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A RAMAN SPECTROSCOPIC INVESTIGATION OF

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# A RAMAN SPECTROSCOPIC INVESTIGATION OF

# SOME HETEROPOLYMOLYBDATES

Ву

Melody Starr Kasprzak

# A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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### ABSTRACT

# A RAMAN SPECTROSCOPIC INVESTIGATION OF

# SOME HETEROPOLYMOLYBDATES

By

Melody Starr Kasprzak

Raman spectroscopy has been used to investigate three aspects of heteropolymolybdate chemistry. Raman spectra have been obtained of 12-molybdophosphoric acid (12-MPA)  $H_3PMo_{12}O_{40}$  and 12-molybdosilicic acid (12-MSA)  $H_4SiMo_{12}O_{40}$  in aqueous solution over a wide pH range. The spectra change as a function of pH; decomposition schemes have been determined based on variations in the Raman band frequencies and intensities, through comparison with literature spectra. Both 12-MPA and 12-MSA are decomposed by concentrated HCl to form <u>cis</u>-(MoO<sub>2</sub>Cl<sub>4</sub>)<sup>2-</sup>. The addition of base to solutions of 12-MPA and 12-MSA

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 $PMO_{11}O_{39}^{7-}$  (12-MPA only), heptamolybdate ( $MO_7O_{24}^{6-}$ ), and orthomolybdate ( $MOO_4^{2-}$ ) as the pH is increased.

The  $\beta$  isomer of 12-MSA has also been investigated by Raman spectroscopy. Although group theoretical considerations of the modified Keggin structure predict 16 more Raman bands in the spectrum of the  $\beta$  form than in that of the  $\alpha$  isomer, few additional bands were observed. Comparison of the spectra of the  $\alpha$ - and  $\beta$ -12-tungstosilicic acid showed similar results.

Resonance Raman spectra of three reduced forms of 12-MPA (the heteropoly blues) have been obtained. The spectrum of the two-electron blue is indistinguishable from unreduced 12-MPA. Experimental limitations allowed only portions of the spectra of the four- and six-electron blues to be observed. The features which were observed indicate that the structure of 12-MPA is unchanged upon further reduction. Raman spectra of three molybdovanadophosphates, which are models for the heteropoly blues, have also been obtained. The spectra are consistent with the Keggin structure for these mixed-valence compounds.



to Mom, Dad, and Dan

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#### to bas fostel

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# CHAPTER I

## INTRODUCTION

The chemistry of Mo(VI) in aqueous solution is complex because the molybdenum can exist in numerous compounds, some of which have several isomers. These compounds and complexes are related through equilibria which are not yet fully characterized. The sensitivity of Raman spectroscopy to changes in structure and its applicability to aqueous samples indicate that the technique can provide valuable insight into the chemistry of molybdenum (VI).

A review of the chemistry of molybdenum (VI) oxo compounds is contained in Chapter II of this dissertation. Isopolymolybdates, heteropolymolybdates, and their relationships to each other are discussed. Attention is focused on the 12-A heteropolymolybdates, specifically 12-molybdophosphoric acid (12-MPA) and 12-molybdosilicic acid (12-MSA). Spectroscopic studies of isopolymolybdates and heteropolymolybdates are also reviewed in Chapter II. Infrared and Raman spectroscopic studies of 12-MPA and 12-MSA are emphasized.

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Raman spectroscopy is discussed in Chapter III. The advantages and disadvantages of the technique as a method for species identification are considered. Special problems arising from the study of colored materials are discussed along with the experimental techniques used to minimize these problems. A brief description of the Raman instrument used in this research is also included.

The degradation of 12-MPA and 12-MSA by hydroxide ion has been studied in the past by techniques, primarily ultracentrifugation (1) and electrochemistry (2), which are not sensitive to molecular structure. Raman spectroscopy has been applied in this work to examine the degradation processes previously reported. Chapter IV contains a discussion of the experiments; degradation schemes based on the Raman spectra of the species in solution at various pH values are presented. A modified version of Chapter IV will appear in the November-December 1978 issue of Applied Spectroscopy.

The existence of two forms of 12-MSA has been documented (3, 4, 5). The stable  $\alpha$  isomer is well characterized; however, the  $\beta$  isomer is unstable and consequently is less well characterized. No structural determination of  $\beta$ -12-MSA has been reported previously. The Raman spectrum of  $\beta$ -12-MSA is reported in Chapter V. Group theoretical arguments are employed to explain the differences between the observed spectra of the  $\alpha$  and  $\beta$ 

isomers. In addition, the Raman spectra of  $\alpha$ - and  $\beta$ -l2tungstosilicic acid (l2-WSA), compounds also known to have the basic Keggin-type structure, are compared with those of the molybdenum compound.

In Chapter VI, resonance Raman spectroscopic studies of some heteropoly blues are presented. The heteropoly blues considered here are reduced forms of 12-MPA. ESR data have been interpreted to indicate that the molecular structure of 12-MPA is unchanged upon reduction. That conclusion has been tested in this work.

The final chapter of this dissertation presents some ideas for further investigations of heteropolymolybdates with Raman spectroscopy as the primary technique.



### CHAPTER II

# Mo(VI) IN AQUEOUS SOLUTION--CHEMISTRY AND SPECTROSCOPY

The chemistry of Mo(VI) is extremely complex and has been extensively reviewed (6-14). This chapter presents a summary of the pertinent facts, including recent developments, and a summary of the spectroscopic studies of the oxo species of Mo(VI).

Molybdenum (VI) compounds containing oxygen can be divided into two basic categories: isopolymolybdates and heteropolymolybdates. Isopolymolybdates are those compounds composed of oxygen and more than one molybdenum, whereas heteropolymolybdates include not only molybdenum and oxygen, but also one or two heteroatoms such as phosphorus and silicon in the molecule.

# Isopolymolybdates

In basic aqueous solution, Mo(VI) exists as the tetrahedral orthomolybdate ion  $(MoO_4)^{2-}$ . Acidification of a solution of molybdate leads to the formation of various isopolymolybdates. The first step appears to

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be the protonation of the molybdate ion by one or two protons to form  $OMO(OH)_5^-$  or  $MO(OH)_6$ , both of which have been reported to be octahedral (15-18). However,  ${}^{95}MO$ and  ${}^{97}MO$  NMR spectra indicate that the species formed upon protonation is not octahedral, but the asymmetric  $\underline{cis}$ -dioxo- $MOO_2(H_2O)(OH)_3^-$  (19). When the bound acid-tomolybdate ratio (Z or  $\bar{n}$ ) reaches 1.14, the heptamer,  $MO_7O_{24}^{6-}$ , is formed. The kinetics of the basic decomposition of heptamolybdates has recently been studied (20).

Further acidification presumably leads to the formation of the octamer, which can be crystallized as the ammonium salt at Z = 1.5 (1, 17, 21-23). However, other workers have found no evidence for the octamer in solution (24, 25).

At the isoelectric point, molybdenum trioxide  $(MoO_3)$  precipitates. Upon further acidification, the molybdenum trioxide redissolves to form various molybdenyl cationic species (27). Evidence for both monomeric (28, 29) and dimeric (24, 30, 31) species has been found. Protonated and unprotonated monomeric and dimeric molybdenyl species have been reported by Krumenacker and coworkers (32-35). The formation constants were determined as a function of acidity (24, 34, 35). Others (36) found the monomer to be singly charged and the dimer doubly charged in perchloric acid solutions at a concentration greater than 3M. Ojo et al. (29)



determined equilibrium constants for the protonation and dimerization of the molybdenyl species which were in agreement with Krumenacker.

In highly acidic solutions in the presence of chloride ion, the molybdenum complexes with the chloride to form  $\underline{\text{cis}}$ - $(\text{MoO}_2\text{Cl}_4)^{2-}$  or  $\text{MoO}_2\text{Cl}_2$  (37).

# Heteropolymolybdates

Heteropolymolybdates, which exist in acid solution and are themselves strong acids, are classified by the ratio of molybdenum to heteroatoms (for example, 2:18 represents  $P_2Mo_{18}O_{62}^{\phantom{6}-}$ ). The structure and reactivity of a heteropoly acid are dependent primarily on the molybdenum to heteroatom ratio, although the heteroatom determines the reactivity to some extent. The heteropolymolybdates are discussed here according to classification; variations due to the nature of the heteroatom may be considered within each classification.

## 12-A Heteropolymolybdates

The 12-A heteropolymolybdates (general formula  $XMo_{12}O_{40}^{(8-n)-}$ , where n is the charge of X) are comprised of a central tetrahedron with the heteroatom, usually P, Si, As, Ti, or Zr, at the center and oxygens at the corners, surrounded by 12 molybdenum octahedra with a molybdenum at the center of each octahedron. The octahedra are linked by shared oxygen atoms. The structure



shown in Figure 1-A, which has T<sub>d</sub> symmetry, was first proposed by Keggin (38) in 1934, and has been confirmed for numerous 12-A heteropolymolybdates by X-ray crystallographic studies (38-44).

The 12-A heteropolymolybdates are known to decompose in solutions more acidic than pH 0.5 or more basic than pH 2 - 6 (exact pH depends on the particular heteropolymolybdate and its concentration). In acidic solution, the heteropolyacid decomposes and the molybdenum is found as various protonated species or as a molybdenum-chloride-oxygen complex in the presence of chloride ion. The addition of 20 to 28 equivalents of hydroxide ion per equivalent of heteropolymolybdate in solution results in degradation to simple orthomolybdate ion,  $MoO_A^{2-}$ , via several hetero- and/or isopolymolybdates (2). The number of equivalents of base required depends on the valence of the heteroatom and the chemistry of its simple acid. It has been proposed that 12-molybdophosphate anion (12-MPA) degrades first into an eleven complex,  $PMO_{11}O_{39}^{7-}$ , then possibly to the 10 heteropolymolybdate (45). Continued addition of hydroxide ion results in the formation of the octamolybdate,  $Mo_8O_{26}^{4-}$ , the heptamolybdate,  $Mo_7 O_{24}^{6-}$ , and finally  $MoO_4^{2-}$ . The degradation of 12-molybdosilicic acid (12-MSA) proceeds in an analogous fashion with the exception that no 11 or 10 complex is known for 12-MSA. The heteropoly acid





Polyhedral diagrams of the 12-A heteropolymolybdates and tungstates: (a) the  $\alpha$  isomer, (b) the  $\beta$  isomer. (Reprinted from reference 51 with permission of the Chemical Society of Japan.) Figure 1.


is thought to decompose directly to the heptamer and then to the orthomolybdate ion (2).

The addition of base to 12-MPA can also result in the conversion of the acid to  $P_2Mo_{18}O_{62}^{6-}$  via the 10-heteropolymolybdate. This conversion occurs only at high concentration (2).

One further complication in the chemistry of the 12-A heteropolymolybdates is the existence of two isomeric forms,  $\alpha$  and  $\beta$ , of these acids. Early analytical colorimetric procedures for determining silicon using 12-MSA were plagued by fading color of the 12-MSA. Strickland (3) interpreted this in terms of the existence of two forms of the 12-MSA. The  $\beta$  form results when the bound acid-to-molybdate ratio is greater than 2; the  $\alpha$ form results when the ratio is less than 1.5 (3-5). The unstable  $\beta$ -12-MSA transforms spontaneously and irreversibly to the  $\alpha$  form at a rate which depends on concentration, solvent, temperature, and pH (46). The  $\beta$ form of 12-MSA can be crystallized into bright yellow crystals which are hygroscopic and light sensitive. The ultraviolet spectra of  $\alpha$  and  $\beta$  12-MSA are identical in shape and position of the maximum (47). The primary difference is in the molar absorbtivity: that of the  $\beta$  isomer is approximately twice that of the  $\alpha$ . An additional distinction between the  $\alpha$  and  $\beta$  forms is in the polarographic half-wave potential, which indicates that the  $\beta$  form is more easily reduced than the  $\alpha$  (48).



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The structure of  $\beta$ -12-MSA has not been determined; however, several hypotheses have been suggested. Chalmers and Sinclair (49) suggest that three of the Mo-O octahedra are rotated 60° with respect to the rest of the molecule, as shown in Figure 1-B, which reduces the symmetry to  $C_{3v}$ . Others suggest that the Mo-O octahedra are distorted but not moved relative to one another. Thus the overall  $T_d$  symmetry of the molecule is maintained (3). The  $\alpha$  and  $\beta$  forms are presumed to exist for other 12-A heteropolymolybdates. The  $\beta$  form of 12-MPA is stable and does not convert spontaneously to the  $\alpha$ -12-MPA (3, 4, 50); the forms of most of the other 12-A heteropolymolybdates have not been investigated.

Sasaki and coworkers (51) have determined the structure of the  $\beta$ -l2-tungstosilicate ion. The structure they detected is that suggested by Chalmers and Sinclair (49) for the corresponding molybdosilicate anion; that is, three Mo-O octahedra are rotated 60° with respect to the rest of the anion. By analogy this conclusion suggests that the  $\beta$ -l2-MSA probably has this structure. Photographs of models of  $\alpha$  and  $\beta$ -l2-tungstosilicate ion from several viewpoints are shown in Figure 2.

### 12-B Heteropolymolybdates

The 12-B heteropolymolybdates have the formula  $(XMo_{12}O_{42})^{n-}$ , where n is 12 minus the charge of the



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Figure 2. Models of the  $\alpha$  and  $\beta$  isomers of the 12-A heteropolymolybdates.

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heteroatom. Metals such as Th and Ce are the heteroatom in this series (2). These compounds are also composed of molybdenum-oxygen octahedra; however, the octahedra share faces and the heteroatom is twelve-coordinate. A polyhedral diagram of the 12-B heteropolymolybdate anion is shown in Figure 3. The 12-B heteropolymolybdates are more stable to base degradation that the 12-A series; the cerium complex does not decompose until the pH is about 9 (57).

