

# RAMAN SPECTRAL STUDY ON ISOPOLYTUNGSTATES IN AQUEOUS SOLUTION<sup>①</sup>

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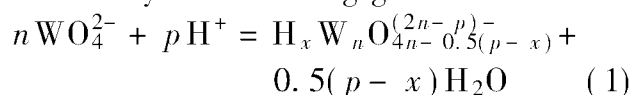
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**ABSTRACT** In the acidic aqueous  $\text{Na}_2\text{WO}_4$  solutions in a range of  $Z(\text{H}^+ / \text{WO}_4^{2-}) = 0 \sim 1.50$ , the chemical state of isopolytungstates has been studied using Raman spectroscopy. It was found that in the solution of  $Z \leq 1.25$ , the dominant polynuclear species at any time is paratungstate A,  $\text{W}_7\text{O}_{24}^{6-}$ , which also exists at  $Z = 1.42$ . During the aging of solution, paratungstate A is slowly transformed to paratungstate B,  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ , which is easily deposited as the crystal  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$ , but the concentration of paratungstate B in the solution is too low to be detected. In the solution of  $Z = 1.42$  and  $1.50$ , there are probably metastable species, but metatungstate,  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ , becomes the dominant species after long aging.

**Key words** Raman spectra isopolytungstate paratungstate metatungstate

## 1 INTRODUCTION

A large number of studies have been done in the field of the aqueous chemistry of isopolytungstate using numerous experimental methods<sup>[1-6]</sup>. The chemical state and subsequent transformation of isopolytungstates in aqueous solution are not well understood because of the slow attainment of equilibrium and the complexity of polymerization. The formation of isopolytungstates by acidification of the  $\text{WO}_4^{2-}$  ion can be described by the following general reaction



Therefore, the acidic ratio,  $Z = p/n$ , not only characterizes the degree of acidification but also every isopolytungstate species.

Although the existence of many isopolytungstate species in aqueous solution has been reported, the important and stable species are paratungstate A, paratungstate B and metatungstate. The latter two species are well known to be  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$  and  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ , corresponding to  $Z = 14/12$  and  $Z = 18/12$  respec-

tively. Paratungstate A is a primary stabilized species on acidification of  $\text{WO}_4^{2-}$  solution, but up to the 1970's its formula was considered to be  $\text{HW}_6\text{O}_{21}^{5-}$  (corresponding to  $Z = 7/6$ ) which was not supported by any direct evidence. Fuchs *et al*<sup>[7]</sup> reported that paratungstate A is  $\text{W}_7\text{O}_{24}^{6-}$  ( $Z = 8/7$ ), which has the same structure as  $\text{Mo}_7\text{O}_{24}^{6-}$ , by the structural analysis of the crystal of  $(\text{C}_5\text{H}_{10}\text{NH}_2)_6\text{W}_7\text{O}_{24}$ . Maksimovskaya *et al*<sup>[8]</sup> affirmed the same conclusion by  $^{183}\text{W}$  NMR.

Hastings *et al*<sup>[6]</sup> reported that when  $\text{pH} > 5$ , the dominant polynuclear species is paratungstate B along with a smaller amount of paratungstate A, and when  $\text{pH} < 4$ , the dominant species is metatungstate. Maksimovskaya *et al*<sup>[8]</sup> found that when the aqueous  $\text{Na}_2\text{WO}_4$  solution was acidified to  $Z \leq 1.17$ , the dominant polynuclear species is  $\text{W}_7\text{O}_{24}^{6-}$ , and the species  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$  can not be detected by NMR but can be deposited as the crystal of  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$ . Shiva<sup>[9]</sup> reported that only paratungstate B and metatungstate are supported by the electrochemical study. Cruywagen

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*et al.*<sup>[5]</sup> found that when the  $\text{Na}_2\text{WO}_4$  solution was acidified to  $Z \leq 1.2$ , the dominant species is  $\text{W}_7\text{O}_{24}^{6-}$  with the  $\text{WO}_4^{2-}$  concentration of 0.001 mol/L, and the dominant species is  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$  with the  $\text{WO}_4^{2-}$  concentration of 0.1 mol/L. Hence there is considerable confusion regarding the dominant polynuclear species in aqueous solution. The purpose of this work is to clarify the dominant polynuclear species in the acidic aqueous  $\text{Na}_2\text{WO}_4$  solution of  $Z \leq 1.50$  by using Raman spectroscopy.

