resonant charge transfer here would seem to be precluded by the difficulty of symmetrizing the ionic atmospheres and this is reflected in the absence of a detectable electronic conduction.[22]

The inability to resolve more than the low-energy side of the presumed band of $Cd_2^{2+}$ in $CdCl_2$ solvent results from the proximity of the presumed charge-transfer band of the solvent (see below) which effectively limits observation to 335–340 m$\mu$ at the 88-$\mu$ pathlength employed. No other feature appears in the spectrum out to 1.0 $\mu$, and so it is concluded, but by no means assured, that the lower energy transition of the same, albeit weakened, $Cd_2^{2+}$ ion accounts for the pronounced visible color of the solutions. The probable energy of the transition to the $^1\Sigma_u$ state in $CdCl_2$ is appropriately about twice the dissociation energy estimated for $Cd_2Cl_2$ in this solution, 40 kcal mol$^{-1}$.[23]

Attempts to verify the previous spectral reports for the chloride system have been unsuccessful. An earlier, qualitative study on a 5% solution in $CdCl_2$ showed a relatively weak band at 455 m$\mu$ and 575° which split into two bands at 450 and 550 m$\mu$ on heating to 618°.[8] In the present work a poorly resolved band was found in this region only with a dilute solution which had been briefly exposed to air; absorption at about 415 m$\mu$ has also been observed (along with precipitation of the brown oxide) after treatment of Cd–$CdCl_2$ solutions with oxygen.[24] Another study[9] indicated that a weak ($\epsilon \sim 150$) band at 345 m$\mu$, with a possible shoulder at 325 m$\mu$, was well resolved from the metal-saturated solution (~15.5 mol % or 2.6 *M*) at 575° using 50-$\mu$ pathlengths. Anything of this magnitude would be very difficult to resolve in the dilute solutions studied here since $\epsilon_{345}$ is already about $10^4$; in fact, if Beer's law were to hold up to saturation, the cutoff would be at substantially lower energies. Nonetheless, Gaussian analyses of solute bands in both $Cd(AlCl_4)_2$ and $NaAlCl_4$ commonly gave small negative deviations from experiment ($\Delta A \leq 0.02$) in the neighboring of 340 m$\mu$, corresponding to molar absorptivities of a few hundred for a $Cd_2^+$ solute. Although the differences are probably of the order of experimental error, the nominally forbidden transition to the $^3\Sigma_u$ state could be involved instead.

The effect of the anion on the positions of the band edges for the sodium and cadmium(II) solvents is quite consistent with a charge-transfer assignment. However, the only thing that can be safely concluded is that in each case the conversion from chloride to tetrachloroaluminate anion should raise the ionization energy of the donor and probably decrease the coulombic loss; the effect of covalency is more difficult to assess although it is possibly quite important in $CdCl_2$.[25] In any case substitution of $AlCl_4^-$ yields a far more useful solvent optically; *e.g.*, at 220 m$\mu$ the molar absorptivity of $NaAlCl_4$ is only 0.034 at 300° and that of the $Cd(AlCl_4)_2$ solute is $2.2 \times 10^3$ at 350°. On the other hand, a charge-transfer assignment for the $Cd_2^{2+}$ spectrum therein is inconsistent although the same cannot be firmly eliminated for the unresolved spectrum in $CdCl_2$.

**Acknowledgment.**—Considerable assistance was given to phases of this work by Douglas Adolphson and Lynn Holloman, Summer Research Participants.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

# A Vibrational Spectroscopic Study of Aqueous Cadmium Nitrate Solutions[1]

BY A. R. DAVIS AND R. A. PLANE

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Raman and infrared spectra of aqueous cadmium nitrate solutions indicate the presence of nitratocadmium species. The intensity variation of the Raman bands at 1404 cm$^{-1}$, originating from solvated nitrate ion, and 1452 cm$^{-1}$, originating from complexed nitrate, has been used to characterize the species present in solution. The observation of a polarized Raman band at 1324 cm$^{-1}$ indicates that the nitrate ion is acting as a monodentate ligand. A vibrational assignment for the monodentate nitrate group, in terms of the $C_{2v}$ point group, is described. The calculated association constant for the $CdNO_3^+$ species is 0.38 ($\pm$0.05) at 44°. No evidence for species higher than $CdNO_3^+$ has been obtained from the molar ratio solutions studied. Nevertheless, this work does not rule out the existence of higher species.

