

Infrared and Computational Investigation of Vanadium-Substituted Keggin $[\text{PV}_n\text{W}_{12-n}\text{O}_{40}]^{(n+3)-}$ Polyoxometallic Anions

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This study investigates complex salts of $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{PVW}_{11}\text{O}_{40}]^{4-}$, $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$, and $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ Keggin anions using Fourier transform infrared spectroscopy under ambient atmospheric and high-vacuum conditions and by computational methods. A detailed vibrational study suggests that the presence and amount of vanadium in these anions can be tested quickly and reliably with the help of infrared spectroscopy because the salts of these anions exhibit distinctly different infrared absorption signatures (particularly in the 1025–1250 cm^{-1} region, where the P–O stretch is surrounded by a set of complex vibrations involving V–O and W–O bonds). Investigation of these salts with different counteranions suggests that the overall appearance of the spectra, and thus the ability to use infrared as a diagnostic tool to identify the presence and number of vanadium atoms in Keggin structure anions, is not affected significantly. Last, it is shown that all the structures investigated are extremely stable across a wide range of temperatures.

1. Introduction

Polyoxometalates (POMs) are a valuable class of inorganic compounds. Tunability of size and charge of a polyoxometallic cage, and the inclusion of a variety of transition metal and main group elements, made them very valuable in catalysis and materials science.^{1–5} Among all the classes of POMs, Keggin-type oxoanions are probably the most investigated.^{3,6} Relatively easy altering of the structure of this type of POMs by substituting other metals, for example, V(V), Cu(II), Ln(III), and Eu(IV) into the anion frame, allows for the controllable changes in electronic, magnetic, and catalytic properties of Keggin compounds.^{2,3,7–14}

Vanadium-substituted Keggin polyoxometalates are known to be highly active and extremely selective oxidation catalysts. The presence, number, and arrangement of vanadium atoms in a Keggin framework have been shown to impact the performance of these materials as oxidation catalysts in oxidation of toluene and nitrobenzene.^{15,16}

Numerous methods have been employed to analyze and understand the structure and properties of these compounds. In particular, X-ray crystallography and solution and solid-state nuclear magnetic resonance were used, specifically, to address the issues of vanadium atom incorporation and arrangement in Keggin polyoxometalate anions.¹⁷ Infrared spectroscopy is one of the simplest, most informative, and robust methods that can be used both in the laboratory and in the field. For many years, it has offered a quick and reliable characterization of POMs and often can be used for structural characterization, studies of the role of the counteranions and water in the salts, and thermal stability.^{18,19} The interpretation of the vibrational spectra of POMs has been aided tremendously by recent computational analysis of unsubstituted Keggin POMs;^{20–23} however, substituting one or more transition metal atoms in a polyoxometallic Keggin cage for another transition metal has not been investigated in such a detail.

This paper provides a new approach and a set of spectroscopic benchmarks for analysis and reliable characterization of vanadium-substituted Keggin structure anions. It also examines the effects of counteranions on the obtained vibrational spectra and addresses the effect of vacuum and temperature on the stability of these compounds.

2. Experimental Section

2.1. Materials. All the POM salts were generously donated by the group of Professor Tatyana E. Polenova (Department of Chemistry and Biochemistry, University of Delaware) and by the group of Professor Lynn C. Francesconi (Department of Chemistry, Hunter College, CUNY, NY). $\text{K}_3[\text{PW}_{12}\text{O}_{40}]$, $\alpha\text{-K}_4[\text{PVW}_{11}\text{O}_{40}]$, $\alpha\text{-Na}_4[\text{PVW}_{11}\text{O}_{40}]$, $\alpha\text{-Na}_2\text{Cs}_2[\text{PVW}_{11}\text{O}_{40}]$, $\alpha\text{-}((n\text{-C}_4\text{H}_9)_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$, $\alpha\text{-}1,2\text{-}((n\text{-C}_4\text{H}_9)_4\text{N})_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$, $\alpha\text{-}1,2\text{-Cs}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$, $\alpha\text{-}1,2\text{-K}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$, $\alpha\text{-}1,2,3\text{-}((n\text{-C}_4\text{H}_9)_4\text{N})_6[\text{PV}_3\text{W}_9\text{O}_{40}]$, $\alpha\text{-}1,2,3\text{-Cs}_6[\text{PV}_3\text{W}_9\text{O}_{40}]$, and $\alpha\text{-}1,2,3\text{-K}_6[\text{PV}_3\text{W}_9\text{O}_{40}]$ were prepared according to previously published protocols as described in ref 17. These compounds were characterized by X-ray crystallography, solution NMR spectroscopy, and solid-state NMR spectroscopy. Water presence in all these salts was confirmed by infrared spectroscopy. In the salts with $((n\text{-C}_4\text{H}_9)_4\text{N})^+$ (TBA⁺) as a counteranion, water was only adventitious and could be eliminated under vacuum, as shown below. Salts with other counteranions have water molecules incorporated in their crystal structure, as described in detail in ref 17, where the exact structures of some of these hydrates are given. For the purpose of clarity, in these studies the salts will be referred to without specifying the number of water molecules associated with the exact structure. Distilled water was used as a solvent.