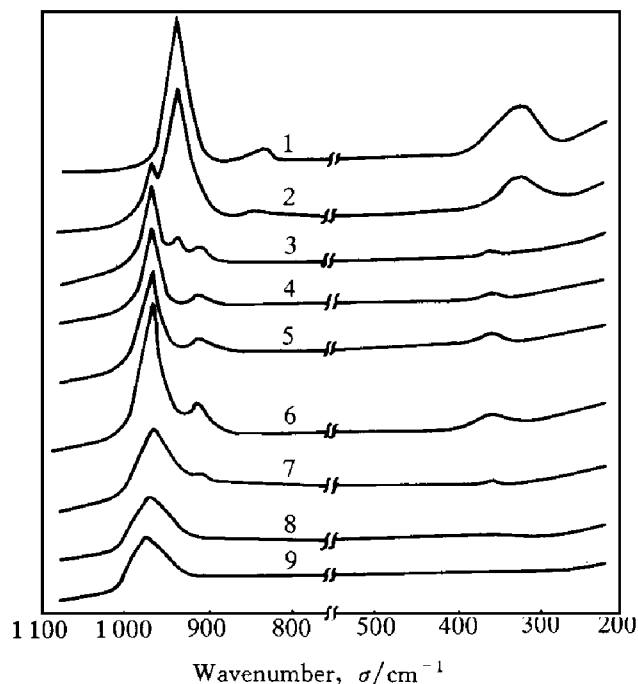
## 2 EXPERIMENTAL

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (A. R.) was recrystallized once and was analyzed by drying to a constant weight at 150 °C and weighing<sup>[3]</sup> as  $\text{Na}_2\text{WO}_4$ . The HCl solution (1.197 mol/L) was used for acidification because it has no Raman line below 1200  $\text{cm}^{-1}$ . The sample solutions with fixed concentration of 0.50 mol/L of  $\text{WO}_4^{2-}$  and acidic degree of  $Z = 0 \sim 1.50$  were prepared by slowly adding the HCl solution to the  $\text{Na}_2\text{WO}_4$  solution with stirring, and then aged in a covered plastic beaker at room temperature,  $(18 \pm 3)$  °C.

Raman spectra were measured with a R500 spectrophotometer (Japan Spectroscopic Co., LTD) using 632.8 nm laser and 0.3  $\text{cm}^3$  sample solution. The measurements were carried out three times for each sample solution, at 0.5~1 h after preparation, at the beginning of crystallization (about 1~2 d) and after aging for 55 d, respectively, the spectra were recorded at the wavenumber below 1200  $\text{cm}^{-1}$  because all Raman lines of species appeared below 1000  $\text{cm}^{-1}$ . It should be noted that in the present work the intensity of Raman lines could not represent quantitatively the concentration of species, since no internal standard was used. The measurement of pH value was carried out with a PHS-3C potentiometer (Shanghai Rex Instruments Factory, P. R. China) at room temperature.

## 3 RESULTS AND DISCUSSION

Raman spectra of the first measurement for sample solutions are collected in Fig. 1.



**Fig. 1** Raman spectra of the fresh acidic  $\text{Na}_2\text{WO}_4$  solutions

- 1— $Z = 0$  (pH 9.5); 2— $Z = 0.50$  (pH 8.3);  
 3— $Z = 1.00$  (pH 7.5); 4— $Z = 1.14$  (pH 6.4);  
 5— $Z = 1.15$  (pH 6.1); 6— $Z = 1.17$  (pH 5.9);  
 7— $Z = 1.25$  (pH 5.3); 8— $Z = 1.42$  (pH 3.9);  
 9— $Z = 1.50$  (pH 2.6)

The mononuclear tungstate ion  $\text{WO}_4^{2-}$  ( $Z = 0$ ) has three Raman lines at 934, 834 and 325  $\text{cm}^{-1}$ . The line at 934  $\text{cm}^{-1}$  is the most obvious and characteristic, and agrees with that reported previously by Basile *et al.*<sup>[10]</sup>. For the solution of  $Z = 0.50$ , a new line appeared at 963  $\text{cm}^{-1}$  apart from the lines of  $\text{WO}_4^{2-}$  at 934 and 325  $\text{cm}^{-1}$ . When  $Z = 1.00$ , the line of  $\text{WO}_4^{2-}$  at 934  $\text{cm}^{-1}$  is detectable, correspondingly the line at 963  $\text{cm}^{-1}$  becomes the most intense one and two weak lines appeared at 908 and 360  $\text{cm}^{-1}$ . The fact shows the formation of new species on acidification of  $\text{Na}_2\text{WO}_4$  solution. The situations at  $Z = 1.14$ , 1.15, 1.17 and 1.25 are similar to that of  $Z = 1.00$  except the disappearance of the line at 934  $\text{cm}^{-1}$ . For the solutions of  $Z = 1.42$  and 1.50, only a broad line appeared at about 968 and 973  $\text{cm}^{-1}$  respectively.