## Introduction

Apart from some earlier work which detected no evidence for complexation in solutions of cadmium nitrate,[2,3] there is evidence from such techniques as conductivity,[4,5] calorimetry,[6] emf measurements,[7,8] and polarography[9] for a mononitratocadmium species. A

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dinitratocadmium species has also been proposed,[9] but no higher complexes.

Although cadmium nitrate has not been previously studied by Raman spectroscopy, results from other metal–nitrate systems have been interpreted in terms of complex species,[10–12] contact ion pairs,[13,14] and solvent-separated ion pairs.[15] For a complete description of a metal–nitrate system it would be advantageous to have information not only about the complexed nitrate but also about the free nitrate ion in solution. Previous workers[14,15] have used variations in the intensities of the bands at *ca.* 720 and 740 $cm^{-1}$ to diagnose species in solution. Even in 4.55 *M* cadmium nitrate solution the 740-$cm^{-1}$ band is only as intense as the 720-$cm^{-1}$ band. It is also probable that the 720-$cm^{-1}$ band is not solely due to free nitrate ion. In view of these two observations, it was decided to study the intensity variations of the *ca.* 1400-$cm^{-1}$ region. The *ca.* 1400-$cm^{-1}$ region has already been extensively studied in the case of the alkali metal nitrates. The splitting of the normally degenerate $\nu_3(E')$ mode in dilute aqueous solutions has been attributed to water perturbation of the nitrate ion.[16] The coordination of nitrate to metal ions may, if the symmetry is lowered to $C_{2v}$, also lead to removal of the degeneracy of this mode and the occurrence of two bands. Therefore, if solvated nitrate ion is in equilibrium with complexed nitrate ion, at least four bands should be observed in this region. This conclusion is borne out in the case of cadmium nitrate and the intensity variations of the bands have been used to diagnose the species present. The observation of four bands in this region may be contrasted with results of previous authors who have also studied the equilibrium between complex nitrato species and free nitrate. In one study of calcium nitrate three bands were reported for the 1400-$cm^{-1}$ region[14] whereas in another only two bands were reported.[14]

## Experimental Section

Raman data were obtained with a Cary Model 81 spectrophotometer using the 4358-Å mercury line as the exciting source. Unwanted mercury lines below 4358 Å were filtered out by means of an Ozalid filter surrounding the sample. Raman intensities were measured relative to the 458-$cm^{-1}$ band of carbon tetrachloride. Spectra were recorded at the ambient temperature of the cell compartment (44 ± 1°).

Infrared spectra were recorded using Beckman IR-9 and Perkin-Elmer Model 521 spectrophotometers with the samples pressed between silver chloride plates.

A standard (2.5 *M*) cadmium perchlorate solution was prepared by dissolution of cadmium oxide in perchloric acid. The cadmium content of the solution was determined by a gravimetric method, the cadmium being precipitated as $Cd(py)_2(SCN)_2$.[17] A stock solution of 7.0 *M* sodium nitrate was prepared by dissolution of the dried and weighed salt in water.

Solutions for the molar ratio method were prepared from stock solutions; the cadmium ion concentration was 1.0 *M* and the nitrate ion concentration varied from 0.8 to 3.07 *M*. Solutions for the Job method of analysis were prepared from stock solutions by standard techniques. Concentrations were adjusted so that the total concentration of cadmium ion plus nitrate ion was equal to 2.5 *M*.