2.2. Methods. **2.2.1. Infrared Measurements.** Experiments were performed using a Nicolet Magna 560 FTIR spectrometer with a liquid nitrogen cooled MCT detector. The spectrometer was equipped with a purging system to free the system of any $\text{CO}_2(\text{g})$ and moisture. Standard KBr pellet preparation techniques were used. The pellets were prepared by careful mixing of the appropriate amounts of polyoxometalates, to produce ap-

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proximately 1% weight mixture, with KBr (Fluka, for IR spectroscopy). The pellets were obtained by applying 40 ft lbs to the screw of a 3/8 in. pellet press to produce a pellet of approximately 0.010 in. thickness as measured by a micrometer. Special precaution was exercised to ensure that the infrared beam of the spectrometer had a diameter smaller than the 3/8 in. opening of the pellet press. Infrared spectra were recorded at room temperature with 4 cm^{-1} resolution and at least 32 scans/experiment. The absorption spectra were obtained by dividing the single-beam spectra of KBr pellets containing polyoxometalates by a single-beam spectrum of pure KBr, maintaining the same parameters throughout the course of the studies.

A home-built infrared cell similar to that previously reported²⁴ with a specially designed attachment assembly²⁵ was used for high-vacuum and temperature-dependent studies. This cell was evacuated by a torbomolecular pump to a pressure of approximately 1×10^{-6} Torr for the experiments reported here. All analytes were prepared by spotting the sample onto a 10×10 mm Si(100) sample covered with native oxide with water solvent and mounting it on a resistive tantalum heater perpendicular to the IR beam with the manipulator. The temperature was measured by a k-type thermocouple spot-welded to the tantalum sample holder. The absorption spectra were obtained by the division of the spectra of the POM-spotted sample by a spectrum of a silicon crystal support without added POM salt recorded at the same conditions. For the annealing studies, the samples were briefly annealed with heating and cooling rate of approximately 3 K/s, and the resulting spectra were recorded at room temperature.

2.2.2. Computational Details. Molecular orbital calculations²⁶ using density functional theory (DFT) were performed using the Gaussian 03 package.²⁷ The Becke three-parameter hybrid functional,^{28,29} combined with the Lee, Yang, and Parr (LYP) correlation functional,³⁰ denoted B3LYP,³¹ was employed in the calculations. Geometries of the naked anions without counter-cations were optimized^{32–34} without any symmetry constraints using the LANL2DZ basis set. This basis set retains some of the outer-core functions when applied to third- and higher-period atoms. The LANL basis sets are available either as a minimum (MB) or a double- ζ (DZ) basis. Our previous computational study of polyoxometalates of Lindqvist structure demonstrated that these two basis sets yield essentially the same optimized structures.¹⁹ The LANL2DZ basis set was used here, and the optimized geometries are in general agreement with each other and with experimental data. In contrast to previous DFT studies of unsubstituted Keggin structure polyoxometalates,³⁵ this study does not use any symmetry constraints. Harmonic vibrational frequencies were calculated analytically for each optimized structure. No scaling factors were used, except for the convenience of the comparison in Figure 6, *vide infra*.