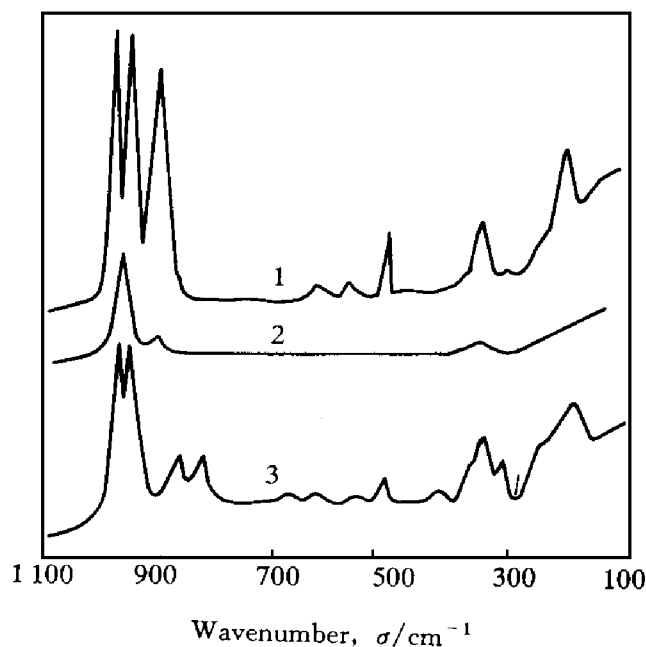
It is commonly considered<sup>[6, 8]</sup> that only

two stable polynuclear species, paratungstate A and paratungstate B, can coexist in the solution of  $Z \leq 1.17$ . Aveston<sup>[3]</sup> reported that in the concentrated lithium tungstate solution of  $Z = 1.17$  the most intense and characteristic Raman line appeared at  $952 \text{ cm}^{-1}$ , other weak lines appeared at the range from  $878$  to  $187 \text{ cm}^{-1}$ . He assigned these lines to paratungstate B, namely  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ . Fuchs *et al*<sup>[7]</sup> reported that in the freshly acidified sodium tungstate solution of  $Z = 1.15$ , Raman lines appeared intensely at  $961 \text{ cm}^{-1}$  and weakly at  $902$  and  $358 \text{ cm}^{-1}$ , which were assigned to paratungstate A,  $\text{W}_7\text{O}_{24}^{6-}$ . As shown in Fig. 1, when  $Z \leq 1.25$ , Raman lines of the new species are in good agreement with those of paratungstate A reported by Fuchs *et al*<sup>[7]</sup>, while those of paratungstate B do not appear. This result indicates that in the fresh acidic  $\text{Na}_2\text{WO}_4$  solution of  $Z \leq 1.25$ , the dominant polynuclear species is paratungstate A.

In contrast to the description by Murata *et al*<sup>[11]</sup> in the aqueous isopolymolybdate, it can be considered that the peak shifting to a higher wavenumber for the solution of  $Z = 1.42$  is caused by the coexistence of paratungstate A and metastable species, and the latter will finally change to the metatungstate<sup>[6]</sup>, rather than by the protonation of  $\text{W}_7\text{O}_{24}^{6-}$ . This suggestion can be supported by the fact that the broad line splits into two lines at  $975$  and  $963 \text{ cm}^{-1}$  after aging for 55 d (refer to Fig. 3), and that the solution of  $Z = 1.42$  can yield the crystal of sodium paratungstate B. Hastings *et al*<sup>[6]</sup> also found that paratungstate A did not protonate. In the solution of  $Z = 1.50$ , paratungstate A does not exist and there are probably metatungstate and metastable species<sup>[6]</sup>.