#### 11 Heteropolymolybdates

The ll heteropolymolybdates, which have  $B^{3+}$ ,  $p^{5+}$ ,  $As^{5+}$ , and  $Ge^{4+}$  as central atoms, are probable degradation products of the 12 heteropolymolybdates. The ll-molybdogermanate ion, which is the only ll-anion definitely known to exist (53), is found in solution at pH values between 4.8 and 5.4 (53, 54). Solid ll-molybdophosphates have been reported, but not confirmed. Baker et al. (55) report that dissolution of l2-MPA in a buffer at pH 4.8 results in the formation of a monomeric ll-molybdophosphate as indicated by ultracentrifugation. Other workers have also reported the existence of ll-molybdophosphates in solution (56).

#### Others

The 10 heteropolymolybdates (central atoms  $P^{5+}$ , As<sup>5+</sup>, and Pt<sup>4+</sup>) are presumed to be degradation products





Figure 3. Polyhedral diagram of the structure of the 12-B heteropolymolybdates. (Reprinted from reference 2 by permission of Climax Molybdenum Co.)



of the l2-heteropolymolybdates. However, their existence is still a matter of debate. The ether adduct of l0-MPA can be isolated (57).

The 9 heteropolymolybdates can exist as monomers (central atom  $Mn^{4+}$ , Ni<sup>4+</sup>) or dimers (central atom  $P^{5+}$ , As<sup>5+</sup>, and possibly  $Be^{2+}$ ) (2). X-ray crystallography and piezoelectric studies show that the monomeric molecules are asymmetric structures based on an XO<sub>6</sub> central octahedron (58). The dimeric 9 heteropolymolybdates contain two XO4 tetrahedra surrounded by MoO6 octahedra as shown in Figure 4. The structures of these compounds have not been determined by X-ray crystallography, although that of  $Na_6(P_2W_{18}O_{62}) \cdot 4H_2O$  has been (59). This molecule is composed of two identical units, each of which can be pictured as the Keggin structure with three octahedra removed (60). The structure of the analogous heteropolymolybdates is presumed to be the same. The dimeric  $(P_2Mo_{18}O_{62})^{6-}$  ion can be converted to  $(PMo_{12}O_{40})^{3-}$  by treatment with acid, and 12-MPA can be converted to the 2:18 molybdophosphate by treatment with hydroxide (43). The 2:18 complexes are formed under slightly less acidic conditions than the 12-anions. Although the range of conditions for formation is considerably narrower than that of the 12-anions, the 2:18 anions will exist under conditions unsuitable for formation (61, 62). The alkaline degradation of  $\alpha - P_2 W_{18} O_{62}^{6-}$  has been shown to









occur in three steps (63). The  $P_2W_{18}$  degrades first to tungstophosphate, then to  $\alpha - P_2W_{16}$  and  $\alpha - P_2W_{12}$ . The equilibria among these species and their isomers are complex.

#### Heteropoly Blues

Most heteropolymolybdates are easily reduced to form intensely blue colored reduction products. These "heteropoly blues" have been studied extensively, although no structural determination has been reported. The electrochemistry of the heteropolymolybdates has been reviewed (64); only pertinent facts related to the 12-A anions are presented here.

The heteropoly blues are formed by the addition of electrons to the oxidized form of the heteropoly acid, the maximum number of electrons being 8 - n, where n is the charge of the anion (65). If the pH of the solution is such that protonation can accompany reduction, additional electrons may be added. Robin and Day (66) have classified mixed valence complexes according to the degree of delocalization of the electrons. The Class II structures have electrons trapped on specific atoms with some delocalization occurring via thermal hopping. In the Class IIIA complexes, the added electrons are completely delocalized in multi-centered molecular orbitals. Pope and coworkers (67) found that when one electron is added to the 1:12 or 2:18 heteropolytungstate complexes,



the Class II model is most appropriate. Rabette et al. (68) studied 12-MSA and found the Class II model was valid for the addition of up to six electrons. ESR studies conducted by Pope and coworkers (69) suggest that the valence trapping model best fits the oneelectron reduction product of 12-MPA. The electron is localized on a single atom at very low temperatures; thermal activation leads to delocalization.

Souchay and coworkers (70, 71) have studied the electrochemical reduction of 12-MPA in strong acid solutions. The  $\beta$  form was reduced at a more positive potential than the  $\alpha$  form. Distinct stages in which two, four, and six electrons had been added were distinguishable.

Chemical reduction can be accomplished by a variety of mild reducing agents. Crouch and coworkers (31) and Yatsimirskii and coworkers (72) studied the reduction of 12-MPA by ascorbic acid. Other reducing agents, primarily iodide, thiourea, hydroquinone, Fe(II), and Sn(II), have also been studied (73). El-Shamy and Iskander (74) used spectrophotometry to study the stoichiometry of the reduction of 12-MPA by stannous chloride. Four steps in which one equivalent of Sn(II) was consumed per step were found. These steps corresponded to the reduction of two, four, six, and eight Mo(VI) atoms to Mo(V).



Mixed valence compounds containing V(V) and Mo(V) have been studied by Pope and coworkers as models for the heteropoly blues (75, 76). Optical and ESR spectra and polarographic redox potentials were interpreted in terms of the Class II structure in which the valence electron is trapped on the Mo(V) or V(V) atom in the molecule.

### Spectroscopic Studies

Spectroscopic techniques such as electron spin resonance, nuclear magnetic resonance, and optical, infrared, and Raman spectroscopy have been particularly useful in studying the heteropolymolybdates.

#### ESR Spectrometry

ESR has been used primarily in examining the heteropoly blues of both heteropolymolybdates and analogous heteropolytungstates (69, 75-77). This work has been discussed previously in this chapter.

#### NMR Spectrometry

Nuclear magnetic resonance spectrometry has also been used to study heteropolymolybdates (78-85). Lebedeva and Vanchikova (78) found that the relaxation time and chemical shift (relative to  $H_3PO_4$ ) in the <sup>31</sup>P NMR spectrum change with pH. This is interpreted as resulting from changes in the number of "ligands" in the complex. Phosphorus 31 NMR studies have also correlated the chemical shift to the structure of



various heteropolyanions of the form  $(PM_{12}O_{40})^{3-}$  or  $(P_2M_{18}O_{62})^{6-}$  (M = Mo, W) (79). The chemical shift of 24 heteropolyanions has been shown to change with the structural defects in the anions or substitutions of metal atoms, and correlates well with the changes in the infrared and Raman frequencies of the P-O vibrations observed for these compounds.

Gazarov and coworkers (80) have used proton NMR to study hydrates of 12-MSA and its sodium salt. Results indicate that 12-MSA is highly hydrated and is considerably less stable than 12-tungstosilicic acid.

Oxygen-17 NMR spectra of 12-MPA show peaks for the terminal oxygens and the two types on nonequivalent bridging oxygen atoms (81). The oxygen atoms bonded to the central phosphorus atom were not detected.

Proton NMR studies on the chain trimolybdate anion,  $(H_2Mo_3O_{11})_n^{2-}$ , have shown that the ratio of OH groups to water molecules is temperature dependent (82).

### Optical Spectroscopy

Optical spectroscopy has been a primary method for identifying the heteropoly blues and also for distinguishing between the  $\alpha$  and  $\beta$  forms of the heteropolymolybdates (2-5, 23, 46-47, 67, 74, 83-87). Kazanskii (88) has correlated the energy of the first electronic transition of heteropolymolybdates with the half-wave potential for reduction. The absorption band is due to



the  $\phi_0 \rightarrow \phi_1^*$  transition, where  $\phi_0$  is composed of the p orbitals of the bridging oxygen atoms and  $\phi_1^*$  also includes some Mo  $d_{xy}$  involvement. The reduction of the heteropolymolybdates involves adding an electron in the  $d_{xy}$  orbital. Kazanskii expected and found a linear relationship between the half-wave potential and the energy of the electronic transition.

### Infrared and Raman Spectroscopy

Infrared and Raman spectroscopy have been applied to the study of isopoly- and heteropolymolybdates and tungstates. Most of the work has been qualitative in nature with little or no attempt to make assignments of observed bands to specific vibrations.

Simple molybdates are known to be either four or six coordinate. Busey and Keller (89) studied several tetrahedral anions, including  $MOO_4^{2-}$  as  $Na_2MOO_4$  and  $Na_2MOO_4 \cdot 2H_2O$ , by both infrared and Raman spectroscopy. Band assignments based on  $T_d$  symmetry were presented. Clark and Doyle (90) studied the infrared spectra of solid anhydrous simple molybdates and tungstates, and interpreted the spectra in terms of site symmetry of the anions. Liegois-Duyckaerts and Tarte (91) combined single crystal and powder X-ray diffraction data with infrared and Raman measurements to make specific assignments of the infrared bands, including the low frequency external modes.



Isopolymolybdates have been investigated by several workers. Kiss, Holly, and Hild (92) studied the mid-infrared spectra of various ammonium polymolybdates. Terminal oxygen-molybdenum bond vibrations were particularly noted; the frequency shifts were correlated with increasing polymerization of the MoO<sub>6</sub> octahedra. The stretching vibrations of Mo-O bonds and Mo-O-Mo bridges were approximately assigned. Aveston, Anacker, and Johnson (1) used Raman spectroscopy along with ultracentrifugation and acidity measurements to identify the heptamolybdate ion,  $Mo_7 O_{24}^{6-}$ , in solution at Z = 1.14 and the octamolybdate ion,  $Mo_8O_{26}^{4-}$ , at Z = 1.5. Identification of these species was accomplished by comparison of the solution spectra with the spectra of solid heptamolybdate and octamolybdate. The structure of the solids had been determined by X-ray crystallography.

The vibrational spectra of heteropolymolybdates have been interpreted primarily in terms of the Keggin structure. One of the first studies of the vibrational spectra of a heteropoly compound was conducted by Sharpless and Munday (93). No specific assignment of the bands of the heteropoly acids or their ammonium salts was attempted, although frequency shifts upon changing the heteroatom (P, Si, As, B) or metal atom (Mo, W) were noted. Brown (94) obtained the infrared spectra of several heteropolytungstates and assigned bands to



the X-O (X = Si, P, B, CO(II)) or W-O vibrations without attempting assignment of a band to a specific vibration. Yuknevich (95) divided the anion into three regions: inner, exterior, and intermediate. He assigned the observed infrared bands to a given region based on the degree of frequency shift on varying the heteroatom or metal atom. However, he neglected to assign any vibrations to the central XO<sub>4</sub> tetrahedron (X = P, Si).

Lange, Hahn, and Dehnicke (96) studied both the Raman and infrared spectra of several heteropolyacids and their ether complexes. Their assignments, which are based on group frequencies, are interpreted in terms of the 15 internal modes expected from local C<sub>s</sub> symmetry at the Mo or W atom.

Rabette and Olivier (97) assigned specific bands to vibrations of different types of M-O bonds (M = Mo, W). Metal to terminal oxygen, metal-oxygen-metal bridges, and metal-oxygen-heteroatom vibrations were distinguished. Assignments were based on comparison with molybdenum trioxide and frequency shifts resulting from substitution of the central or metal atom, or changes in going from 12-MPA to the salt of  $P_2Mo_{18}O_{62}^{6-}$ .

Thouvenot and coworkers (98) reported the infrared and Raman spectra of 12-MPA, 12-MSA, and their tungsten analogs. They observed bands characteristic of the Keggin structure in the 650-800 cm<sup>-1</sup> and



300-400 cm<sup>-1</sup> region. Their band assignments are based on observed frequency shifts and comparison of Raman and infrared data. Thouvenot et al. (99) also studied the anions of the above acids. Vibrations of the XO<sub>4</sub> tetrahedron were observed; little influence of the rest of the molecule was noted. Comparisons of the molybdenum and tungsten anions were made again, with frequency shifts being noted. Spectra were interpreted to indicate that the molybdenum atom is closer to the center of the octahedron than is the tungsten atom. Rocchiccioli-Deltcheff and coworkers (100) made a complete assignment of the type of vibrations to specific observed bands.

Kazanskii (101) studied both crystalline and aqueous 12-MPA, 12-MSA, 12-WPA, and 12-WSA. Assignments, which are based on group frequencies, agree with previous workers. Complete coincidence of solid and solution spectra indicate that the anion maintains the Keggin structure in aqueous solution.

Lyhamn and coworkers (102-103) have also recorded the Raman spectrum of 12-MPA. In addition, they have constructed symmetry coordinates for the anion and executed approximate force field calculations based on dividing the molecule into four "ligands." The calculated values for the 12-MPA frequencies do not agree well with observed values. However, they are distributed in the same region as the observed frequencies.



## Conclusions

In this chapter, a summary of the relevant chemistry of molybdenum (VI) has been presented. Both isopolymolybdates and heteropolymolybdates have been discussed, with emphasis on the 12-A heteropolymolybdates which are the subject of this work. In addition, spectroscopic studies of molybdates, primarily the 12-A heteropolymolybdates, have been reviewed.



#### CHAPTER III

# LASER RAMAN SPECTROSCOPY AS A TECHNIQUE FOR IDENTIFYING SPECIES IN SOLUTION

Raman spectroscopy has long been recognized as a technique which is indicative of the structure of molecules. Before the advent of lasers, the experimental problems associated with Raman spectroscopy were monumental. The Raman effect is extremely weak (for a strong vibrational transition, approximately one in 10<sup>6</sup> photons undergoes Raman scattering [104]), thus a strong monochromatic source is required. The Toronto mercury arc was the primary source before the use of lasers. A filter was required to isolate a single line from those available from the arc; the intensity was barely sufficient. Photographic detection was generally used, and this involved the problems of nonlinear integration of the signal and the difficulties of measuring the wavenumber shifts accurately. The use of lasers as excitation sources has led to the simplification of the experimental procedures and to the rapidly expanding



utilization of Raman spectroscopy as a routine probe for identifying the predominant species in solution.

