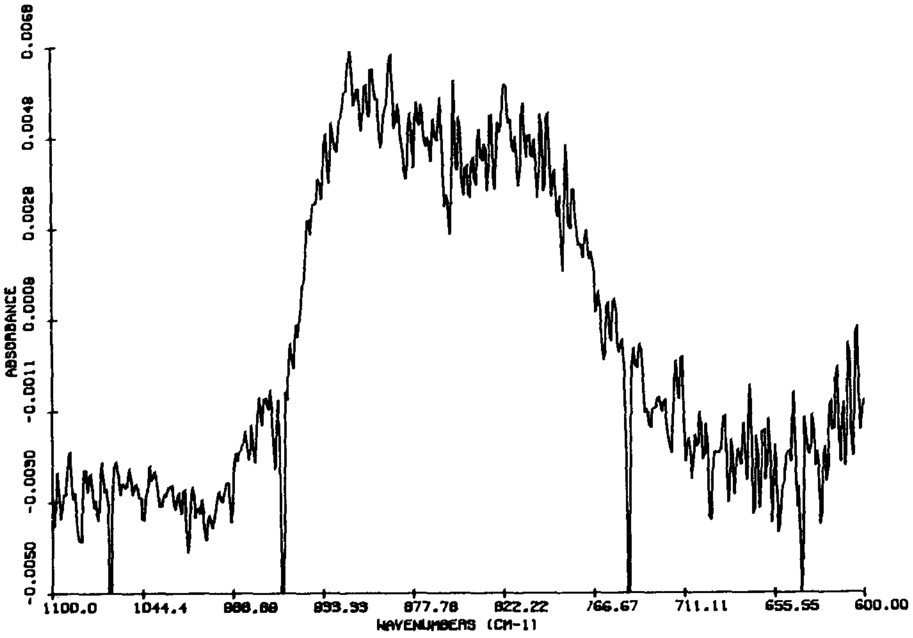

Fig. 9. A typical difference spectrum obtained by subtracting the spectrum during transport from the windows. Some unsubtracted solid is probably also present in this spectrum.

P_2Cl_4 [27]. The band at 506 cm^{-1} could also indicate that PCl_3 is present [28]. However, it is probably not a major contributor to this peak.

The band at 975 cm^{-1} is clearly in the Mo–O stretching region. It has a definite *P–R* structure. Since the band is not well resolved, it is possible that a weak *Q* branch may also be present. Since P_2Cl_4 is a product of this reaction, this molecule is probably an oxychloride of molybdenum. In one experiment, MoO_2Cl_2 was also observed from the reaction between Mo and $POCl_3$, suggesting that the 975 cm^{-1} band is a reaction intermediate in the mechanism to form MoO_2Cl_2. Although MoOCl, MoO_2Cl and $MoOCl_2$ would be logical reaction intermediates (Each of these compounds has been reported in the solid phase. However, there is some evidence that $MoOCl_2$ may disportionate when heated; see ref. 29.), MoOCl is more consistent with the observed conditions and the 975 cm^{-1} band is assigned as MoOCl. MoO_2Cl could form via the reactions

$$Mo + 2POCl_3 \rightarrow MoO_2Cl + PCl_3 + PCl_2$$

$$2PCl_2 \rightarrow P_2Cl_4$$

However, it would be expected to have two IR active Mo–O stretching modes. Since the spectrum appears to contain only one band with *P* and *R* structure, it is unlikely that this band is from MoO_2Cl. In contrast, $MoOCl_2$ would have

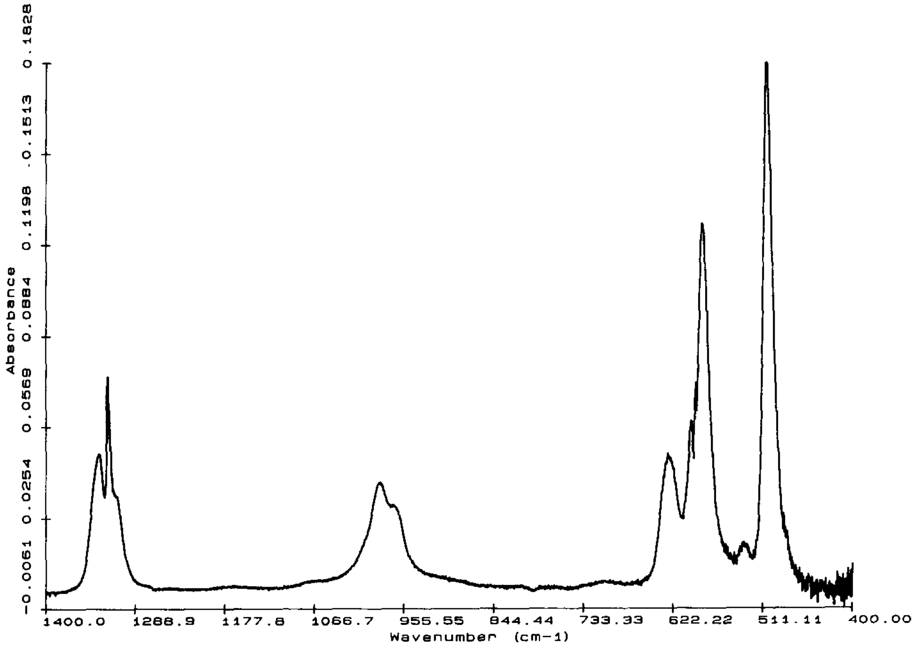

Fig. 10. The IR spectrum observed from the reaction between Mo and $POCl_3$.