3. Results and Discussion

Figure 1 shows the structure of a Keggin-type polyoxoanion. It suggests that there are several distinctly different types of oxygen atoms in the structure of this cage. Substitution of the native tungsten in this structure for a vanadium atom would lead to complex changes in the vibrational characteristics of the polyoxoanions. The mono-, di-, and tri-vanadium-substituted POM salts analyzed in this study had vanadium atoms at neighboring metal center positions in the “crown” within the anion, denoted M_{crown} , (for example, α -1,2- $K_5[PV_2W_{10}O_{40}]$ and α -1,2,3-((n -C₄H₉)₄N)₆[PV₃W₉O₄₀],) as described in ref 17. In fact, Figure 1 depicts an example of the trisubstituted α -isomer

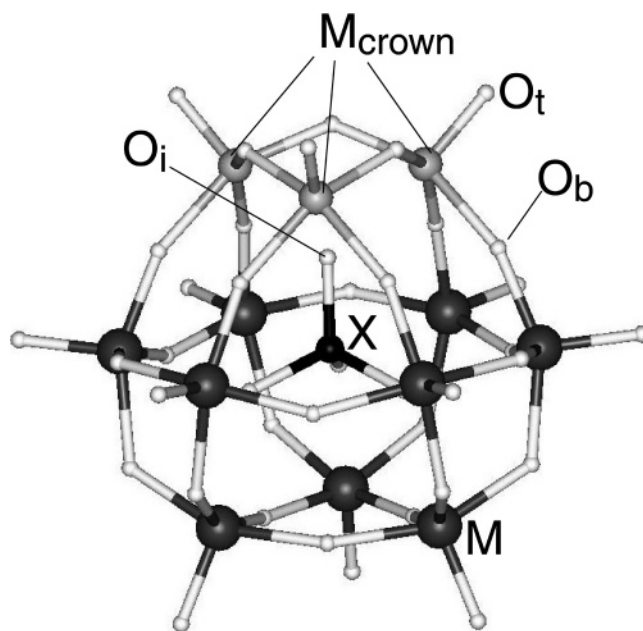


Figure 1. Schematic representation of the Keggin structure anion of the α -isomer.

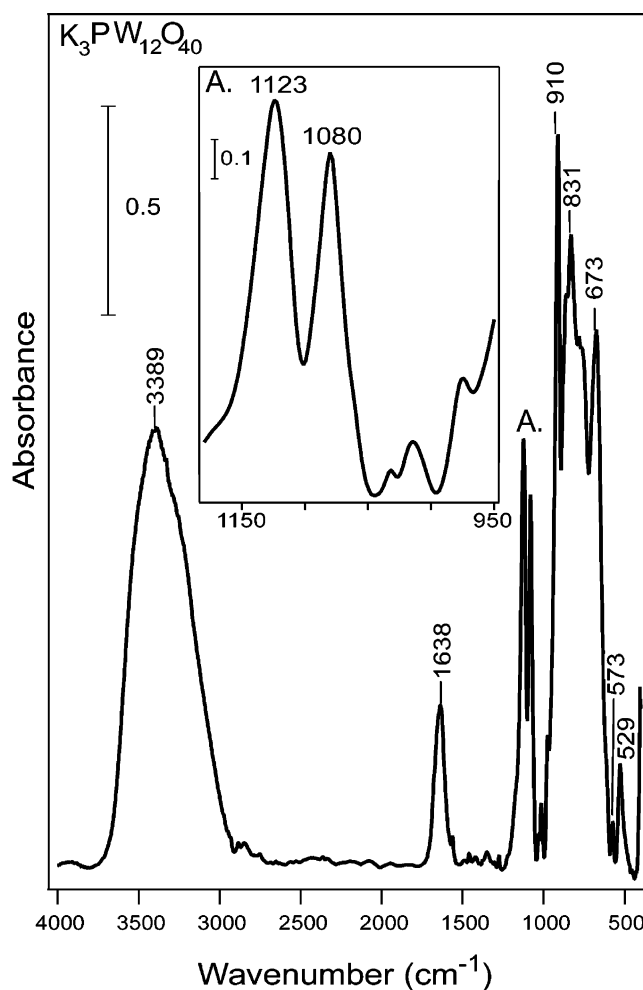


Figure 2. Infrared studies of the unsubstituted $[PW_{12}O_{40}]^{3-}$ anion with K^+ as a counteranion. The inset shows the enlarged $950\text{--}1200\text{ cm}^{-1}$ spectral region.