The combination of Raman and infrared vibrational spectroscopy has proved to be extremely powerful for determining the structure of molecules. The observation of Raman bands depends on a polarizability change during the vibration of a molecule (104); the observation of infrared bands depends on a change in dipole moment (105, 106). This difference results in complementary, rather than identical, information in the spectra. The knowledge of the polarization of the Raman bands and the positions and intensities of the Raman and infrared bands allows the use of group theory to evaluate the symmetry of the molecule. In addition, normal coordinate analysis can provide such information as force constants for given bond stretches and angle deformations (107). The data resulting from the mathematical and group theoretical analyses provide a reasonably complete picture of the molecular structure.

For the routine determination of the structure of complex molecules, a complete detailed analysis may be difficult or impossible because of the many parameters involved; even where such analysis is possible it may be extremely time consuming and will provide more information than is normally desired. Functional group analysis or identification by comparison of the spectra of a


standard and an unknown compound are more appropriate. The latter approach has been taken in this work.

This chapter contains a discussion of the advantages and disadvantages of Raman spectroscopy as a technique to identify species in solution. Both 12-MPA and 12-MSA are yellow solids and form yellow aqueous solutions; therefore, problems associated with the study of colored materials are described along with experimental solutions to these problems. Resonance Raman spectroscopy, which takes advantage of the absorption of light by colored materials, is also discussed. Finally, the chapter contains a brief description of the instrument used in this research. Details of the individual experiments are not provided here, but in the chapters in which the projects are discussed.

## Advantages of Raman Spectroscopy

Raman spectroscopy has several advantages over other techniques for probing the structure of molecules. The primary advantage is the ability to handle aqueous solutions (104). Water is a very poor Raman scatterer and consequently does not produce a spectrum which interferes with or obscures the spectrum of the molecules of interest. The need to extract the analyte into nonaqueous solvents is eliminated. The utilization of aqueous solutions is particularly important for biological samples which are almost universally in aqueous media.



The range of sample types which can be analyzed by Raman spectroscopy is virtually unlimited. Samples can be liquids, solutions, gases, powders, or single crystals (104). For example, the resonance Raman spectrum of  $\beta$ -carotene has been obtained from purified  $\beta$ carotene, carrot juice, and a whole carrot (108-110). Several Raman microprobes, which combine light microscopy and Raman spectroscopy, have been developed. Blaha and Rosasco (111) recently reported the spectra of individual microcrystals and fibers of various silicate minerals, including talc and tremolite. The instrument developed by Delhaye and Dhamelincort (112, 113), which is now commercially available, has been applied to the study of minerological samples and to biological samples. Raman spectra of specific parts of a cell are obtainable through use of a Raman microprobe (114).

A third advantage of Raman spectroscopy is sample size (104, 115, 116). The limit of minimum sample size is determined by the diameter of the laser beam, which can be focused down to a few micrometers. Liquid samples on the order of microliters are sufficient to obtain reasonable spectra. This is particularly important when only small amounts of sample are available.

Another advantage of Raman spectroscopy is that it is normally nondestructive. Although damage to the sample may occur due to the intensity of the laser



excitation beam, often this can be avoided and the sample recovered undamaged. This allows the spectra of <u>in vitro</u> or <u>in vivo</u> samples to be recorded, as exemplified by studies of the visual pigments in intact bovine retinas (117).

The final advantages of Raman spectroscopy to be discussed are the ease of obtaining low frequency spectra and the wide range of the instrument. Spectra can be obtained down to 20 cm<sup>-1</sup> with ease, and the complete 20 to 4000 cm<sup>-1</sup> range can be covered in a single scan on a single instrument. The ease of obtaining low frequency data is advantageous for the study of inorganic molecules or crystal effects.

## Disadvantages of Raman Spectroscopy

There are, of course, several disadvantages of Raman spectroscopy which limit the utility of the technique in an analytical laboratory. These disadvantages are low sensitivity, the dependence of absolute intensities on the instrument, fluorescence interference, and difficulties associated with the study of colored samples (104).

The problem of low sensitivity is inherent to the nature of the technique. The majority of the photons incident on the sample are transmitted; of those scattered, most experience no net energy transfer between the sample and the radiation beam (Rayleigh or elastic scattering).



Only a small fraction (at best one in 10<sup>6</sup>) of the incident photons undergo Raman inelastic scattering (104). The Raman scattered photons are divided between Stokes and anti-Stokes scattering. Stokes scattering occurs when the molecule is excited by one vibrational level and the photon has less energy by the amount corresponding to the vibrational excitation. In anti-Stokes scattering, the molecule is in a lower vibrational state after the scattering, and the photon has more energy by an amount corresponding to the vibrational transition. The weakness of the Raman effect necessitates the use of a very intense light source. The advent of lasers has virtually solved the light source problem but not the entire sensitivity problem. The relative abilities of the solvent and solute to act as Raman scatterers will determine the concentration necessary to obtain spectra. Resonance Raman spectra have been obtained of various heme proteins at or near physiological concentrations (118); however, solution concentrations are generally in the  $10^{-3}$  to 1.0 M range. The presence of solid particles in liquids or solutions causes light to be scattered into the monochromator; this Rayleigh scattering can obliterate the Raman spectrum, especially at low wavenumber shifts. Fortunately, this problem can usually be avoided by filtering the sample.

The intensity of the measured scattering depends heavily on instrument parameters such as monochromator



efficiency and photomultiplier sensitivity. Sample positioning is critical, as is focusing the scattered light onto the entrance slit of the monochromator. The first two parameters vary widely among instruments, and the latter two vary from sample to sample on a given instrument. This makes the establishment of standard spectra containing absolute intensities rather difficult. The relative intensities of bands within spectra are usually constant, however, and can be used in spectral characterization.

Fluorescence is frequently observed under the same experimental conditions as Raman scattering (104). The fluorescence signal is usually much stronger than the Raman signal; the Raman spectrum is then either totally obscured by the fluorescence or is observed superimposed on the fluorescence background. There are an increasing number of techniques to eliminate fluorescence interference. If the fluorescence is due to an impurity in the sample, it can be "burned out" by placing the sample in the laser beam for some time (which depends on the sample) until the impurity is destroyed (104). The introduction of quenchers which suppress the lifetime of the electronic state from which fluorescence arises also serves to reduce the fluorescence background (119). A more recent technique is to use a pulsed laser with picosecond pulses to discriminate between the Raman



scattering and fluorescence on the basis of their lifetime differences (107, 120-121); however, the extremely short pulses cause problems in detection. Coherent anti-Stokes Raman spectroscopy (CARS) is also utilized to avoid the fluorescence problem (122). CARS is a threewave mixing technique which allows the observation of an extremely intense anti-Stokes signal (123). Fluorescence is not a problem, since it is observed only in Stokes Raman scattering.

The final disadvantage of Raman spectroscopy to be considered is the difficulty of studying colored materials. The importance of this problem dictates that it be discussed in the following separate portion of this chapter.

# Problems Associated with Colored Samples

In the early days of Raman spectroscopy (before 1970), a rule of thumb for researchers interested in studying colored materials was "use a laser that is the same color as the sample." A green laser focused on a red sample quickly results in a decomposed sample.

There are two intimately related problems associated with studying colored materials: absorption and decomposition. The incident laser beam can be absorbed by the sample, which leads to a diminished signal and possibly to a destroyed sample. If the incident beam is



absorbed, fewer photons are available to be scattered. The scattered photons can also be absorbed, which again leads to a diminished signal. The incident beam can burn the sample if it is crystalline (this can occur even when white crystalline solids are studied) or cause solution samples to boil and to form a bubble where the laser beam impinges on the sample. In either case, if a Raman spectrum is obtained it is not that of the desired sample but rather that of a slightly charred material.

The incident laser beam can also induce photochemical reactions in the sample. Both 12-MPA and 12-MSA, for example, are subject to photoreduction. Unless an obvious physical change accompanies the photochemical reaction, this can be difficult to detect.

## Experimental Solutions

Fortunately, these problems usually can be solved without extraordinary effort. The simplest solution is to have the laser beam and the sample in motion relative to one another, in effect constantly bringing fresh sample into the laser beam. This can be accomplished by motion of the laser beam or by motion of the sample. A system has been designed which uses a rotating lens to scan the laser beam across the sample; the scattered light is simultaneously focused on the entrance slit of the monochromator (124, 125).



In actual practice, it is usually easier to move the sample than to move the laser beam. Since the original development of rotating cells by Kiefer and Bernstein (126, 127), rotating sample cells for both liquids and solids have been developed (128-130), as have cells for special applications including high temperature gas phase studies (131), Raman difference spectroscopy (132, 133), the superimposition of an external standard spectrum (134), and low temperature studies (135). Flow systems have also been developed (136); however, most of these require large sample volumes.

## Cell Design

As mentioned previously, 12-MPA and 12-MSA are susceptible to photoreduction, the extent of which is a function of laser wavelength, laser power, and solvent. The reduction problem was noted early in this research. Solid 12-MPA or 12-MSA in glass capillary tubes would "burn" under 500 mW of 514.5 nm radiation; aqueous solutions in capillaries would turn blue or green. Cooling the sample by blowing cold nitrogen over the capillary proved ineffective in preventing the destruction of the sample. A modification of the spinning cells described by Kiefer and Bernstein (126, 127) was employed to minimize the problem.

Two cells were constructed, one of glass, one of quartz, for aqueous solutions. Figure 5 shows the





Figure 5. Diagram of the spinning quartz cell.



cell design with dimensions for the quartz cell. Quartz windows are used for both top and bottom surfaces; quartz tubing comprises the body of the cell. The entrance port is a 10/18 standard taper ground glass fitting with small quartz protrusions on the female receptacle. These protrusions are used to bind the male plug securely to the cell. The glass cell is of similar construction.

The cell is mounted on a motor and spun rapidly; thus, the solution in the cell is forced into a one to three mm layer against the cell wall (the thickness of the layer depends on the sample volume). Figure 6 is a photograph of the spinning quartz cell in its normal position; Figure 7 shows the cell at an angle used for obtaining spectra of the heteropoly blues. The laser beam is focused through the layer of sample when the cell is in its normal position or focused onto the sample layer for the tilted cell. The scattered light is collected at 90° from the incident radiation. No photoreduction problems were noted using these cells for solutions with water as a solvent.

Heteropolymolybdate solutions in a 1:1 waterdioxane solvent exhibited photoreduction with 514.5 nm excitation even with spinning. The problem was noted first with  $\beta$ -12-MSA, but also occurred with  $\beta$ -12-MPA. However, no photoreduction was noted using 647.1 nm excitation. The 514.5 nm radiation is in or near the

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Figure 6. Photograph of the spinning cell in the upright position.

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Figure 7. Photograph of the spinning cell in the tilted position.



tail of the absorption profiles of both 12-MPA and 12-MSA  $(\lambda_{max} = 283 \pm 1 \text{ nm})$  and the absorption of the exciting light leads to the reduction.

## Resonance Raman Spectroscopy

In some instances the absorption of light by a sample can be advantageous. Resonance Raman spectroscopy is a technique which utilizes this absorption to obtain spectral information which is otherwise inaccessible. The theory of resonance Raman spectroscopy has been thoroughly described (137-144); its inclusion here is not appropriate.

Pre-resonance Raman scattering occurs when the excitation wavelength is near an absorption profile of the sample; in resonance Raman scattering the excitation wavelength is within an absorption band (143). In both cases, the Raman bands due to vibrations which are coupled to the electronic transition associated with the absorption are enhanced by a factor up to  $10^6$ . This is of particular importance for large molecules such as heme proteins (116, 145-153) and vitamin  $B_{12}$  (154). Only those vibrations associated with the chromophore (i.e., heme in hemoglobin) are enhanced. This allows the observation of a particular portion of the molecule with no interference from the remainder of the molecule.

The observed resonance enhancement of Raman bands allows the study of less concentrated samples than those



used in normal Raman spectroscopy (146), and thus enables the study of biological samples at or near physiological concentrations. Resonance Raman spectroscopy can also be used to monitor air pollutants because of the increased sensitivity arising from resonance (155, 156). The research on the heteropoly blues utilizes this practicality of lower concentration; a discussion of the use of resonance Raman spectroscopy in this research is included in Chapter VI.

## Description of the Instrument

The Raman spectrophotometer used in this project has been described previously (157); therefore, only a summary will be presented here.

The basic instrument is composed of a Jarrell-Ash 25-100 scanning double Czerny-Turner monochromator and associated optics followed by a thermoelectricallycooled RCA 31034A photomultiplier and a Hewlett-Packard 7100B strip chart recorder. A digital counter which monitors the wavenumber of the light passing through the monochromator has been constructed. A description of the counter is contained in the Appendix. Lasers available for use as the excitation sources are a Spectra-Physics Model 164 argon ion laser (1.1 W at 514.5 nm and 488.0 nm) and a Spectra-Physics Model 165 krypton ion laser (600 mW at 647.1 nm). Appropriate instrument

parameters will be provided in conjunction with the individual experiments.

The sample cell is placed in the laser beam as shown in Figures 6 and 7. The scattered light is collected at 90°, and is focused on the entrance slit of the monochromator. Since the laser beam normally passes through 15 mm of sample, a line rather than a point is focused on the slit. This has the advantage of filling the entire slit rather than only a small vertical portion.

Spectra are recorded in the normal manner. All options available on the instrument (such as polarization measurements) are usable with the spinning cell.