All solutions were filtered through a fine-porosity glass frit prior to recording their spectra.

## Results

The Raman and infrared spectra of a 4.55 *M* solution of cadmium nitrate are recorded in Table I.

Table I

Raman and Infrared Frequencies of a 4.55 *M* Cadmium Nitrate Solution (in $cm^{-1}$)

| Raman | Infrared | Raman | Infrared |
|---|---|---|---|
| 348 wp | | 1050 sp | 1043 m |
| 720 m | 720 vw | 1324 mp | 1328 m |
| 739 mp | 740 vw | 1348 m | 1348 m |
| 822 vw | 818 m | 1404 m | 1404 m |
| | 830 sh | 1452 m | 1456 m |

Intensity variations have been studied for the 1404- and 1348-$cm^{-1}$ bands, originating from free nitrate, and the 1324- and 1452-$cm^{-1}$ bands, originating from complexed nitrate. A Du Pont 310 curve resolver has facilitated the resolution of the spectral envelope containing the bands at 1324, 1348, 1404, and 1452 $cm^{-1}$. For all of the spectra measured, it was found that the experimental curves could be resolved into four Gaussian components of apparently fixed frequency and half-width (Figure 1). Furthermore the amplitudes of the two components characteristic of free nitrate (1348 and 1404 $cm^{-1}$) were found to remain in fixed ratio. Band changes such as were found in alkali metal nitrate solutions[16] were not apparent in the present system which is dominated by the larger effects due to the presence of $Cd^{2+}$.

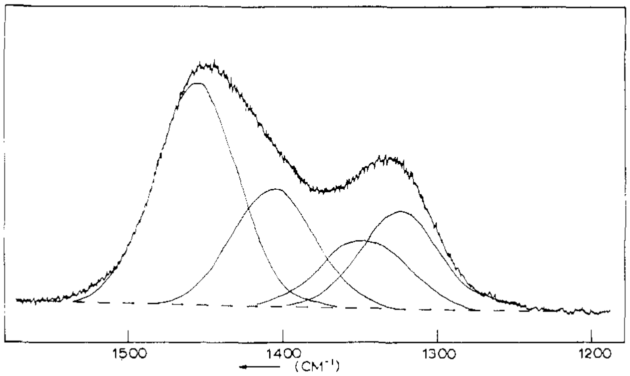

Figure 1.—The Raman spectrum of a 4.55 *M* cadmium nitrate solution (1200–1600 $cm^{-1}$) resolved into four Gaussian components.

The relative amplitudes of the bands originating from the Job series of solutions are shown plotted *vs.* *f* (Figure 2, open circles). The total concentration of cadmium ions plus nitrate ions was fixed at 2.5 *M*, and *f* is the fraction of these ions which is nitrate. The solubility of cadmium perchlorate, approximately 2.5

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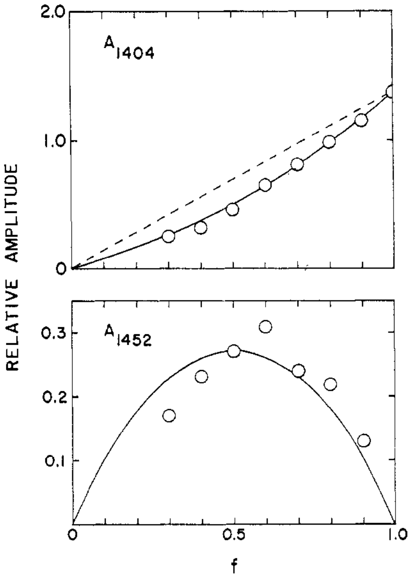

Figure 2.—Relative amplitude *vs.* the ratio $f$ (the total concentration of nitrate ion divided by the sum of the total concentrations of nitrate and cadmium(II) ions). $[Cd^{2+}] + [NO_3]$ is 2.5 $M$ for all values of $f$. Circles are experimental points and lines are calculated results.