TABLE 5

Observed IR product bands from the reaction between Mo and $POCl_3$

Frequency (cm^{-1})	Assignment
976	MoOCl
506	P_2Cl_4 + PCl_3 (?)
535	
627	

only one Mo–O stretching frequency, but it is not possible to write a chemical reaction which would produce it without postulating that unobserved products are also formed. Like $MoOCl_2$, MoOCl would have only one IR active Mo–O stretching band. Also, the reaction sequence

$$Mo + POCl_3 \rightarrow MoOCl + PCl_2$$

$$2PCl_2 + M \rightarrow P_2Cl_4 + M$$

easily explains its formation without introducing any unobserved stable products. Further support for this assignment comes from the estimated temperature of the system calculated using the equation [30]

$$\Delta\nu_{PR}=2.358\ [BT]^{1/2}$$

If the rotational constant (B) estimated from the molecular constants found for MoO_2Cl_2 is used with the observed P–R separation in this equation, the rotational temperature (T) is estimated to be ca. 700 K. Since this value is a reasonable estimate for the temperature in the cell, it adds further support to this assignment.

The spectrum observed from the reaction between W and $POCl_3$ is very similar to the spectrum observed from the Mo reactions (see Fig. 11 and Table 6). By analogy, the W containing molecule has been assigned as WOCl.

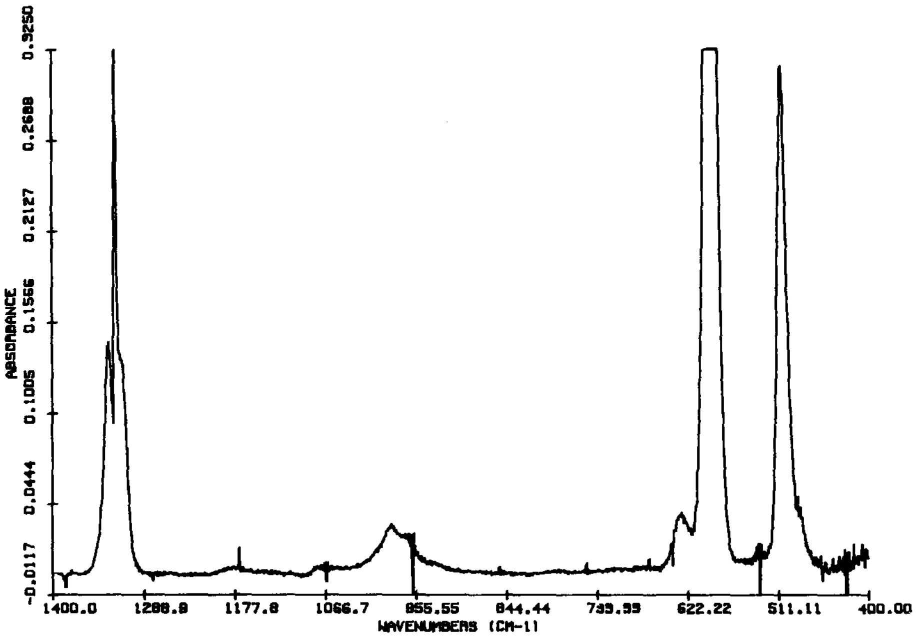

Fig. 11. The IR spectrum observed from the reaction between W and $POCl_3$.

TABLE 6

Observed IR product bands from the reaction between W and $POCl_3$

Frequency (cm^{-1})	Assignment
975	WOCl
506	P_2Cl_4
535	+
627	PCl_3 (?)

TABLE 7

Summary of force constants (N m^{-1}) observed for the molybdenum and tungsten oxides and oxyhalides

Metal-oxygen stretch				Ratio	Metal-Chlorine stretch				Ratio
WOCl	830	MoOCl	765	1.08	WO_2Cl_2	300[b]	MoO_2Cl_2	300[a]	1.07[c]
WO_2Cl_2	864	MoO_2Cl_2	785	1.10					
WO_2[a]	797	MoO_2	692	1.15					
WO_3	774 [16]	MoO_3	690	1.12					

[a] $f_{rr} = 19$. [b] $f_r - f_{rr}$. [c] Calculated from $f_r - f_{rr}$.

CONCLUSIONS

The IR spectra of several molybdenum and tungsten oxides and oxyhalides have been obtained at 0.5 cm^{-1} resolution. In general, this resolution was sufficient to resolve band contours and to permit accurate assignments for the bands in the metal oxide stretching region and part of the bands in the metal chloride stretching region. In the cases where there was a conflict between previous gas phase spectra and the matrix isolation data, the current spectra support the matrix isolation results. In general a matrix red shift of ca. 5 cm^{-1} or less was found for all the bands observed here.

The metal oxygen stretching force constants calculated using the high energy approximation are summarized in Table 7. These values indicate that the tungsten oxide bond is approximately 10% stronger than the molybdenum oxygen bond. Since W is approximately 9% less electron negative than is Mo, this difference may reflect the increased covalency of the tungsten oxygen bond. Replacing an oxygen with chlorine or adding chlorine to the molecule also increases the strength of the metal–oxygen bond. Since these changes usually involve a change in geometry as well as a change in electronegativity around the metal, the reason for these changes could not be determined.

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