# Raman Spectroscopic Evidence of Dimeric Molybdenum(VI) Species in Acidic Solutions

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It is known that Mo(V) forms a number of dimeric oxygen-bridged complexes, and the structures of the complexes have been established. On the other hand, little is known with certainty on the nature of dimeric Mo(VI) species. In acidic solutions, there is only indirect evidence for the presence of Mo(VI) dimers. In ultraviolet (UV) spectrophotometric measurements, absorption coefficients per molybdenum change with an increase in the Mo(VI) concentration [1–4]. The change has been interpreted in terms of the formation of dimeric Mo(VI) species, and monomer-dimer equilibrium constants have been calculated [5, 6]. In addition, the formation of various dimeric cations has been postulated to explain the data obtained by diffusion [7], polarographic [8], distribution [9], and solubility [10] measurements.

The present study was undertaken to obtain direct information on the formation of Mo(VI) dimers in acidic solutions. Raman spectroscopy was thought to be a powerful technique for the characterization of Mo(VI)–oxygen bridged systems. Evidence was obtained for the existence of dimeric species with a single-oxobridge.

## Experimental

Raman spectra (1200–100 cm$^{-1}$) were obtained with a Spex Raman spectrophotometer, Model Ramalog 5. The argon line at 488 nm was used for excitation.

Reagent grade chemicals were used without further purification. Molybdenum(VI) solutions were prepared from $Na_2MoO_4 \cdot 2H_2O$.

## Results and Discussion

Raman spectra were recorded for a series of solutions containing 0.5 *M* Mo(VI) and different concentrations of $HNO_3$ (0.8–6 *M*). In the region where the ratio of [H$^+$] to [Mo(VI)] ranged from 1.7 to 2.1, the Raman spectra in the Mo–O stretching region were characterized by bands at 978, 950 and 898 cm$^{-1}$. Tytko *et al.* concluded that these three bands were associated with $Mo_{36}O_{112}{}^{8-}$ [11], but Murata and Ikeda [12] and Mattes *et al.* [13] claimed that $Mo_6O_{19}{}^{2-}$ existed in the acidity range. With an increase in the $HNO_3$ concentration, the intensity of the band at 978 cm$^{-1}$ decreased with a simultaneous shift of the band at 898 cm$^{-1}$ toward higher frequencies, to about 918 cm$^{-1}$. Above 2.5 *M* $HNO_3$, three bands assigned to a *cis*-$MoO_2$ group were observed: 950, 918 and 369 cm$^{-1}$; the 950 cm$^{-1}$ band is assigned to the symmetric stretch $\nu^s(MoO_2)$, the 918 cm$^{-1}$ band to the asymmetric stretch $\nu^{as}(MoO_2)$, and the 369 cm$^{-1}$ band to the deformation $\delta(MoO_2)$ [14]. In addition to the three bands, two broad bands appeared near 820 and 450 cm$^{-1}$. The spectra were essentially independent of the $HNO_3$ concentration up to 6 *M*. The two bands near 820 and 450 cm$^{-1}$ are of particular interest.

Two dimeric Mo(VI) complexes with a mono-oxobridge have been isolated [15, 16]. The preparations are fortuitous; the Mo(VI) complexes were unexpectedly obtained by keeping an aqueous solution of an Mo(V) oxalate complex in air, and in the crystallization process of $MoO_2Cl_2(dmf)_2$. Infrared spectra of the Mo(VI) oxalate complex show bands at 960, 920 and 860 cm$^{-1}$ [15]. The first two bands are assigned to the symmetric and asymmetric stretching vibrations of the *cis*-$MoO_2$ group. The band at 860 cm$^{-1}$ is assigned as the asymmetric stretching band of a linear mono-oxobridge. The structure of the oxalate complex has been determined by an X-ray diffraction study [17]. No dimeric Mo(VI) complexes with the dioxobridge have been prepared so far.