## Conclusions

The foregoing has included a brief discussion of the utility of Raman spectroscopy as a technique for identifying species in solution. The use of spectra of known reference compounds to identify the species in a solution provides one means of characterization. The wide variety of sample types, the small permissible size of the sample, the feasibility of studying aqueous samples, the nondestructive nature of Raman spectroscopy, and the ease of obtaining spectra at low wavenumber shifts are advantageous; however, the low sensitivity, fluorescence interference, and problems associated with intensity limit the utility of the technique.

Problems associated with the study of colored materials such as 12-MPA, 12-MSA, and the heteropoly blues have also been discussed. Judicious choice of solvent, sample cell, and excitation wavelength have been seen to minimize sample destruction and maximize the Raman signal. A brief description of the Raman instrument has also been included.



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#### CHAPTER IV

RAMAN SPECTROSCOPIC STUDY OF AQUEOUS SOLUTIONS OF 12-MPA AND 12-MSA OVER A WIDE pH RANGE

The 12-A heteropolymolybdates, including 12-MPA and 12-MSA, are known to decompose in aqueous solution at both lower and higher pH values than those of the dissolved solids, which are approximately 1.0 (2). Although decomposition schemes based on indirect techniques such as electrochemistry or ultracentrifugation have been proposed for heteropolymolybdates (1, 2), no method which characterizes molecular structure has yet been applied to the decomposition process. The study described here was conducted to determine the utility of Raman spectroscopy as a technique to identify the major molybdate species in solution and to test the decomposition schemes based on the indirect ultracentrifugation and electrochemical techniques.

In this chapter the Raman spectra of 0.1  $\underline{M}$ aqueous solutions of 12-MPA and 12-MSA over a wide pH range are described. The assignment of species to a

given pH range is discussed, and the pH-dependent decomposition schemes for the two compounds are presented.

#### Experimental Method

The heteropoly compounds were obtained from commercial sources (12-MPA: Climax Molybdenum Co.; 12-MSA: Pressure Chemical Co.). Spectra of recrystallized 12-MPA and 12-MSA were indistinguishable from the spectra of unrecrystallized material. Therefore, both were used without further purification. Both compounds are reduced on contact with metal surfaces and must be handled with glass or plastic implements and storage vessels.

Both 12-MPA and 12-MSA are highly hydrated (up to 31 waters of hydration). The compounds used in this research had an undetermined amount of water in the crystals. Karl-Fischer determination of the water is inappropriate because the samples are highly acidic. Since 29-31 moles of water are usually present unless measures are taken to eliminate them, 30 moles of water were assumed in the calculation of the solution concentration. The concentration of the heteropolymolybdate solutions was approximately 0.1 <u>M</u>. Evaluation of Raman spectra of 12-MPA and 12-MSA solutions at different concentrations (no pH adjustment) revealed no differences due to concentration changes. The pH of 0.1 <u>M</u> solutions of 12-MPA and 12-MSA was approximately 0.9. The pH of

each solution studied was adjusted to the desired value over the pH range of -1.0 to 13.5 to within ±0.1 pH unit with either 50% NaOH or concentrated HCl. The pH of solutions less than pH = 1 (except those with no adjustment) were calculated from the amount of added acid ignoring activity effects; the pH of other solutions was measured using a standard glass pH electrode and a Heath pH meter. The solutions were stored in glass initially but were transferred to plastic containers to eliminate leaching of silicon by free molybdate. The pH of each solution was checked immediately before the Raman spectrum was obtained.

Attempts to find the monomeric and dimeric molybdenyl species described in Chapter II were unsuccessful because solid 12-MPA and 12-MSA do not dissolve in acids other than HCl. If the heteropoly acid is made in solution and then acidified with  $H_2SO_4$ ,  $HNO_3$ , or  $HClO_4$ , it decomposes as evidenced by a change from yellow to colorless solution (158). However, the structural consequences could not be monitored by Raman spectroscopy because the concentration of the heteropoly acid was too low.

The Raman instrument is described in Chapter III. Spectra were recorded for each solution in the 70 cm<sup>-1</sup> to 1100 cm<sup>-1</sup> region using 514.5 nm excitation. All spectra reported were obtained using the 514.5 nm line



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of the argon ion laser unless otherwise noted. Intensities were calibrated relative to the strongest peak in each spectrum. No attempt was made to determine absolute intensities. Polarization data were obtained using a polaroid film analyzer.

The absorbance of the concentrated solutions in the visible region was measured with a Perkin-Elmer Model 572 spectrophotometer; the electronic absorption maxima were obtained for  $10^{-5}$  <u>M</u> solutions using a Cary 17 spectrometer.

# Electronic Spectra of 12-MPA and 12-MSA and Implications

The electronic absorption maximum,  $\lambda_{max}$ , is 283 ± 1 nm for both 12-MPA and 12-MSA. The molybdophosphate solution is light yellow, and 0.1 <u>M</u> solutions show detectable absorbance into the visible range to 520 nm; the yellow green molybdosilicate solution absorbs out to 500 nm. It is thus possible that resonance or preresonance enhancement of the Raman scattering might be observable, and we therefore compared the Raman spectra of 0.1 <u>M</u> solutions of 12-MPA and 12-MSA (no pH adjustment) obtained with 647.1, 514.5, and 488.0 nm excitation. However, within the experimental uncertainty of the relative intensity measurements, none of the Raman bands was intensified as the excitation energy more closely matched the electronic absorption maximum. Indeed, the



overall Raman scattering intensity was diminished at 488.0 nm in comparison to that at 514.5.

Spectra could not be obtained using 441.6 nm excitation (159). The extremely high absorbance (> 3) of 12-MPA necessitated dilution to the extent that only the Raman bands at ~1000 cm<sup>-1</sup> were observable. There appeared to be no resonance enhancement of these bands.

### 12-Molybdophosphoric Acid

The spectrum of aqueous 0.1 <u>M</u> 12-MPA with no pH adjustment is shown in Figure 8. Peak frequencies of the Raman spectra of 12-MPA at various pH values are listed in Table 1. The spectrum of 12-MPA at the "normal" pH of 0.9 agrees well with previous reports (98, 99, 101-103). A detailed analysis of this spectrum is unwarranted. However, the following general features should be noted. The P-O stretch is found at 996 cm<sup>-1</sup>; Mo-O stretches are in the 600 to 975 cm<sup>-1</sup> region; and the bridge stretches and deformations are in the 250 to  $600 \text{ cm}^{-1}$  region (102, 103).

When dissolved in concentrated HCl, the Raman spectrum is completely different. Comparison of the spectra at pH 0.9 and -0.9 shows the disappearance of the 998 and 979 cm<sup>-1</sup> peaks, which are due to the vibrations of the PO<sub>4</sub> tetrahedron and the "breathing" motion of the entire anion, and the appearance of a new band at 962 cm<sup>-1</sup>. This is readily apparent in the spectra