of the Keggin-structure anion. Here, all the terminal oxygen atoms are denoted O_t , the bridging oxygen atoms of all types

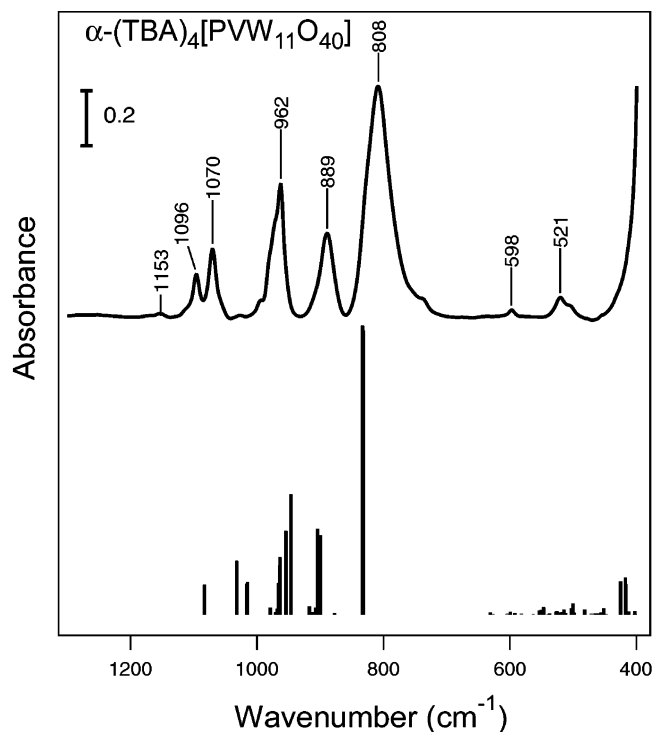


Figure 3. Vibrational experimental (top) and computational (bottom) studies of the $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ anion with $(\text{TBA})^+$ as a counteranion.

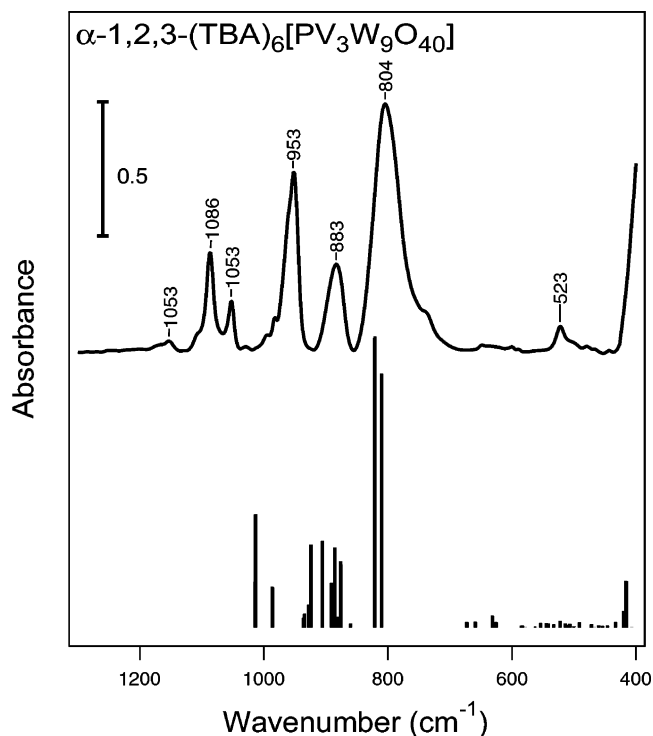


Figure 5. Vibrational experimental (top) and computational (bottom) studies of the $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ anion with $(\text{TBA})^+$ as a counteranion.