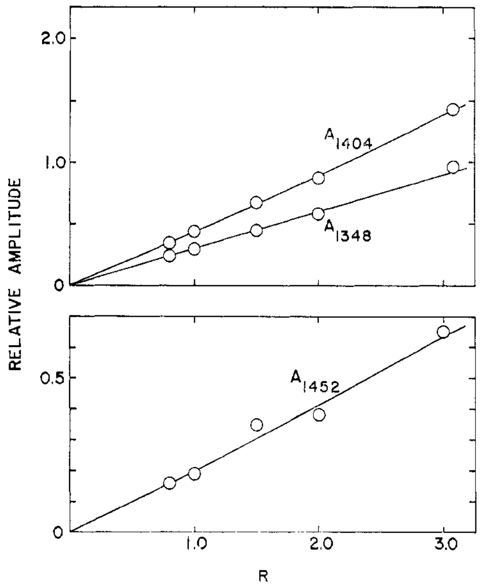

Figure 3.—Relative amplitude *vs.* the ratio $R$ (the total concentration of nitrate divided by the total concentration of cadmium(II) ion). The concentration of cadmium(II) ion is 1.0 $M$ for all values of $R$.

$M$, represents the total maximum concentration of cadmium ions plus nitrate ions. This low concentration severely limited the accuracy with which the least intense band, 1324 cm$^{-1}$, could be measured. Therefore the intensity variation of the 1324-cm$^{-1}$ band is not recorded.

The relative amplitude variations for the molar ratio solutions are shown in Figure 3. The cadmium ion concentration was fixed at 1.0 $M$ and the nitrate ion concentration varied from 1.0 to 3.0 $M$.

## Discussion

**Stoichiometric Solutions.**—A study[16] of the vibrational spectra of solutions of the alkali metal nitrates has shown that the solvated nitrate ion generates the following vibrational spectrum: 1404 cm$^{-1}$ (infrared, Raman); 1348 cm$^{-1}$ (infrared, Raman); 1049 cm$^{-1}$ (Raman); 825 cm$^{-1}$ (infrared); 719 cm$^{-1}$ (infrared, Raman). The 56-cm$^{-1}$ split of the normally degenerate $\nu_3(E')$ mode has been ascribed to interaction of water with the nitrate ion. The four bands in the *ca.* 1400-cm$^{-1}$ region of the infrared and Raman spectra of 4.55 $M$ cadmium nitrate solution clearly indicate the presence of complex species and solvated nitrate ion (Table I).

A Raman spectroscopic study[16] of the aqueous alkali metal nitrates showed that only for solutions of lithium and sodium nitrates above 7.0 $M$ was the $\nu_4(E')$ mode of the nitrate ion split into two bands. In these solutions of low water content it is probable that the nitrate ion occupies a position in the first coordination sphere of the metal ion. It has been suggested[16] that the presence of a band at *ca.* 740 cm$^{-1}$ implies direct metal–nitrate interaction. The observation of a band at 740 cm$^{-1}$ for all solutions of cadmium nitrate supports the conclusion that the species in these solutions are not solvent-separated ion pairs but contact ion pairs.

The 818-cm$^{-1}$ infrared band may be attributed to the complex species. For a nitrate ion of $D_{3h}$ symmetry the $\nu_2(A_2'')$ mode occurs at *ca.* 830 cm$^{-1}$. The lower frequency observed for this mode is consistent with previous work.[10,12,15] The infrared spectrum of a 4.55 $M$ solution of cadmium nitrate shows a band at 818 cm$^{-1}$, originating from complexed nitrate, with a shoulder at 830 cm$^{-1}$ originating from free nitrate. This observation indicates considerable complex formation.