During the aging of a sample solution at room temperature, a block-like crystal was deposited. The time for crystallization was about 1 ~ 2 d for the solutions of  $Z = 0.5 \sim 1.25$ , about 7 d for  $Z = 1.42$ , and no crystal was deposited for  $Z = 1.50$  even after 55 d. At the beginning of crystallization for  $Z \leq 1.25$  and at 2 d for  $Z = 1.42$  and  $1.50$ , the Raman spectra of all solutions are the same as that shown in Fig. 1 and no

change could be observed (only pH value changed obviously to higher for  $Z = 0.5 \sim 1.42$ ). It indicates that paratungstate A is still the dominant species and that paratungstate B is also undetectable in the solutions of  $Z \leq 1.25$  when the crystal is deposited. Each deposited crystal has the same thermal behavior<sup>[12]</sup> and the same Raman spectrum as the curve 2 shown in Fig. 2. The peaks appearing at  $965$ ,  $950$ ,  $870$ ,  $830$ ,  $690$ ,  $640$ ,  $575$ ,  $520$ ,  $430$ ,  $355$ ,  $320$  and  $195 \text{ cm}^{-1}$  are in agreement with those of the crystal of  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$  reported by Aveston<sup>[3]</sup>. The results of elemental analyses of a typical crystal also correspond with those of  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$  (found:  $\text{Na}_2\text{O}$  8.56%,  $\text{WO}_3$  77.28%,  $\text{H}_2\text{O}$  14.13%; calculated:  $\text{Na}_2\text{O}$  8.62%,  $\text{WO}_3$  77.36%,  $\text{H}_2\text{O}$  14.03%). Hence during the aging, the solutions with a wide range of  $Z$  values ( $0.5 \sim 1.42$ ) can yield the crystals of sodium paratungstate B, which has been reported by Janina *et al*<sup>[13]</sup>.



**Fig. 2** Raman spectra of the crystal and acidic solution

- 1 —  $\text{Na}_6\text{W}_7\text{O}_{24} \cdot 21\text{H}_2\text{O}$ ;  
2 — Solution of  $Z = 1.17$  (pH 6.1);  
3 —  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$

In another experiment, adding acetone to a fresh acidic  $\text{Na}_2\text{WO}_4$  solution (pH = 6.8), a needle-like crystal was quickly deposited. The

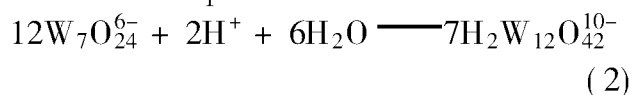
composition of this crystal corresponds to that calculated from  $\text{Na}_6\text{W}_7\text{O}_{24} \cdot 21\text{H}_2\text{O}$  (found:  $\text{Na}_2\text{O}$  8.42%,  $\text{WO}_3$  74.09%,  $\text{H}_2\text{O}$  17.41%, calculated:  $\text{Na}_2\text{O}$  8.50%,  $\text{WO}_3$  74.20%,  $\text{H}_2\text{O}$  17.30%), its Raman spectrum is shown as the curve 1 in Fig. 2. The peaks appearing at 975, 950, 905, 640, 585, 520, 360, 315 and  $215\text{ cm}^{-1}$  are different from those of  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$ . The preparation of  $\text{Na}_6\text{W}_7\text{O}_{24} \cdot 21\text{H}_2\text{O}$  has been reported<sup>[14]</sup> but the description of its Raman spectrum can not be found in the literature. Since in a pH 6.8 solution, only mononuclear tungstate ion  $\text{WO}_4^{2-}$ , paratungstate A and paratungstate B can coexist probably, it may be suggested that the above crystal is sodium paratungstate A. Its Raman mode can be assigned to  $\text{W}_7\text{O}_{24}^{6-}$  in the crystal when we consider that the lines of the crystal at 975 and  $950\text{ cm}^{-1}$  degenerate in the solution to a single line of  $\text{W}_7\text{O}_{24}^{6-}$  at  $963\text{ cm}^{-1}$  (see the curve 2 in Fig. 2). The vibration in a complex ion often has this degeneracy, which has been used to explain the difference of paratungstate B in the crystal and solution by Aveston<sup>[3]</sup>.

After aging for 55 d, only Raman line of  $\text{WO}_4^{2-}$  at  $934\text{ cm}^{-1}$  could be detected for the solution of  $Z = 0.50$ , and only the line of  $\text{W}_7\text{O}_{24}^{6-}$  at  $963\text{ cm}^{-1}$  could be observed for the solutions of  $Z = 1.00, 1.14, 1.15$  and  $1.17$ . It shows that the main polynuclear species is paratungstate A, but its concentration decreases because of the crystallization of paratungstate B. For the solution of  $Z = 1.25$ , a weak line at  $975\text{ cm}^{-1}$  can be detected apart from the line at  $963\text{ cm}^{-1}$ ; for  $Z = 1.42$ , a line at  $975\text{ cm}^{-1}$  and a weak line at  $963\text{ cm}^{-1}$  can be detected; and for  $Z = 1.50$ , only the line at  $975\text{ cm}^{-1}$  is observed, which are collected in Fig. 3.