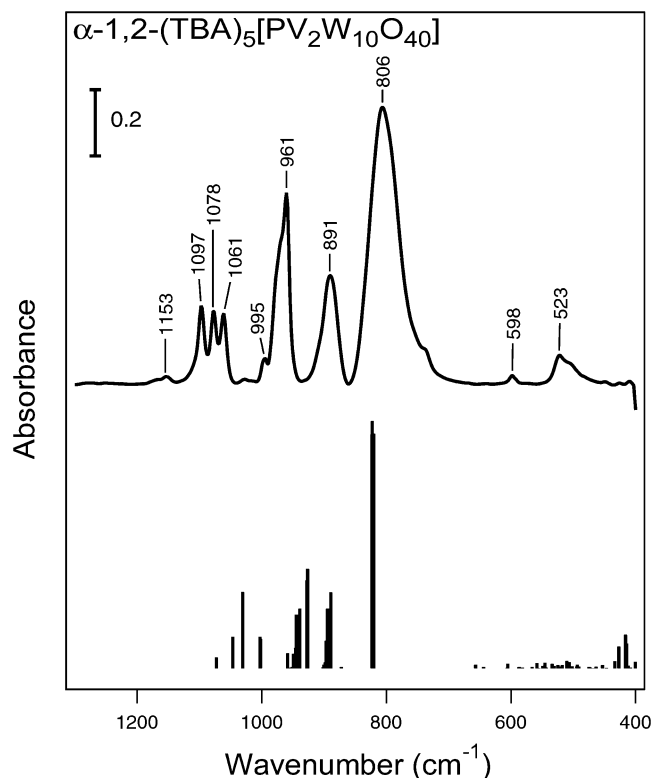


Figure 4. Vibrational experimental (top) and computational (bottom) studies of the $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anion with $(\text{TBA})^+$ as a counteranion.

are denoted O_b , and the oxygen atoms of the internal PO_4 group are denoted O_i . It should be emphasized that, in vanadium-substituted structures, there are several distinctly different kinds of oxygen atoms corresponding to each type.

An infrared spectrum of $\text{K}_3[\text{PW}_{12}\text{O}_{40}]$ is shown in Figure 2. Since the vibrational modes produced by this type of structure

are very complex, only spectral features that are significantly different in the infrared spectra of mono-, di-, and tri-vanadium-substituted POMs will be outlined below. Most importantly, only a doublet of features at 1123 and 1080 cm^{-1} is observed in the 1025–1250 cm^{-1} range. This range will be shown below to be the most informative for the assignment of the number of vanadium atoms in the Keggin cage. The majority of the vanadium-related absorption features in this range involve $\text{V}=\text{O}_t$ vibrations (terminal oxygen shown in Figure 1), similar to the previously studied six-coordinate oxotungstates.¹⁹ Since the vibrational spectrum of the unsubstituted Keggin-structure oxotungstate has been analyzed previously, and since the absorption features corresponding to this structure have already been assigned and published,³⁵ these assignments will not be repeated here. It is worth noting that the absorption features of the unsubstituted Keggin-structure oxotungstates in the 1025–1250 cm^{-1} spectral region are blue-shifted as compared to the corresponding features of vanadium-substituted structures and thus can be easily distinguished from the rest of the structures analyzed here, *vide infra*.

Comparison of the results in Figure 2 with the spectroscopic studies of a mono-V-substituted POM in Figure 3 shows that in the case of one of the tungsten atoms replaced with vanadium, the vibrational spectrum exhibits a set of completely different absorption features at 1096 and 1070 cm^{-1} as compared to the unsubstituted POM. If two vanadium atoms are incorporated into the Keggin cage of the polyoxotungstate, then the triplet of the vibrations is recorded at 1097, 1078, and 1061 cm^{-1} , as shown in Figure 4. Finally, Figure 5 demonstrates that when three vanadium atoms are present in the polyoxometalate structure, the absorption feature at 1086 cm^{-1} completely dominates the spectrum with a satellite feature at 1053 cm^{-1} . The absorption band around 1103 cm^{-1} is only observed as a shoulder. For each vanadium-substituted POM compound, the naked anions, $[\text{PVW}_{11}\text{O}_{40}]^{4-}$, $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$, and $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$, have been fully optimized and characterized by frequency