						wavenu	umber (cm	-1)*						
6.3         336(5)         897(10)         842(2) </th <th>12.8</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th>896(10)</th> <th></th> <th>835(3)</th> <th></th> <th></th> <th></th> <th></th> <th></th>	12.8						896(10)		835(3)					
5.6       97(10)       95(4)       96(4)       719(2)       649(1)       603(-1)         3.4       970(10)       955(5)       922(3)       868(3)       551(3)       603(-1)         3.4       970(10)       956(7)       926(7)       902(3)       868(3)       651(3)       691(3)         1.5       97(1)       974(10)       956(7)       901(3)       870(2)       651(3)       691(4)         0.9       986(10)       978(1)       956(7)       901(3)       870(2)       651(1)       657(1)       631(1)         0.9       986(10)       978(1)       956(7)       901(3)       870(2)       651(1)       631(1)       631(4)         0.9       986(10)       978(1)       954(8)       902(3)       868(3)       657(4)       632(1)       631(4)         0.9       986(10)       978(1)       868(1)       868(3)       868(3)       657(4)       631(1)       631(4)<	6.3				939(6)		897(10)		842(2)					
	5.6				941(10)		896(4)							
$3.4$ $900(10)$ $956(7)$ $926(3)$ $866(3)$ $657(1)$ $657(1)$ $493(\frac{1}{3})$ $1.5$ $974(10)$ $956(7)$ $901(3)$ $870(2)$ $657(1)$ $657(1)$ $494(\frac{1}{3})$ $0.2$ $996(10)$ $974(10)$ $956(7)$ $900(2)$ $870(\frac{1}{3})$ $657(\frac{1}{3})$ $657(\frac{1}{3})$ $494(\frac{1}{3})$ $0.2$ $996(10)$ $974(7)$ $954(8)$ $900(2)$ $870(\frac{1}{3})$ $653(1)$ $603(2)$ $494(\frac{1}{3})$ $0.2$ $962(10)$ $954(8)$ $900(2)$ $927(3)$ $800(\frac{1}{3})$ $617(2)$ $496(\frac{1}{3})$ $0.2$ $952(10)$ $952(10)$ $923(3)$ $901(\frac{1}{3})$ $901(\frac{1}$	4.4		976(10)		955(sh)(4)		903 (2.)	865(2)			719(2)	649(1)	603(<1)	465
1.5         974(10)         974(10)         974(10)         956(7)         961(3)         870(2)         867(3)         867(3)         863(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         930(1)         931(1)         653(1)         603(2) $494(3)$ 0.3         960(10)         978(7)         963(10)         963(10)         963(10)         923(3)         902(3)         800(1)         803(1)         603(2)         494(3)           10.3         962(10)         962(10)         962(10)         923(3)         319(3)         808(1)         303(1)         601(2)         963(1)         104(4)           12.8         362(1)         362(1)         319(3)         216(2)         216(2)         216(2)         104(4)           12.8         332(1)         361(1)         335(3)         216(2)         216(2)         104(1)         104(1)           14.4         339(1)         335(3)         335(3)         218(2)         218(2)         218(2)         104(1)         104(1)           15.1         335(3)         335(3)         335(3)         318(3)         136(1)         104(1)	3.4		970(10)		959(9)		902(3)	868(3)				651 (I <sub>3</sub> )		
0.9       998(10)       979(8)       968(4)       902(3)       867( $\frac{1}{3}$ )       653(1)       603(2)       494( $\frac{1}{3}$ )         0.3       996(10)       978(7)       954(8)       902(3)       902(3)       653(1)       601(2)       496( $\frac{1}{3}$ )         0.3       996(10)       978(7)       952(10)       923(3)       316(5)       308( $\frac{1}{3}$ )       653(1)       601(2)       496( $\frac{1}{3}$ )         12.8       362(1)       923(3)       319(3)       319(3)       216(2)       216(2)       104(-1)         13.4       313(1)       362(1)       319(3)       216(2)       216(2)       216(2)       104(-1)         14.4       319(1)       339( $\frac{1}{3}$ )       216(2)       216(2)       216(2)       104(-1)       107(1)         3.4       317(1)       313( $\frac{1}{3}$ )       313( $\frac{1}{3}$ )       216(2)       216(2)       216(1)       107(4)         1.5       317(1)       313( $\frac{1}{3}$ )       313( $\frac{1}{3}$ )       216(2)       217(2)       104(-1)       107(4)         1.5       317(1)       344( $\frac{1}{3}$ )       344( $\frac{1}{3}$ )       217(2)       206(1)       196(1)       107(4)         1.5       317(1)       246(2)       217(2)       210(1)	1.5	667(1)	974(10)		956(7)		901(3)	870(2)				657(1)	4	93( ½)
-0.3       966 (10) $737 (1)$ 953 (3)       902 (3) $653 (1)$ $601 (2)$ $496 (\frac{1}{2})$ -0.3       962 (10)       962 (10)       923 (3)       908 ( $\frac{1}{2} )$ 653 (1)       601 (2) $496 (\frac{1}{2} )$ 12.8       1362 (1)       319 (3)       316 (5)       216 (2)       216 (2)       104 (-1)         12.8       335 (1)       319 (3)       216 (2)       216 (2)       216 (2)       104 (-1)         14.4       379 (1)       233 (1)       335 (\frac{1}{2} )       233 (2)       216 (2)       104 (-1)       104 (-1)         3.4       374 (1)       374 (1)       335 (\frac{1}{2} )       233 (2)       216 (2)       157 (1)       102 (1)         1.5       374 (1)       344 (\frac{1}{2} )       335 (\frac{1}{2} )       233 (2)       216 (2)       164 (1)       107 (4)         1.5       372 (1)       344 (\frac{1}{2} )       344 (\frac{1}{2} )       249 (2)       217 (2)       206 (1)       159 (1)       107 (4)         0.3       372 (1)       374 (\frac{1}{2} )       249 (2)       217 (2)       206 (1)       196 (1)       107 (4)         0.3       371 (1)       344 (\frac{1}{2} )       245 (2)       217 (2)       206 (1)       196 (1) <td>0.9</td> <td>998(10)</td> <td>979(8)</td> <td>968(4)</td> <td></td> <td></td> <td>900(2)</td> <td>867(I<sub>3</sub>)</td> <td></td> <td></td> <td></td> <td>653(1)</td> <td>603(2) 49</td> <td>94 (<sub>15</sub> ) 461</td>	0.9	998(10)	979(8)	968(4)			900(2)	867(I <sub>3</sub> )				653(1)	603(2) 49	94 ( <sub>15</sub> ) 461
-0.9       962(10)       923(3)       808( $\frac{1}{3}$ )         12.8       316(5)       216(2)       104(-1)         12.8       362(1)       316(5)       216(2)       104(-1)         6.3       356(1)       319(3)       216(2)       104(-1)         6.3       379(1)       239(1)       214(2)       107(1)         9.4       379(1)       237(1)       214(2)       107(1)         3.4       379(1)       335( $\frac{1}{3}$ )       235( $\frac{1}{3}$ )       107(1)         3.4       379(1)       335( $\frac{1}{3}$ )       235( $\frac{1}{3}$ )       107(1)         3.4       370(1)       343( $\frac{1}{3}$ )       249(2)       233(2)       156(1)       107(4)         0.9       372(1)       343( $\frac{1}{3}$ )       249(2)       217(2)       206(1)       156(1)       107(4)         0.1       371(1)       344( $\frac{1}{3}$ )       249(2)       217(2)       206(1)       156(1)       107(4)         0.1       413(1)       249(1)       248(1)       217(2)       206(1)       156(1)       107(4)	-0.3	601)966	978(7)		954(8)		902(3)					653(1)	601(2) 49	96 (1 <sub>5</sub> ) 461
12.8 $316(5)$ $316(5)$ $316(5)$ $316(5)$ $316(2)$ $316(2)$ $104(1)$ 5.6 $415(1)$ $329(1)$ $319(3)$ $216(2)$ $216(2)$ $104(1)$ 5.6 $415(1)$ $379(1)$ $214(2)$ $214(2)$ $104(1)$ 4.4 $379(1)$ $379(1)$ $214(2)$ $214(2)$ $104(1)$ 3.4 $379(1)$ $335(1)$ $335(1)$ $214(2)$ $214(2)$ $104(1)$ 1.5 $374(1)$ $374(1)$ $374(1)$ $378(2)$ $218(2)$ $218(2)$ $104(1)$ 0.9 $375(1)$ $343(1_3)$ $343(1_3)$ $343(1_3)$ $210(1)$ $107(2)$ $104(1)$ 0.9 $372(1)$ $344(1_3)$ $344(1_3)$ $249(2)$ $217(2)$ $206(1)$ $107(1)$ 0.9 $371(1)$ $249(1)$ $249(1)$ $206(1)$ $107(1)$ $107(1)$ 0.9 $311(1)$ $248(1)$ $249(1)$ $206(1)$ $107(1)$ $105(2)$	-0.9			962(10)		923(3)				808( 1/2)	-			
$6.3$ $362(1)$ $319(3)$ $216(2)$ $216(2)$ $104(4)$ $5.6$ $415(1)$ $214(2)$ $214(2)$ $107(1)$ $107(1)$ $4.4$ $379(1)$ $218(2)$ $233(2)$ $157(1)$ $107(1)$ $4.4$ $374(1)$ $335(t_3)$ $335(t_3)$ $248(2)$ $233(2)$ $157(1)$ $107(1)$ $3.4$ $374(1)$ $335(t_3)$ $335(t_3)$ $248(2)$ $233(2)$ $157(1)$ $107(1)$ $3.4$ $374(1)$ $335(t_3)$ $335(t_3)$ $348(t_3)$ $248(2)$ $233(2)$ $154(1)$ $107(4)$ $0.9$ $370(1)$ $344(t_3)$ $344(t_3)$ $249(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ $0.3$ $371(1)$ $248(1)$ $249(2)$ $217(2)$ $206(1)$ $154(1)$ $105(2)$ $0.3$ $371(1)$ $248(1)$ $217(2)$ $206(1)$ $154(1)$ $105(2)$ $105(1)$ $105(2)$ $105(1)$ $105(2)$ $105(1)$ $105(2)$ $105(1)$ $105(2)$ $105(1)$ $105(2)$ $105(1)$ <td< td=""><td>12.8</td><td></td><td></td><td></td><td></td><td></td><td>316(5)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></td<>	12.8						316(5)							
5.6 $415(1)$ $214(2)$ $214(2)$ $214(2)$ $107(1)$ 4.4 $379(1)$ $248(2)$ $233(2)$ $157(1)$ $107(1)$ 3.4 $374(1)$ $335(_3)$ $335(_3)$ $248(2)$ $233(2)$ $157(1)$ $107(1)$ 3.4 $374(1)$ $335(_3)$ $335(_3)$ $248(2)$ $233(2)$ $154(1)$ $102(3)$ 1.5 $376(1)$ $343(_3)$ $343(_3)$ $343(_3)$ $249(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ 0.9 $372(1)$ $344(_3)$ $249(_2)$ $217(2)$ $206(1)$ $154(1)$ $107(4)$ 0.3 $371(1)$ $344(_3)$ $249(_2)$ $217(2)$ $206(1)$ $154(1)$ $107(4)$ 0.3 $371(1)$ $249(_3)$ $249(_2)$ $217(2)$ $206(1)$ $154(1)$ $105(2)$	6.3			362(1)			319(3)				216(2)			
$4.4$ $379(1)$ $248(2)$ $233(2)$ $157(1)$ $107(1)$ $3.4$ $374(1)$ $335(t_3)$ $335(t_3)$ $335(t_3)$ $154(1)$ $102(3)$ $3.4$ $376(1)$ $343(t_3)$ $335(t_3)$ $218(2)$ $158(1)$ $104(4)$ $1.5$ $376(1)$ $343(t_3)$ $243(t_3)$ $229(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ $0.9$ $372(1)$ $344(t_3)$ $249(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ $0.3$ $371(1)$ $341(t_3)$ $211(1)$ $248(1)$ $206(1)$ $154(1)$ $105(2)$ $0.9$ $413(1)$ $241(1)$ $248(1)$ $206(1)$ $154(1)$ $105(2)$	5.6	415(1)							251(1)		214(2)			104(<1)
$3.4$ $374(1)$ $335(\frac{1}{2})$ $335(\frac{1}{2})$ $154(1)$ $102(3)$ $1.5$ $376(1)$ $343(\frac{1}{2})$ $343(\frac{1}{2})$ $229(2)$ $158(1)$ $104(4)$ $0.9$ $372(1)$ $343(\frac{1}{2})$ $249(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ $0.3$ $372(1)$ $344(\frac{1}{2})$ $249(2)$ $217(2)$ $206(1)$ $154(1)$ $105(2)$ $0.3$ $371(1)$ $341(\frac{1}{2})$ $311(1)$ $248(1)$ $201(1)$ $154(1)$ $105(2)$	4.4		379(1)						248(2)	233(2)			157 (1 )	(1)/01
1.5 $376(1)$ $343(i_3)$ $243(i_3)$ $158(1)$ $104(4)$ 0.9 $372(1)$ $344(i_3)$ $344(i_3)$ $249(2)$ $217(2)$ $206(1)$ $159(1)$ $107(4)$ -0.3 $371(1)$ $245(2)$ $206(1)$ $154(1)$ $105(2)$ -0.9 $413(1)$ $241(1)$ $241(1)$ $241(1)$ $221(1)$	3.4		374(1)		335(1 <sub>2</sub> )						218(2)		154 (1 )	102(3)
0.9     372(1)     344(1 <sub>3</sub> )     249(2)     217(2)     206(1)     159(1)     107(4)       -0.3     371(1)     245(2)     206(1)     154(1)     105(2)       -0.9     413(1)     241(1)     248(1)     221(1)	1.5		376(1)		343(1 <sub>2</sub> )					229(2)			158(1)	104(4)
-0.3     371(1)     245(2)     206(1)     154(1)     105(2)       -0.9     413(1)     2413(1)     221(1)	0.9		372(1)		$344(_{1_2})$				249(2)		217(2)	206(1)	159(1)	107(4)
-0.9 413(1) 248(1) 221(1)	-0.3		371(1)						245(2)			206(1)	154(1)	105(2)
	-0.9	413(1)						311(1)	248(1)		221(1)			

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 $\sim$ 

Table l



shown in Figure 9. The spectrum at pH = -0.9 corresponds to that of <u>cis</u>- $(MoO_2Cl_4)^{2-}$  reported by Griffith and Wickins (37). Spectra of 12-MPA in less concentrated HCl are identical to those of the "normal" 12-MPA.

As the pH is raised by addition of NaOH, the first change in the Raman spectrum occurs in the pH range 1.5<pH<5.0. The bands at 998, 603, 465, 249, and 208  $\rm cm^{-1}$  have disappeared, and the peak at 974  $\rm cm^{-1}$ has increased in intensity. New bands appear at 959, 335, and 216 cm<sup>-1</sup>. Previous reports have indicated that 12-MPA decomposes to an ll-complex  $(PMO_{11}O_{39})^{7-}$ then to  $(Mo_8O_{26})^{4-}$  (2). The spectrum in the 1.5 -5.0 pH range does not agree with the spectrum of the octamer; and, therefore, the predominant species in the solution cannot be  $(Mo_8O_{26})^{4-}$ . The most likely candidate is, therefore, the ll complex  $(PMO_{11}O_{39})^{7-}$ whose Raman spectrum has not been reported previously. The anion  $(PMO_{11}O_{39})^{7-}$  is known to exist in buffers in the pH 4.8 region (2). However, the spectrum of  $(PMO_{11}O_{39})^{7-}$  could not be verified independently since the strongest bands in the Raman spectrum of the most applicable buffer (acetic acid-acetate) are in the 900-1000 cm<sup>-1</sup> region and obscure the spectrum of the heteropolymolybdate. The spectra of the buffer and 12-MPA dissolved in the buffer are shown in Figure 10. The band at  $\sim 1000 \text{ cm}^{-1}$  in the spectrum of 12-MPA at













pH 4.8 of Figure 11 is definitely asymmetric. It appears to be composed of two bands, a very sharp component at 976 cm<sup>-1</sup> and a broader band at 965 cm<sup>-1</sup> which are unresolvable. These two bands are assigned to the P-O (976 cm<sup>-1</sup>) and Mo-O<sub>terminal</sub> (965 cm<sup>-1</sup>) stretches in correspondance with the assignment of bands in 12-MPA (102, 103). The presence of the P-O band indicates that the phosphorus atom is still contained in the anion, and thus lends credence to the assignment of this spectrum to  $(PMO_{11}O_{39})^{7-}$ . The spectrum of  $(PMO_{11}O_{39})^{7-}$  in the region 50 to 1100 cm<sup>-1</sup> is shown in Figure 11. No Raman spectrum of this anion has been reported previously.

A buffer at pH 4.8 was made by combining KHP and NaOH in appropriate ratios in an attempt to find a buffer which did not obscure the bands of the molybdate species (55). Addition of 12-MPA to the buffer resulted in the immediate formation of an opaque yellow solution from which a yellow solid precipitated. The 12-MPA apparently reacts with the phthalate ion to form the precipitate, which is consistent with the known reactions of 12-MPA and certain carbonyl compounds (3).

A search was made for  $(Mo_8O_{26})^{4-}$  by repeatedly adding small amounts of NaOH to the molybdate solution and recording the Raman spectrum after each addition. No evidence for species other than  $(PMo_{11}O_{39})^{7-}$  was found in this pH range.





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The next distinct change occurs at a pH of 5.6. The spectrum consists of six bands (939, 897, 842, 362, 319, and 216 cm<sup>-1</sup>) whose frequencies and relative intensities agree well with those of  $Mo_7O_{24}^{6-}$  on the basis of comparison with the spectrum of solid  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1). The Raman spectra of solid ammonium heptamolybdate, aqueous ammonium heptamolybdate (pH 5.6) and 12-MPA at pH 5.6 obtained in this laboratory are shown in Figure 12. The identity of the molybdate species in the 12-MPA solution at this pH is readily apparent.

The Raman spectrum is distinctly different in media of high pH. Only three bands appear, at 896, 835, and 316 cm<sup>-1</sup>. This simple spectrum is characteristic of the tetrahedral orthomolybdate ion,  $MoO_4^{2-}$  (89).

The changes in the Raman spectra suggest the following decomposition scheme which confirms conclusions drawn from electrochemical data (2):

 $\underbrace{\operatorname{cis-(MoO_2Cl_4)}^{2-}}_{(PMO_{11}O_{39})}^{2-} \underbrace{\operatorname{conc. HCl}}_{(PMO_{12}O_{40})}^{(PMO_{12}O_{40})} \xrightarrow{3-} \underbrace{\operatorname{base}}_{(MoO_4)}^{2-} \underbrace{\operatorname{base}}_{(MoO_7O_{24})}^{6-} \underbrace{\operatorname{base}}_{(MoO_4)}^{2-}$ 

The pH at which these changes occur is somewhat dependent on the overall molybdate concentration; therefore, the pH values given in the above discussion must be considered approximate.

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Figure 12. Raman spectra of heptamolybdate: (a) 12-MPA at pH 5.6, (b) 0.1  $\underline{M}$  (NH<sub>2</sub>)<sub>6</sub> Mo<sub>7</sub>O<sub>24</sub>, pH = 5.6, (c) solid (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub> O<sub>24</sub>. \* indicates laser plasma line.



### 12-Molybdosilicic Acid

The changes in the Raman spectra of aqueous solutions of 12-MSA over the pH range of -0.9 to 13.5 are in most respects analogous to those of 12-MPA. The peak frequencies and relative intensities of the spectra of 0.1  $\underline{M}$  12-MSA solutions at various pH values are listed in Table 2.

In concentrated HCl the spectrum is again that of  $\underline{\operatorname{cis}} - (\operatorname{MoO}_2 \operatorname{Cl}_4)^{2-}$  (37). In less acidic media the spectra are essentially the same as that of 12-MSA in aqueous solution with no pH adjustment (pH = 0.9, Table 2), which agrees well with literature reports (98, 99).

In contrast to 12-MPA, no change in the spectrum of the 12-MSA solutions is noted at pH < 6. There is no evidence of another species containing the silicon atom or of  $(Mo_8O_{26})^{4-}$ . At pH = 6, the Raman spectrum is again that of  $(Mo_7O_{24})^{6-}$ . At pH > 10, the spectrum is the simple, three-band  $(MoO_4)^{2-}$  spectrum.