The relative intensities of the infrared bands at 830 cm$^{-1}$, normally infrared allowed, and at 1043 cm$^{-1}$, normally infrared forbidden, have been used to distinguish between complex formation and cationic perturbation of the nitrate ion.[10,15,16] The ratio $I_{1043}/I_{830}$ is 0.34 for saturated sodium nitrate.[16] For two systems which have been shown to exhibit complex formation, as evidenced by the observation of a metal–oxygen stretch vibration, the ratio varies from 7.7 for saturated cerium(IV) nitrate[10] to 20.0 for saturated thorium nitrate.[18] A calculated intensity ratio of 4.0 for saturated cadmium nitrate appears to indicate some complex ion formation.

**Molar Ratio Solutions.**—The molar ratio plots (Figure 3) demonstrate that the band amplitudes of the free ($A_{1404}$, $A_{1348}$) and complexed ($A_{1452}$) nitrate increase with nitrate ion concentration. Although the plots give no direct information as to the stoichiometry of the species, it is possible to calculate $\bar{n}$, the average number of nitrate ions bound per cadmium ion, for the solutions studied. The value of $\bar{n}$, assuming all of the cadmium ion in solution exists as complex nitrato species, never rises above 0.5. This low value would seem

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[18] A. R. Davis, unpublished results.

to preclude the existence of species with more than one nitrate per cadmium ion.

Using the spectral information relating to uncomplexed nitrate for the molar ratio solutions it is possible to calculate formation constants. From the Job method, at $f = 1.0$, the solution contains only nitrate ion. Therefore, the molar intensity, $J$, of the 1404-cm$^{-1}$ band, originating from free nitrate, may be calculated

$$J_{1404} = \frac{A_{1404}}{[NO_3^-]} = \frac{1.3}{2.5} = 0.55$$

This result may be used to calculate the concentration of free nitrate present in the molar ratio solutions

$$[\text{free nitrate}] = C_f = \frac{A_{1404}}{0.55}$$

Assuming that $CdNO_3^+$ is the important species present, then the main equilibrium is

$$Cd^{2+} + NO_3^- \rightleftharpoons CdNO_3^+$$

$$\frac{[CdNO_3^+]}{[Cd^{2+}][NO_3^-]} = \frac{C_{TOT} - C_f}{[1.0 - (C_{TOT} - C_f)]C_f}$$

where $C_{TOT}$ is total nitrate concentration and total $Cd^{2+}$ concentration is 1.0 $M$. If $CdNO_3^+$ is the important species and its equilibrium quotient $K_1$ remains constant, then a plot of $C_{TOT} - C_f$ *vs.* $[1.0 - (C_{TOT} - C_f)]C_f$ should give a straight line of slope $K_1$ passing through the origin. As shown in Figure 4, a straight line of slope 0.38 (±0.05) passing through the origin is obtained. Other workers have reported $CdNO_3^+$ formation constants ranging from 0.61[8] (at 45°) to 2.5[4,5] (at 25°). Thus the calculated constant is in reasonable agreement with previous work.

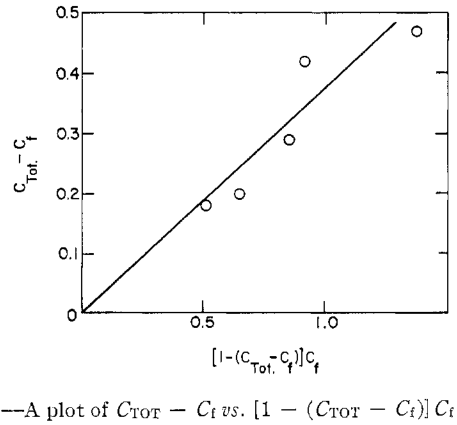

Figure 4.—A plot of $C_{TOT} - C_f$ *vs.* $[1 - (C_{TOT} - C_f)]C_f$ for data obtained from the molar ratio solutions.

A similar calculation was carried out assuming that $Cd(NO_3)_2$ was an important species. A nonlinear plot was obtained which did not pass through the origin.