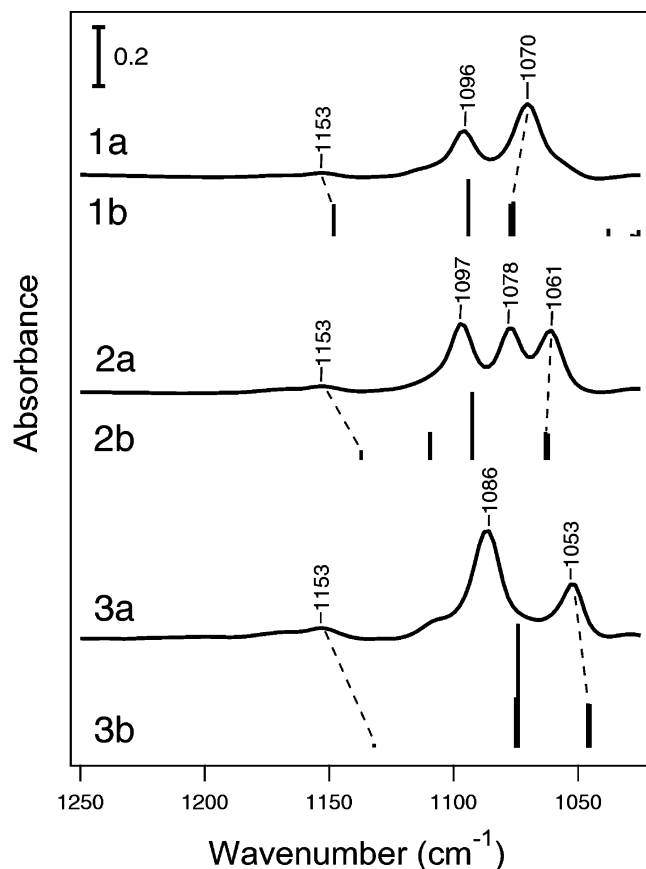


Figure 6. Comparison of the measured (a) and calculated (b) spectra of the 1025–1250 cm^{-1} spectral region for (1a) $\alpha\text{-(TBA)}_4[\text{PVW}_{11}\text{O}_{40}]$, (1b) $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ anion, (2a) $\alpha\text{-1,2-(TBA)}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$, (2b) $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anion, and (3a) $\alpha\text{-1,2,3-(TBA)}_6[\text{PV}_3\text{W}_9\text{O}_{40}]$, 3b) $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ anion. A scaling factor of 1.06 is used for a more convenient comparison.

calculations. The computed unscaled IR spectra are compared with the experimental data in the bottom part of Figure 3, Figure 4, and Figure 5, respectively. Although various absorption bands in the infrared spectrum of vanadium-substituted POMs could potentially be used for identification of these compounds, the spectral signatures between 400 and 1025 cm^{-1} involve complex vibrations of the multiple atoms in the Keggin cage, largely independent of the vanadium presence, while the 1025–1250 cm^{-1} region seems to be the most informative and reliable, as suggested by a comparison in Figure 6. In this figure the computed frequencies were multiplied by a scaling factor of 1.06 for a more convenient comparison. Complete lists of all the frequencies and corresponding calculated intensities of the infrared spectra are available in the Supporting Information. The studies presented in Figure 6 show a very good qualitative comparison between computational and experimental data and capture all the trends in changes of vibrational signatures of mono-, di-, and trisubstituted POMs. Each experimental spectrum has a peak at 1153 cm^{-1} , which can be assigned to a combination of stretching vibrations of $\text{P}=\text{O}_i$ and $\text{V}=\text{O}_i$. This feature is absent in a spectrum of $\text{K}_3[\text{PW}_{12}\text{O}_{40}]$ presented in Figure 2 because of the absence of vanadium in this structure. The two absorption bands at 1096 and 1070 cm^{-1} observed for $\alpha\text{-(TBA)}_4[\text{PVW}_{11}\text{O}_{40}]$ shown in plot 1a in Figure 6 correlate well with the computed vibrational frequencies predicted in 1b characterizing a combination of $\text{P}=\text{O}_i$ stretch and $\text{M}_{\text{crown}}=\text{O}_i$ and a combination of $\text{P}=\text{O}_i$ and $\text{W}=\text{O}_i$ with $\text{V}=\text{O}_i$, respectively. A triplet of the features describing $\alpha\text{-1,2-(TBA)}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$