The decomposition scheme for 12-MSA based on the changes in the Raman spectra may be written:

 $\underbrace{\operatorname{cis}}_{\operatorname{MoO}_2\operatorname{Cl}_4}^{\operatorname{Cis}} (\operatorname{MoO}_2\operatorname{Cl}_4)^{2-} \underbrace{\operatorname{conc. HCl}}_{\operatorname{Koo}_{12}\operatorname{O}_{40}}^{\operatorname{SiMO}_{12}\operatorname{O}_{40}}^{4-} \underbrace{\operatorname{base}}_{\operatorname{Koo}_4}^{\operatorname{MoO}_2\operatorname{Cl}_4}^{\operatorname{MoO}_2\operatorname{Cl}_4} (\operatorname{MoO}_4)^{2-} \underbrace{\operatorname{MoO}_4}^{2-} \underbrace{\operatorname{M$ 



Hd								wavenumb	er (cm <sup>-1</sup> )*				
13.3					892(10)	839(2)							
6.7			936(4)		895(10)	836(2)							
4.8	979(10)	958(7)		915(1)	892(2)		807(< <sup>i</sup> )	678(1)	616(3)	489(1)	459(1)		368(1)
2.8	981(10)	959(4)		914(7)	891(1)		812(< <sup>1</sup> <sub>2</sub> )	678(1)	615(2)	(1)067	460(1)		368(' <sub>2</sub> )
1.9	982(10)	961(7)		919(1)	893(2)		810(< <sup>1</sup> <sub>2</sub> )	681(1)	619(2)	493(1)	462(1)		367(1)
0.9	979(10)	958(7)		918(1)	890(2)		807 (< <sup>i</sup> <sup>2</sup> )	676(1)	619(2)	(I)767	459(2)		369(1)
-0.4	983(10)	961(7)		917(1)	893(2)		807 (< <sup>1</sup> <sub>2</sub> )	675(1)	617(2)	( <sup>7</sup> )867	463(2)		365(1)
-0.9	983(8)	961(10)		922 (< <sup>1</sup> <sub>2</sub> )				.9	25(< <sup>1</sup> ,)			( <sup>7</sup> ) 905	
13.3	316(8)												
6.7	315(3)				213(1)								
4.8				244(4)	207(4)	160(2)	107(5)						
2.8			291 (< <sup>1</sup> <sub>2</sub> )	245(2)	207(2)	159(1)	107(3)						
1.9				246(2)	209(2)	160(1)	109(3)	68(1)					
0.9				247(3)	209(3)	161(1)	107(3)	70(1)					
-0.4			291 (< <sup>1</sup> <sub>2</sub> )	247(2)	208(2)	161(1)	109(3)						
-0.9		309 (1 <sub>2</sub> )		250(1)	218(1)								

Table 2

Raman Spectra of 12-MSA at Representative pH Values



This scheme is analogous to that of 12-MPA with the exception of the 11 anion and again confirms that proposed on the basis of electrochemical data (2).

Infrared spectra of aqueous solutions of 12-MPA and 12-MSA yielded little information because of the absorbance of water (160). Only the bands above 800 cm<sup>-1</sup> could be observed, and these only as small peaks superimposed on the water background. The spectra show qualitatively the same changes as the Raman spectra.

## The Fate of the Heteroatom upon Decomposition

When acid or base is added to the heteropolymolybdate solution, the heteroatom is no longer found in the molybdate species. No peaks were observed in the Raman spectra which could be attributed to phosphate or silicate species.

The phosphorus atom can exist as several soluble phosphates, primarily  $PO_4^{3-}$  and  $HPO_4^{2-}$ . The Raman spectra of  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^{-}$ , and  $H_3PO_4$  have been recorded (161-163), and no evidence of any of these species was observed in the Raman spectra of the heteropolymolybdates. The absence of phosphate bands in the Raman spectra is most likely due to concentration effects. The phosphate concentration is less than the molybdate concentration by a factor of 12 ( $C_p \approx 0.1 \text{ M}$ ,  $C_{MO} \approx 1.2 \text{ M}$  based on the analytical concentration of



the solution). In addition, the phosphorus is distributed among the various phosphate species according to the pH of the solution. Since the concentration differential is so large, the Raman bands due to the vibrations of the phosphate species which are present are not sufficiently intense to be observed.

The silicate case is different. No simple silicates are known to be soluble in the pH regions of interest (pH < -0.5, 6.0 < pH < 13.5). If the solutions of 12-MSA were allowed to sit for several weeks or months, a precipitate appeared. The solutions were discarded when the precipitate was present on the premise that they were "bad." However, the precipitate was not the molybdate, but rather insoluble silicates. (No precipitate was noted in the 12-MPA solutions.) The Raman spectra of the 12-MSA solutions were recorded before the precipitate appeared, and no vibrations which could be attributed to silicate species were observed. As in the case of 12-MPA, a concentration differential argument can be employed to explain the lack of silicon bands in the Raman spectra.

#### Conclusions

Decomposition schemes for 12-MPA and 12-MSA have been derived from changes in the Raman spectra of the two compounds in aqueous solution over a wide pH range. The degradation process was found to proceed



through analogous molybdate species in each case, with the exception that no ll anion was observed for 12-MSA. The species observed through the use of Raman spectroscopy are the same as those detected by electrochemical techniques and ultracentrifugation, and thus the Raman spectra provide confirmation of the degradation process.

The most significant result from this study is the Raman spectrum of  $(PMo_{11}O_{39})^{7-}$ . Although the identity of the species could not be verified independently, experimental conditions and analysis of the spectrum indicate that the spectrum is of the ll anion.

The identification of the species in the various pH ranges was not difficult because of the striking nature of the changes in the Raman spectra. Raman spectroscopy is shown to be a very useful technique to identify the major species in aqueous solution at any given point in the complex molybdenum (VI) equilibria.



#### CHAPTER V

RAMAN SPECTRUM OF  $\beta$ -12-MOLYBDOSILICIC ACID

The 12-A heteropolymolybdates can exist in two isomeric forms,  $\alpha$  and  $\beta$ . The  $\beta$  isomer of 12-MSA is unstable and slowly converts spontaneously and irreversibly to the  $\alpha$  form. Beta 12-MSA is light sensitive, and the crystals are hygroscopic. Undoubtedly because of its instability, no crystal structure of  $\beta$ -12-MSA has been reported.

The  $\alpha$  forms of the 12-A heteropolytungstates have the Keggin structure and react in a manner equivalent to the 12-A heteropolymolybdates. The  $\beta$  isomers of the heteropolymolybdates and tungstates are believed to be similar. The crystal structure of  $K_4(SiW_{12}O_{40})$ . 14H<sub>2</sub>O has recently been reported (51).

This chapter summarizes experiments designed to investigate the structure of  $\beta$ -l2-MSA through its Raman spectrum and by comparison of its Raman spectrum to that of  $\beta$ -l2-WSA. The syntheses of  $\beta$ -l2-MSA and  $\beta$ -l2-WSA are described. The Raman spectra of both  $\beta$  isomers are reported, and special problems associated with  $\beta$ -l2-MSA



are discussed. The differences in symmetry between the  $\alpha$  and  $\beta$  isomers of 12-MSA and 12-WSA and the effects of symmetry on the spectra are considered.

### Synthesis of $\beta$ -12-MSA and $\beta$ -12-WSA

The major products of the synthesis of 12-A heteropolymolybdates and heteropolytungstates from molybdate or tungstate salts and the heteroatoms are determined by the pH of the solutions and the order of addition of the reactants (47, 164). For 12-MSA, the pH of the solution is the critical parameter (47). The molybdate ions are added to a solution of pH approximately 1, followed by the addition of the heteroatom. For 12-WSA, however, the order of addition of reactants determines the products. According to Souchay (164), the following reactions occur (note the order of addition of acid and heteroatom):

> $SO_4^{2-} + SiO_3 \xrightarrow{\text{acid}} \alpha - 12 - WSA$  $WO_4^{2-} \xrightarrow{\text{acid}} paratungstate A \xrightarrow{SiO_3} \beta - 12 - WSA$

#### $\beta$ -12-MSA

The synthetic method for preparing  $\beta$ -12-MSA was adapted from that reported by Tsigdinos (47). The solvent is composed of 87.5 mL of 1,4-dioxane, 15 mL concentrated HCl, and 18 mL H<sub>2</sub>O. To the solvent 25 g of



 $Na_2MoO_4 \cdot 2H_2O$  in 40 mL  $H_2O$  are added.  $Na_2SiO_2 \cdot 9H_2O$  (2.5 g) in 15 mL water is slowly dripped into the reaction mixture. The solution is swirled after each addition to minimize the formation of a white precipitate. The addition of the silicate produces a yellow color which indicates the formation of  $\beta$ -12-MSA. The reaction mixture is left undisturbed for 24 hours, after which it is passed through an ion exchange column (Dowex 50W-X8 in the H<sup>+</sup> form) at approximately 20 mL/min. The column is prepared by first washing the resin with 500 mL of 3M HCl, followed by 500 mL of 1 M HCl in 1:1 water-dioxane. The effluent from the column is cooled to -20 °C in an acetone-dry ice bath. Concentrated HCl (215 mL) is added rapidly to precipitate the free  $\beta$ -12-MSA. The temperature of the solution is not allowed to rise above -20°C during this addition. The product is then filtered (the solution being kept cold to prevent the  $\beta$ -12-MSA from dissolving), and the bright yellow crystals are placed in a vacuum dessicator to dry. After approximately eight hours in the dessicator, the product begins to decompose as evidenced by the appearance of a green color. Hence, the Raman experiments were conducted immediately upon completion of the synthesis.

#### β-12-WSA

The method for synthesizing  $\beta$ -12-WSA was reported by Souchey, Tézé, and Hervé (164). Fifty grams of


 $Na_2WO_4$  were dissolved in 100 mL of water, and the solution was heated while 15 mL of concentrated HCl were added. A yellow precipitate formed and subsequently dissolved when the flask was swirled. After the addition of the acid, the pH of the solution was approximately 6, which is the pH for the formation of paratungstate ion.  $Na_2SiO_3$  (1.4 g) in 10 mL of water was added to the solution, which was then filtered to remove particulate matter. An additional 15 mL of concentrated HCl were added to the reaction vessel. The free heteropoly acid was extracted with ether by the Drechsel method (165), and the product was recrystallized from water.

# $\frac{\text{Symmetry of the } \alpha \text{ and } \beta \text{ Isomers of}}{12\text{-}\text{MSA and } 12\text{-}\text{WSA}}$

The  $\alpha$  form of 12-MSA and 12-WSA has  $T_d$  symmetry. As can be seen in Figures 1 and 2, the anion is composed of four Mo<sub>3</sub>O<sub>13</sub> groups of three molybdenum-oxygen octahedra. Each group is centered about one corner of the Si-O tetrahedron in such a way as to retain  $T_d$  symmetry.

Rotation of one of the four groups of octahedra by 60° yields the structure reported by Matsumoto, Kobayashi, and Sasaki (51) for  $K_4(SiW_{12}O_{40}) \cdot 14H_2O$ . This is presumed to be the structure of  $\beta$ -12-MSA. The 60° rotation destroys some  $C_3$  axes and planes of reflection, which reduces the symmetry of the anion to  $C_{3v}$ . Models of the  $\alpha$  and  $\beta$  isomers are shown in Figure 2. The



difference in structure is readily apparent. The group of octahedra which has been rotated by  $60^{\circ}$  is shown in blue for the  $\beta$  isomer.

Classification of the molecular vibrations according to group theory leads to the representation:

$$\Gamma = 9A_1(Raman) + 4A_2(inactive) + 13E(Raman) + 16T_1(inactive) + 22T_2(IR, Raman)$$

for the  $T_d$  isomer. This indicates that 44 Raman bands and 22 infrared bands coincident with Raman bands could be observed. Of course, accidental degeneracies and low intensities preclude the observation of some of the expected modes.

For the  $\beta$  isomer, classification of the vibrations leads to the representation:

 $\Gamma = 31A_1(IR, Raman) + 20A_2(inactive) + 51E(IR, Raman).$ 

In this case, 82 bands are both Raman and infrared active.

A brief consideration of the correlation between the symmetry operations of  $T_d$  and  $C_{3v}$ , which is a subgroup of  $T_d$ , clarifies the symmetry relationship between the two isomers and the expected changes in the spectra. The character tables for  $T_d$  and  $C_{3v}$  are shown in Tables 3 and 4, respectively (166). The correlation

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т <sub>d</sub>	Е	8C3	3C <sub>2</sub>	65 <sub>4</sub>	6σ <sub>d</sub>		
A <sub>1</sub>	1	1	1	1	1		$x^2 + y^2 + z^2$
<sup>A</sup> 2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2),$ $x^2 - y^2)$
т <sub>l</sub>	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
<sup>т</sup> 2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

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Table	3

Character Table for the Point Group  $T_d$  (7)

Table	e 4
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Character Table for the Point Group  $C_{3v}$  (7)

c <sub>3v</sub>	E	2C <sub>3</sub>	3σ <sub>v</sub>			
Al	1	1	1	Z		$x^{2} + y^{2}, z^{2}$
<sup>A</sup> 2	1	1	-1	$R_{z}$		
Е	2	-1	0	(x, y)	(R <sub>x</sub> , R <sub>y</sub> )	$(x^{2} - y^{2}, xy) (xz, yz)$

diagram shown in Figure 13 can be obtained either by inspection or by the method outlined by Fateley and coworkers (167). Comparison of the characters in the table for  $C_{3v}$  with those in the portion of the  $T_d$  table for the E,  $C_3$ , and  $\sigma_d$  operations shows the following relationships, which are represented graphically in the correlation diagram:

$$\frac{T_d}{A_1} = \frac{C_{3v}}{A_1}$$

$$A_2 = A_2$$

$$E = E$$

$$T_1 = E + A_2$$

$$T_2 = E + A_1$$

The triply degenerate  $T_1$  and  $T_2$  modes in  $T_d$  are split into doubly and singly degenerate modes in  $C_{3v}$ . This change in the symmetry is expected to affect the number of bands observed in the Raman and infrared spectra of the  $\alpha$  and  $\beta$  isomers. Only 22 vibrations ( $T_2$ ) are expected to be infrared active in the  $\alpha$  isomer. However, in the  $\beta$  isomer, 82 vibrations ( $A_1$  and E) are infrared active. Unfortunately, the strong absorbance of water in the infrared region obscures the infrared spectra of  $\beta$ -12-MSA and  $\beta$ -12-WSA; the changes in the infrared spectra thus cannot be determined. In the  $\alpha$  isomer,









Figure 13. Correlation diagram for  $T_d$  and  $C_{3v}$ .