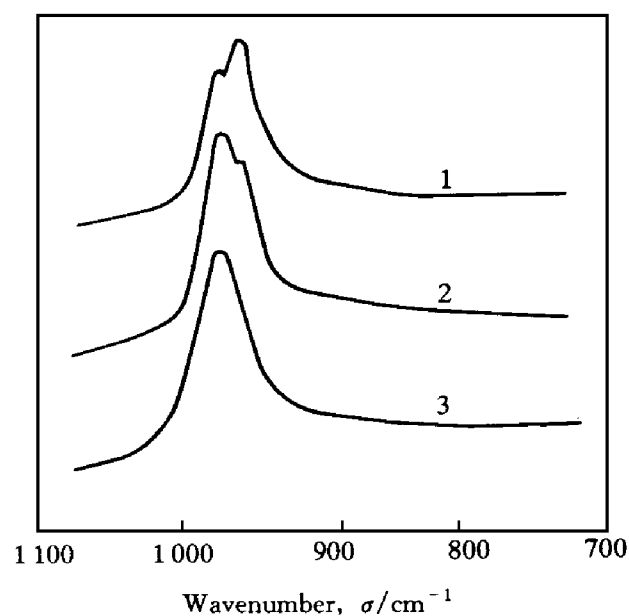
The solution of  $Z = 1.50$  is suitable for the formation of metatungstate ion<sup>[15]</sup>, and below  $\text{pH} \approx 4$ , after aging, metatungstate  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$  is the dominant species in any case<sup>[6]</sup>. Therefore, it is reasonable to assign the line at  $975\text{ cm}^{-1}$  to metatungstate as shown in Fig. 3. Consequently, the results in Fig. 3 indicate that in the solutions of  $Z = 1.42$  and  $1.50$ , the dominant

species is metatungstate, which also exists at  $Z = 1.25$  ( $\text{pH} = 6.0$ ) after aging.

The deposition of the crystal of paratungstate B from sample solutions shows the existence of paratungstate B in the aged solution, but its concentration should be low and it is not a dominant species. The fact that paratungstate A could not be deposited in aqueous solution and its concentration decreased with the deposition of sodium paratungstate B indicates that paratungstate A is slowly transformed to paratungstate B during the aging. This transformation is incomplete and can be described as



The pH value was observed to increase slowly during the aging for the solution of  $Z = 0.5 \sim 1.42$ .



**Fig. 3** Raman spectra of the aged solutions

1— $Z = 1.25$  ( $\text{pH} 6.0$ );

2— $Z = 1.42$  ( $\text{pH} 5.5$ );

3— $Z = 1.50$  ( $\text{pH} 2.5$ )

On the measurement of the pH value, it was also found that the pH value increased rapidly within about 30 min after preparation of the sample solution for  $Z \leq 1.42$ . The larger the  $Z$  value, the larger the change in the pH value. This result may indicate that the formation of paratungstate A in the present work is not so

rapid as that reported by Dewan *et al*<sup>[4]</sup>.

#### 4 CONCLUSION

In an acidified aqueous  $\text{Na}_2\text{WO}_4$  solution up to  $Z \leq 1.25$ , paratungstate A,  $\text{W}_7\text{O}_{24}^{6-}$ , is a primary stable and dominant polynuclear species, which also exists in the solution of  $Z = 1.42$ . During the aging of the solution, paratungstate A is slowly transformed to paratungstate B,  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ , which is deposited as the crystal of  $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$ . However, in the solution, paratungstate B is undetectable in the present work, which at least shows that its concentration is low. These results are in agreement with those reported by Maksimovskaya *et al*<sup>[8]</sup> using NMR. In the fresh acidic  $\text{Na}_2\text{WO}_4$  solutions of  $Z = 1.42$  and  $1.50$ , there are probably metastable species, but eventually the dominant species should be metatungstate, which also exists in the solution of  $Z = 1.25$  (pH 6.0) after aging and has the characteristic Raman line at about  $975 \text{ cm}^{-1}$ .

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