On the other hand, it is well known that the dimeric Mo(V) complexes contain two types of oxygen-bridged groups; a mono-oxobridge, linear or bent, and a di-oxobridge [18–24]. According to Wing and Callahan [22], the stretching vibrations of the mono-oxobridge occur outside the frequency range of 750–500 cm$^{-1}$, while those of the di-oxobridge are expected at 750–500 cm$^{-1}$. In our recent Raman studies on the Mo(V) species in HCl solutions, a dimer shows bands at 870, 802 and 436 cm$^{-1}$, bands which are assigned to the stretching frequencies of the mono-oxobridge, while the other dimer shows bands at 742 and 532 cm$^{-1}$ due to those of the di-oxobridge [25].

On this basis we can assign bands near 820 and 450 cm$^{-1}$ to the asymmetric and symmetric stretching modes of the mono-oxobridge, which means the formation of a dimeric Mo(VI) species in 2.5–6 *M* $HNO_3$.

Table I lists the frequencies observed for 0.5 *M* Mo(VI) in various acids. The bands in parentheses are due to the absorption of solvent anions. In the acid

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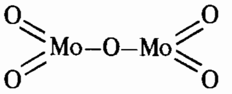
TABLE I. Vibrational Frequencies (cm$^{-1}$) of Mo(VI) in Various Acids.

| | $\nu$(MoO$_2$) | $\nu$(Mo$_2$O) | $\delta$(MoO$_2$) | $\nu$(Mo–Cl) | $\nu$(O···H–O) |
|---|---|---|---|---|---|
| HNO$_3$ | | | | | |
| 2.5–6 *M* | 950 918 | 820 (720) 450 | 369 | | 216 |
| HClO$_4$ | | | | | |
| 3 *M* | 953 (937) | 825 (631) (465) | 378 | | 220 |
| H$_2$SO$_4$ | | | | | |
| 3 *M* | 951 917 (903) | 830 (598) (435) | 379 | | 228 |
| HCl | | | | | |
| 3 *M* | 949 918 | 830 455 | 373 | 291 | 215 |
| conc. | 957 917 | | 387 | 307 | 213 245 |

solutions of 3 *M*, the spectra contain the bands near 950, 920 and 370 cm$^{-1}$ assigned to the *cis*-MoO$_2$ group; the $\nu_1$ band of ClO$_4^-$ (937 cm$^{-1}$) obscures the stretching band near 920 cm$^{-1}$ in perchloric acid. In addition, the appearance of the bands near 830 cm$^{-1}$ shows the formation of dimeric Mo(VI) species with the mono-oxobridge. In 3 *M* HCl, we observed a broad band at 455 cm$^{-1}$, due to the symmetric stretching mode. In perchloric and sulfuric acids, however, the band near 450 cm$^{-1}$ is obscured by strong absorption of the solvent anions. It is concluded that the principal species in these acid solutions is a dimer with the



core.

In concentrated HCl, the bands from the mono-oxobridge are not observed. The spectra are similar to those reported by Aveston *et al.* [26] and Griffith and Wickins [14], who have concluded the formation of monomeric Mo(VI)–Cl complexes. The appearance of the bands at 950, 920 and 370 cm$^{-1}$ excludes the possibility of the presence of Mo(OH)$_4^{2+}$, but suggests a *cis*-dioxo structure [27].

Another region of interest is 210–230 cm$^{-1}$. The band in this region has been assigned as the Mo(VI)–Cl stretching vibration [14]. Since the bands are found in all the acids (Table I), however, they cannot be ascribed to coordinated solvent anions, but to water which coordinates or is hydrogen-bonded to the MoO$_2$ group [28].

The bands at 291 and 307 cm$^{-1}$ in HCl solutions can be assigned to Mo(VI)–Cl stretching vibrations [29, 30]. No assignment can be made to the band at 245 cm$^{-1}$ in concentrated HCl.

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