**Job Solutions.**—For the Job solutions the intensity of the 1404-cm$^{-1}$ band, due to free nitrate, increases with $f$ (Figure 2, open circles). It has been shown that the intensity of the 1404-cm$^{-1}$ band varies linearly with concentration of sodium nitrate.[16] In the Job method of analysis, $f$ is directly proportional to the total concentration of nitrate ion. Therefore, if no complexation occurs, the intensity of the band at 1404 cm$^{-1}$ should increase linearly with $f$, shown by the dashed line in the upper part of Figure 2. The departure from linearity of the plot of $f$ *vs.* the intensity of the 1404-cm$^{-1}$ band may be interpreted in terms of complex formation. The band at 1452 cm$^{-1}$ exhibits an amplitude maximum at $f$ equal to 0.58 (Figure 2, open circles). The single maximum suggests the occurrence of but one species, although conclusions concerning the stoichiometry of the species from the Job results must at best be tentative.

Using the association constant of $CdNO_3^+$ derived from the molar ratio study, it is possible to calculate the theoretical concentrations of the $CdNO_3^+$ and $NO_3^-$ ions present in the Job solutions. This calculation rests on the assumption that $CdNO_3^+$ and $NO_3^-$ are the only nitrate-containing species in the solutions. The calculated molar intensity of the 1404-cm$^{-1}$ band is 0.55. This value may be used to compute the theoretical intensity of the 1404-cm$^{-1}$ band, originating from free nitrate ion, for the Job solutions. The results from these calculations are shown by the plot of the solid line in the upper part of Figure 2. The agreement between the experimental open circles and the calculated solid line is extremely good. It was not possible to calculate directly the molar intensity of the band at 1452 cm$^{-1}$. Instead, the concentration of $CdNO_3^+$ ion, obtained using the value of 0.38 for the association constant, has been normalized to the experimental data at an $f$ value of 0.5. At this point the molar intensity of the 1452-cm$^{-1}$ band, originating from complexed nitrate, was calculated to be 0.88. This value was used to compute the theoretical intensity of the 1452-cm$^{-1}$ band originating from the Job solutions. The computed variation of intensity of the 1452-cm$^{-1}$ band with $f$ is shown by the solid line in the bottom half of Figure 2. The agreement between the computed and measured intensities is not as good as for the 1404-cm$^{-1}$ band. The reason for this may be the existence of complexes higher than $CdNO_3^+$, but is more likely due to inaccuracy in the experimental measurement of band intensity.

**Band Assignment.**—A band assignment may be made on the assumption that stoichiometric cadmium nitrate solutions may be regarded as containing the species $Cd^{2+}$, $CdNO_3^+$, and $NO_3^-$. The bands due to free nitrate may be assigned as shown in Table II.

Table II

Frequency Assignments for the Free and Bound Nitrate in Solutions of Cadmium Nitrate

| Solvated nitrate ion ($D_{3h}$) | | | Bound nitrate ($C_{2v}$) | | |
|---|---|---|---|---|---|
| Infrared | Raman | Assignment | Infrared | Raman | Assignment |
| 720 | 720 | $\nu_4(E')$ | 720 | 720 | $\nu_5(B_1)$ |
| | | | 740 | 740 | $\nu_3(A_1)$ |
| 830 | | $\nu_3(A_2'')$ | 818 | 822 | $\nu_6(B_2)$ |
| | 1050 | $\nu_1(A_1')$ | 1043 | (*Ca.* 1043)[a] | $\nu_2(A_1)$ |
| | | | 1328 | 1324 | $\nu_1(A_1)$ |
| 1348 | 1348 | | | | |
| | | $\nu_3(E')$ | | | |
| 1404 | 1404 | | | | |
| | | | 1456 | 1452 | $\nu_4(B_1)$ |

[a] Appears as asymmetry of the 1050-cm$^{-1}$ band.

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.

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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

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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

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[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.

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