44 vibrations are expected to be Raman active, while 82 vibrations are Raman active for the  $\beta$  isomer. However, since the actual nuclear reorientations which effect this symmetry change are rather subtle, the "splittings" of the previously T<sub>2</sub> modes is likely to be small, and unresolvable under the present experimental conditions. Likewise, the positions and intensities of the 9A<sub>1</sub> modes in T<sub>d</sub> symmetry will probably remain about the same under C<sub>3v</sub> symmetry. However, new Raman active bands should result in the lower-symmetry case from the 16 T<sub>1</sub> modes which were inactive in T<sub>d</sub>. We would, therefore, expect to see 16 E vibrations in the Raman spectra of the  $\beta$ isomers which were not observed in the spectra of the  $\alpha$  isomers. The wavenumber shifts of these bands, however, are not predicted by group theory.

### Raman Spectra of $\beta$ -12-MSA and $\beta$ -12-WSA

The Raman spectra of both  $\beta$ -12-MSA and  $\beta$ -12-WSA were obtained with approximately 0.1 <u>M</u> solutions. A 1:1 water dioxane solution was used as the solvent for  $\beta$ -12-MSA because the dioxane slows down the transformation of the  $\beta$  isomer into the  $\alpha$  isomer. Water was the solvent for the  $\beta$ -12-WSA solutions.

As mentioned earlier,  $\beta$ -12-MSA is light sensitive. For example, the solutions would turn from yellow to green in approximately three minutes when exposed to 500 mW of 514.5 nm radiation. The sample did not turn



green as rapidly when the solvent was water. However, the transformation from  $\beta$  to  $\alpha$  was more rapid. The use of 647.1 nm excitation did not cause sample decomposition. Thus, all of the spectra of  $\beta$ -12-MSA reported here were obtained with 647.1 nm excitation.

The spectra of  $\alpha$ - and  $\beta$ -12-MSA and 12-WSA are shown in Figures 14 and 15. The band positions and relative intensities of these spectra are listed in Table 5. The frequencies which correspond are on the same line; polarized bands are underlined. The spectra reported for  $\alpha$ -12-MSA and  $\alpha$ -12-WSA are in agreement with literature reports (98, 99, 101-103).

The regions in which new bands should be expected to appear in the spectrum of the  $\beta$  isomer can be predicted by a consideration of the structural differences between the  $\alpha$  and  $\beta$  isomers. One of the four  $Mo_3O_{13}$ groups in the  $\alpha$  isomer is rotated to form the  $\beta$  isomer. The other three groups are identical in both cases. Vibrations which involve symmetric motions are unaffected by the rotation, as are Si-O vibrations. Vibrations within individual octahedra and bridge vibrations within groups of three octahedra are also unaffected by the relative positions of the  $Mo_3O_{13}$  units. The vibrations which are affected by the relative positions of the units are the vibrations of Mo-O-Mo bridges which span the junction of two groups. There are six such













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a-12-MSA	β-12-MSA	a-12-WSA	β-12-WSA
70(1)		67(1)	71(1)
	83(1)	87(5)	82(1)
107(21)	100(1)	102(7)	99(2)
107(<1)	108(1)	103(7)	111(1)
			134(3)
	148(1/2)		
161(1)		157(3)	152(7)
000(0)	191(1)	0.0.6 ( 0 )	0.00 ( 0 )
209(3)	210(1)	206(2)	209(2)
247(3)	241(4)	222(3)	234(1)
217(0)	270 (3)	209(0)	201(1)
		287(5)	
	297 ( 5)		
369(1)	364 (芝) 202 (北)	374(5)	
459(2)	392 (Z) *	456(3)	
494(1)	*	450(5)	
		531(1)	
			552(戈)
619(2)	624(2)		
6/6(1) $807(\frac{1}{2})$	680(6)		
007(2)		820(2)	
890(2)			895(1/2)
918(1)	920(1)	915(3)	929(5)
958(7)	953(3)	982(7)	981(3)
979(IO)	9/4(10)	998(10) 1016(1)	998(IO)
		TO TO (T)	

Table 5

Raman Spectra of the  $\alpha$  and  $\beta$  Isomers of 12-MSA and 12-WSA

\*Region obscured by solvent peaks.



bridges which are different in the  $\alpha$  and  $\beta$  isomers, and six which are unchanged. Therefore, half of the vibrations of bridges linking two Mo<sub>3</sub>O<sub>13</sub> groups would be affected by the difference in symmetry.

The spectra of the  $\beta$  isomers should thus have more bands in the bridge stretching and deformation region (<300 cm<sup>-1</sup>) than those of the  $\alpha$  isomers. The most detailed analysis of the spectrum of a Keggin structure reported to date does not provide any insight as to which bands are due to vibrations of bridges within Mo<sub>3</sub>O<sub>13</sub> units, and which are due to vibrations of bridges which span two units (102, 103).

Inspection of the spectra shown in Figures 14 and 15 and listed in Table 5 shows that there are more bands in the spectra of the  $\beta$  isomers than in those of the  $\alpha$  isomers in the low frequency region (<300 cm<sup>-1</sup>). The bands at 111 and 134 cm<sup>-1</sup> ( $\beta$ -12-WSA) and 148 and 191 cm<sup>-1</sup> ( $\beta$ -12-MSA) have no counterparts in the spectra of the  $\alpha$  isomers. The relative intensities of the bands in this region in the spectra of the two isomers are not the same. The peaks due to the breathing motion of the anion (958 cm<sup>-1</sup>, 12-MSA; 982 cm<sup>-1</sup>, 12-WSA) and the Si-O vibrations (979 cm<sup>-1</sup>, 12-MSA; 998 cm<sup>-1</sup>, 12-WSA), as well as the Mo-O vibrations, are the same in the spectra of both the  $\alpha$  and  $\beta$  isomers. The differences in the spectra are not as great as would be expected from the mathematical analysis.



### Conclusions

In this chapter, the structure of  $\beta$ -12-MSA has been probed with Raman spectroscopy. Since  $\beta$ -12-MSA is unstable, its synthesis was necessary. The syntheses of  $\beta$ -12-MSA and  $\beta$ -12-WSA, which was chosen for comparative purposes, are reported here. The few changes in the spectra are discussed in terms of the symmetry difference between the  $\alpha$  and  $\beta$  isomers of 12-MSA and 12-WSA.



### CHAPTER VI

## RESONANCE RAMAN STUDIES OF SOME HETEROPOLY BLUES

The 12-A heteropolymolybdates are easily reduced to form intensely blue compounds known as "heteropoly blues." Each heteropolymolybdate can form several blues, which differ by the number of electrons which have been added to the oxidized form.

Heteropoly blues are colloids and have never been crystallized (74). Consequently, an X-ray crystallographic determination of the structure of a blue has not been possible. ESR data have been interpreted in terms of the Keggin structure of the oxidized form. Raman or resonance Raman spectra of a heteropoly blue could, therefore, provide valuable information about the structure of the reduced forms of heteropolymolybdates.

This chapter describes experiments to obtain resonance Raman spectra of some heteropoly blues. The study has been restricted to the blues formed by the addition of two, four, and six electrons to 12-MPA. The electrochemistry of 12-MPA is briefly discussed,

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as is the preparation of the three blues. The resonance Raman spectra of the blues are discussed. Finally, the synthesis and Raman spectra of some molybdovanadophosphates, which are models for the blues, are described.

### Electrochemistry of 12-Molybdophosphoric Acid

Tsigdinos (64) has reported direct current linear sweep voltammetry, alternating current linear sweep voltammetry, and cyclic voltammetry of  $\alpha$ -12-MPA in  $1 \text{ \underline{N}} H_2 SO_4$  (1:1 water-dioxane) at a platinum electrode. Four waves were found in the direct current voltammogram; the first three are of equal height. The half-wave potentials are +0.29, +0.16, +0.09, and -0.25 V versus the standard calomel electrode (SCE). The ac voltammogram shows four waves with half-wave potentials at +0.303, +0.175, -0.065, and -0.218 V versus SCE. Each wave corresponds to the addition of two electrons to yield products with two, four, six, or eight electrons more than the oxidized form. Cyclic voltammetry indicates that the first three waves are reversible. However, no conclusions can be drawn about the fourth wave, which occurs close to the evolution of hydrogen.

The cyclic voltammogram of  $10^{-3}$  <u>M</u>  $\alpha$ -12-MPA in 1 <u>N</u> H<sub>2</sub>SO<sub>4</sub> (1:1 water-dioxane) was obtained in this laboratory. The cell was a modified H cell with coiled platinum wire electrodes and a silver-silver chloride reference electrode (+0.208 V vs SHE). The cell is

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shown in Figure 16. The voltammogram was obtained on a Princeton Applied Research Model 174 electrochemical bench at a scan rate of 10.4 mV/sec. The half wave potentials found were consistent with those reported by Tsigdinos (64). The voltammogram is shown in Figure 17.

### Synthesis of the Heteropoly Blues

The heteropoly blues of 12-MPA were synthesized by electrochemical reduction of 12-MPA. A  $10^{-3}$  M solution of 12-MPA was made in 1:1 water-dioxane solution with  $1 \text{ \underline{N}} \text{ H}_2 \text{SO}_4$  as the supporting electrolyte. The controlled potential coulometry was carried out on a system composed of an AMEX Model 550 Potentiostat and Model 731 Integrator. The number of coulombs which have passed through the circuit can be read directly from a digital display on the integrator; thus, the need to integrate a current vs. time curve is eliminated. The cell and electrodes used were the same as those used in the cyclic voltammetry. The solvent and supporting electrolyte were placed in the cell and electrolyzed at each voltage for approximately one hour to determine the background. The  $10^{-3}$  M 12-MPA solution was used to prepare three solutions, one each at +0.38, +0.25, and -0.01 V versus the silver-silver chloride electrode. These voltages were chosen on the basis of the cyclic voltammetry to reduce to 12-MPA selectively to products with approximately two, four, and six electrons added to the





Figure 16. The cell used for electrochemical synthesis of the heteropoly blues.

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starting oxidized form. The number of electrons added to each solution was calculated from Faraday's law:

$$n = q/FCV$$

where n is the number of electrons, q is the number of coulombs, F is Faraday's constant, C is the concentration, and V is the volume of the cell (168). The calculations resulted in values of 2.11, 4.05, and 6.08 electrons added to solutions 1, 2, and 3 respectively. Once prepared, the solutions were stored in polyethylene bottles. No color fading was noted during the course of the experiments.

### Spectra of the Heteropoly Blues

The near infrared-visible absorption spectra of the heteropoly blues are shown in Figure 18. These spectra correspond to those of El-Shamy and Iskander (74) who studied the successive reduction of 12-MPA by stannous chloride. The wavelengths of the three most powerful laser lines available for excitation (647.1, 514.5, and 488.0 nm) are marked by arrows on the spectra.

The choice of laser line for use in the Raman experiments is determined by the near infrared-visible spectrum. The 647.1 nm line is well within the absorption profile of the blues. However, the Stokes scattered radiation tends to be strongly absorbed by the solution. Only the scattering from the quartz cell can be seen in






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the Raman spectrum of the blues using 647.1 nm excitation. The 514.5 nm line is in the tail of the absorption profile for solutions 2 and 3, and is near the absorption profile of solution 1. The absorption of the Stokes radiation and the exciting line is less of a problem using 514.5 nm excitation. Therefore, all spectra reported were obtained using 514.5 nm excitation.

Because the 514.5 nm line is near or within the absorption profile of the heteropoly blues, resonance enhancement of the Raman scattering can be expected. Indeed, since Raman scattering is observed from solutions which are less concentrated than those in Chapter IV by a factor of 100, we feel that some resonance enhancement must be occurring. The bands of dioxane and sulfuric acid are observed because they are more concentrated than the blues.

The spectra of the water-dioxane solvent and sulfuric acid, 12-MPA  $(10^{-3} \text{ M})$  in the solvent and sulfuric furic acid, and solution 1 in the solvent and sulfuric acid are shown in Figure 19. The spectra of the oxidized and reduced forms of 12-MPA are identical. This confirms the hypothesis, at least for the two-electron blue, that the structure of the reduced form remains the Keggin structure.

The spectrum of solution 1 was obtained with the spinning cell in its normal upright position as described









in Chapter III (Figure 6). However, none of the laser beams at 647.1, 514.5, and 488.0 nm would penetrate solutions 2 or 3. The spinning cell was thus tilted and the Raman spectra were obtained by total reflectance (169). The optimum cell angle, determined experimentally, was approximately 15<sup>°</sup> from vertical. The major limitation of the total reflectance method is that bands from the quartz cell dominate the spectra.

Resonance Raman spectra of the quartz cell and solutions 2 and 3 are shown in Figure 20. Peaks due to the heteropoly blues can be seen superimposed on the quartz cell spectrum at 249, 978, and 998 cm<sup>-1</sup>. These bands correspond to the three strongest bands of the oxidized form of 12-MPA; the relative intensities of these peaks are also in agreement with those of 12-MPA. The data are not sufficient to make definitive statements about the structure of the four- and six-electron blues. However, the presence of the two bands at 998 and 979 cm<sup>-1</sup>, which were seen in Chapter IV to be sensitive to the presence of the Keggin structure, indicates that this structure is maintained.

#### Models for the Heteropoly Blues

The heteropoly blues are mixed valence compounds; that is, some molybdenum atoms have a valence of VI, some V. Valid models for the heteropoly blues are the molybdovanadophosphates, in which one or more Mo(VI)







atoms has been replaced by V(V). These compounds also have the Keggin structure (77). Three molybdovanadophosphates have been synthesized and their Raman spectra recorded for comparison with the spectra of the heteropoly blues.

## Synthesis of the Molyvdovanadophosphates

The ll-molybdovanadophosphate, l0-molybdo-2vanadophosphate, and 9-molybdo-3-vanadophosphate anions were prepared by a modification of the syntheses reported by Tsigdinos and Hallada (170). The stoichiometry of the molybdovanadophosphates was shown by Tsigdinos and Hallada to be dependent only on the initial amounts of molybdenum and vanadium. For ll-molybdovanadophosphate, 3.05 g  $Na_3VO_4$  were dissolved in 50 mL  $H_2O$  and boiled, and 3.55 g of  $Na_2HPO_4$  in 50 mL water were added. The solution was cooled to room temperature, and 2.5 mL of concentrated sulfuric acid were added. A dark red solution resulted.  $Na_2MoO_4 \cdot 2H_2O$  (66.5 g) in 100 mL water was added to the solution followed by the slow addition, with vigorous stirring, of concentrated  $H_2SO_4$ (42.5 mL). The solution was cooled to room temperature and the molybdovanadophosphate was extracted with ethyl The red etherate layer was collected and the ether. ether removed by bubbling air through the solution. The remaining solid was dissolved in 15 mL  $\rm H_{2}O$  and placed in



a vacuum dessicator over concentrated  $H_2SO_4$ . The solution was concentrated to the appearance of crystals, and then allowed to crystallize further in open air. The orange crystals were filtered, washed with cold water, and air dried.

The synthesis of  $PV_2Mo_{10}O_{40}^{5-}$  and  $PV_3Mo_9O_{40}^{6-}$ followed the same procedure, but the amounts of vanadium and molybdenum were varied. For  $PV_2Mo_{10}O_{40}^{5-}$ , 12.2 g of  $Na_3VO_4$  in 50 mL H<sub>2</sub>O and 60.5 g of  $Na_2MoO_4 \cdot 2H_2O$  in 100 mL of water were used. For  $PV_3Mo_9O_{40}^{6-}$ , 18.3 g of  $Na_3VO_4$  in 100 mL water and 27.25 g of  $Na_2MOO_4$  in 75 mL H<sub>2</sub>O were used. The amounts of  $Na_2HPO_4$  and sulfuric acid remained constant.

The products could be distinguished easily by the color of the crystals--the more vanadium the crystals contained, the redder the product. The ultravioletvisible spectra of all three compounds in aqueous solution show an absorption maximum at 310 nm in agreement with the findings of Tsigdinos and Hallada (170), and long wavelength absorption tails consistent with the appearance of the solutions.

## Raman Spectra of the Molybdovanadophosphates

Raman spectra of approximately 0.1  $\underline{M}$  solutions of the three molybdovanadophosphates were recorded. The



Raman spectra are shown in Figure 21; the band positions and relative intensities are listed in Table 6.

As for the heteropoly blues, the choice of laser line for Raman excitation is determined by the absorption characteristics of the solution. The 488.0 and 514.5 nm lines of the  $Ar^+$  laser were absorbed by the molybdovanadophosphate solutions; however, the material did not absorb the 647.1 nm line of the Kr<sup>+</sup> laser. The spectra reported, therefore, were recorded with 647.1 nm excitation.

The molybdovanadophosphates maintain the Keggin structure in solution and are more stable to base degradation than 12-MPA (170). Therefore, the Raman spectra should reflect the Keggin structure. Any changes in peak position, shape, or intensity could be due to the variation in the number of vanadium atoms present in the structure.

Examination of Figure 21 and Table 6 shows that the spectra of the three molybdovanadophosphates are virtually identical. The V-O stretch may be obscured by the Mo-O vibration at 972 cm<sup>-1</sup>, as in the infrared spectra of these compounds reported by Tsigdinos and Hallada (170). Comparison of the spectra of 12-MPA (see Figure 8) and the molybdovanadophosphates in the 900 to 1000 cm<sup>-1</sup> region reveals that the composite metaloxygen stretch at ~972 cm<sup>-1</sup> in the molybdovanadophosphate









PVM011040	<sup>PV2<sup>M0</sup>10<sup>0</sup>40<sup>5-</sup></sup>	PV3 <sup>M09040</sup> 6-	
105(6)	105(6)	108(7)	
155(2)	154(2)	156(3)	
214(2)	213(2)	213(2)	
250(5)	252(5)	255(5)	
378 (½)	382 (½)	-	
451(½)	453 (½)	450(1)	
605(2)	608(2)	607(3)	
649(1)	657(1)	-	
897(1)	896(1)	892(1)	
972(4)	972(5)	973(5)	
995(10)	992(10)	992(10)	

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Table 6

Raman Spectra of the Molybdovanadophosphates



spectra is broader and less well resolved from the P-O vibration at slightly higher wavenumber. The strong peaks at 992, 972, 250, and 108 cm<sup>-1</sup> agree with those of 12-MPA. Although the molybdovanadophosphate anions maintain their integrity in solution, the Raman spectra cannot be used to distinguish among these compounds. For the ions containing multiple V(V) atoms, they provide no information with regard to the placement of the vanadium atoms relative to one another. The general shape of the Raman spectra are consistent with the Keggin structure for the mixed valence compounds.

 $PV_2Mo_{10}O_{40}^{5-}$  is isoelectronic with the twoelectron heteropoly blue,  $PMo_{12}O_{40}^{5-}$ . The existence of  $PV_2Mo_{10}O_{40}$  and the other molybdovanadophosphates in the Keggin structure indicates the feasibility of the heteropoly blues maintaining that structure upon reduction of the parent heteropolymolybdate.

#### Conclusion

The synthesis of three heteropoly blues by controlled potential coulometry is briefly described. The spectrum of the two-electron blue confirms that the structure remains the Keggin structure of the oxidized form of 12-MPA. The spectra of the four- and sixelectron blues, obtained using the tilted spinning cell, indicate qualitatively that the Keggin structure is retained upon further reduction. However, this deduction



is based on only three bands in each of the Raman spectra. The syntheses and Raman spectra of three molybdovanadophosphates, which are models for the heteropoly blues, are also presented. The Raman spectra of the three compounds are identical and indicate the feasibility of mixed valence compounds existing in the Keggin structure.

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#### CHAPTER VII

#### FUTURE PROSPECTIVES

There are at least two areas in which the marriage of Raman spectroscopy and molybdenum chemistry could prove fruitful. The first is the study of the kinetics of formation of heteropolymolybdates; the second is the study of molybdenum-containing enzymes.

Conventional Raman spectroscopy with continuous sources has proven to be a viable technique for kinetic studies of reactions which occur on a minute or hour time scale (171). Bands which appear with the products or disappear with the reactants can be monitored over an appropriate time period, and kinetic information derived from the changes in peak height or peak area with time. This is normally accomplished by repetitive scans, each requiring several minutes, of portions of the reactant and product spectra. This approach is, therefore, not applicable to reactions, such as the formation of heteropolymolybdates, which occur on a millisecond or shorter time scale.

Time-resolved resonance Raman spectroscopy (TR<sup>3</sup>), however, allows time resolution limited by the laser



pulse width. A recent report (172) has demonstrated the sensitivity of  $\text{TR}^3$ . The resonance Raman spectrum of 5.5 x  $10^{-4}$  <u>M</u> cytochrome c obtained with a single 7 ns pulse of a doubled Q-switched Nd:YAG laser (531.8 nm) and a vidicon Raman spectrometer was reported. The application of this technique in conjunction with stopped-flow kinetic studies could provide considerable information about the transient species involved in heteropolymolybdate formation. In principle, the differences in intermediates which lead to the formation of the  $\alpha$  and  $\beta$  isomers of the 12-A heteropolymolybdates could be determined.

The major limitation of TR<sup>3</sup> in the study of the kinetics of heteropolymolybdates is the low intensity of the Raman scattering. Since no resonance enhancement of the scattering from 12-MPA and 12-MSA was observed, the intensity probably would be insufficient. However, use of the reduced heteropolymolybdates (heteropoly blues) could circumvent the intensity problem because of resonance enhancement of the Raman scattering.

Another potential application of Raman spectroscopy is the study of molybdenum-containing enzymes. Of these enzymes, nitrogenase is one of the most important and well characterized (173). In spite of extensive scrutiny, however, the exact role of the molybdenum atom in the enzyme is not known. The molybdenum is presumed



to be the key to the electron transfer role of the enzyme, but how the electrons are transferred and stored is not understood. Recent evidence (174) indicates that the molybdenum is not actually in the enzyme but is contained in a cofactor essential for enzymatic activity. Raman spectroscopic studies of the enzyme before, during, and after exposure to nitrogen, as well as studies of the cofactor itself, could provide information about the changes which occur in the enzyme near the molybdenum atoms. Changes in the vibrational modes may provide clues to the nature of the electron transport mechanism.

Additional areas for the application of Raman spectroscopy will develop as the technique becomes increasingly refined and the imagination of chemists is sparked by the desire to learn just a little bit more.

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APPENDIX

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#### APPENDIX

# DIGITAL COUNTER FOR MONITORING THE WAVENUMBER OF THE MONOCHROMATOR

A digital counter which monitors the wavenumber of the light passing through the monochromator has been constructed. The counter unit is composed of two virtually identical circuits containing MK50395 six-decade up-down counter/display decoders and the appropriate support components. One counter follows the absolute wavenumber; the other monitors the wavenumber relative to a user defined zero.

This appendix describes the entire counter, the individual counter circuits, and the support circuitry. Appropriate schematic diagrams are included. A simple operating procedure is given. It is assumed that the reader is familiar with the operation of the Raman instrument. Additional details concerning the construction and operation of the counter can be found in the instruction manual for the counter.

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### Front Panel

The front panel has an on-off switch, pilot light, six-digit thumbwheel switch, pushbutton switches to load the counters, a six-digit display for the absolute wavenumber, and a five-digit display for the relative wavenumber. The front panel is diagrammed in Figure 22.

#### Counter Circuits

Two circuits based on manufacturer's literature for the MK50395 counter have been constructed. A schematic diagram for the circuit is shown in Figure 23.

The count and direction signals from the monochromator are directed via coaxial cable to the counter. The count signal is connected directly to both counter chips. The direction signal is sent to the up/down input on counter A (absolute wavenumber) and inverted before connection to counter B (relative wavenumber). During normal scanning of the monochromator, counter A counts down, counter B counts up. The current value of the count is displayed on the seven segment LED's mounted on the front panel.

The circuit design for a single counter, along with the driver and LED's, is contained in the manufacturer's literature for the MK50395 chip. However, the use of a single thumbwheel switch to load two










The circuit diagram for the digital counter. Figure 23.



counters is not well documented by MOSTEK. The notable features of the circuit constructed in this work follow.

The MK50395 has an internal oscillator whose frequency is dependent on the value of an external timing capacitor. Since two capacitors with the same nominal capacitance do not necessarily have the same actual capacitance, the scan rates of the two counters is not the same. An external oscillator, which consisted of a 555 monostable multivibrator connected as an astable multivibrator, was thus constructed. The output of the oscillator was connected to the SCAN input of both counters. This causes them to scan at the same frequency.

A series of monostables controls the SET and LOAD COUNTER functions of both counters. Pressing the LOAD ABSOLUTE button shown in Figure 22 sets both counters (causes the counter to start strobing at the most significant digit), and loads the value in the thumbwheel switch into counter A. Pressing the LOAD RELATIVE button sets both counters and loads the value in the thumbwheel switch into counter B. One-shot monostables (74121) are used to provide the signals to the counters. Both pushbutton switches are connected to a single monostable which is used to set the counters, and both counters are set when either pushbutton is pushed. The pulse from the 74121 was made approximately



0.1 msec, which is of the same order of magnitude as the scanning frequency. Each pushbutton is also connected to a 74121 which has an external capacitor and resistor to produce a pulse of approximately 50 msec. This pulse holds the LOAD COUNTER input high long enough to load all five or six digits. Thus, each pushbutton is connected to two monostables, one of which is common to both, which cause the SET and LOAD COUNTER functions to be performed.

## Monochromator Board

A driver circuit has been mounted in the monochromator control circuitry to send the count and direction signals to the counters. The circuit consists of a single 7406 and flipflop in the monochromator. At the counter end of the cable are receivers (7406, 7407) and pull-up resistors connected to +5 and +12 V. The schematic diagram of this part of the circuit is shown contained in Figure 23.

## Operating Procedures

- Activate the counter by switching the toggle switch mounted on the front panel to the "ON" position.
- Locate the peak of the laser exciting line and leave the monochromator in this position.

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- 3. Enter the wavenumber of the laser line into the thumbwheel switch. (For example, the 514.5 nm line of the Ar<sup>+</sup> laser would be entered as 19434.9.)
- 4. Press the "LOAD ABSOLUTE" button on the front panel. The number in the thumbwheel switch should be visible in the absolute display.
- 5. Enter 0000.0 in the thumbwheel switch.
- Press the "LOAD RELATIVE" button on the front panel. The lower display should read 0000.0.
- 7. Operate the Raman instrument as usual.

The counter should continuously display the position of the monochromator.

Both counters must be recalibrated each time the instrument is turned on. The relative counter must be reset to zero each time a different laser line is used.



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