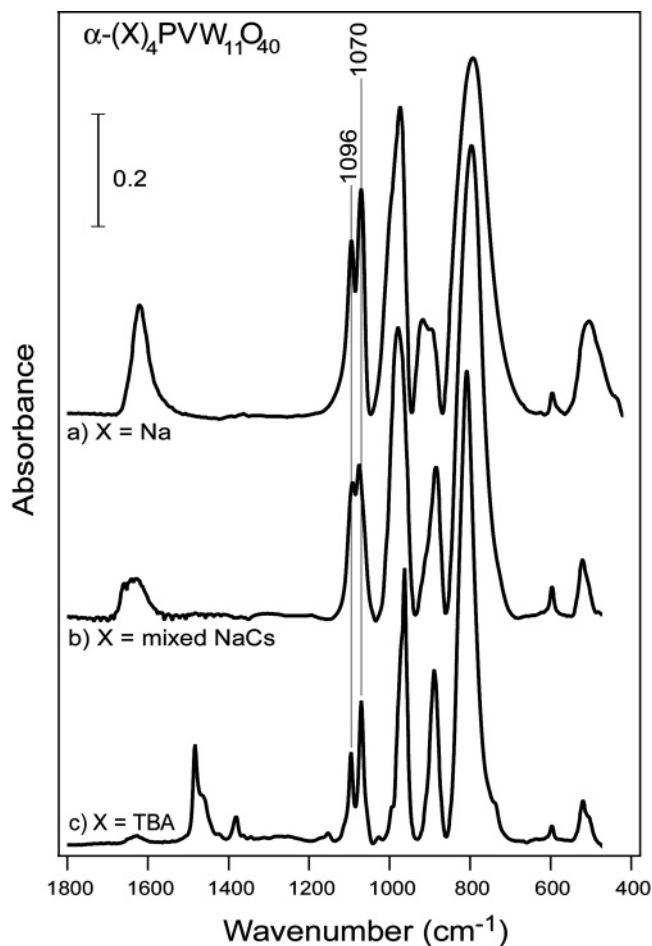


Figure 7. Comparison of the infrared spectra of the $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ anion with (a) Na^+ , (b) mixed Na^+Cs^+ , and (c) $(\text{TBA})^+$ as counteranions.

in plot 2a in Figure 6 originates from the possibility of symmetric and asymmetric vibrations involving $\text{V}=\text{O}_i$. Thus, while the 1097 cm^{-1} absorption feature corresponds to the asymmetric $\text{V}=\text{O}_i$ vibration, the peak at 1078 cm^{-1} can be described as a combination of the $\text{P}=\text{O}_i$ and a symmetric $\text{V}=\text{O}_i$ stretch with a small contribution from the $\text{W}_{\text{crown}}=\text{O}_i$. The 1061 cm^{-1} feature can be viewed as a complex combination of $\text{P}=\text{O}_i$, $\text{W}=\text{O}_i$ and $\text{V}=\text{O}_i$. For a trisubstituted POM anion, there is also a combination of symmetric and asymmetric vibrations corresponding to $\text{V}_{\text{crown}}=\text{O}_i$; however in this case there are two different kinds of asymmetric stretch vibrations involving three vanadium atoms in the “crown”. The 1086 cm^{-1} absorption feature involves largely the asymmetric vibration, while the 1053 cm^{-1} corresponds to symmetric vibrations.

This quick overview produced a set of unique signatures that can serve to distinguish mono-, di-, and tri-vanadium-substituted $[\text{PV}_x\text{W}_{12-x}]^{(3+x)-}$ anions. However, in our previous work on six-coordinate oxotungstates, we demonstrated that the appearance of the infrared spectrum can depend drastically on the nature of the counteranion. Thus, a systematic analysis of the effect that the counteranions may have on the spectral region of 1000–1150 cm^{-1} of vanadium-substituted Keggin POMs should be performed.

Figure 7 compares the spectra of $[\text{PVW}_{11}]^{4-}$ anions with Na^+ , mixed Na^+Cs^+ , and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations. Only the features corresponding to the water incorporated in $\alpha\text{-Na}_4[\text{PVW}_{11}\text{O}_{40}]$ and $\alpha\text{-Na}_2\text{Cs}_2[\text{PVW}_{11}\text{O}_{40}]$ as opposed to $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ in $\alpha\text{-((n-C}_4\text{H}_9)_4\text{N)}_4[\text{PVW}_{11}\text{O}_{40}]$ provide the difference between the

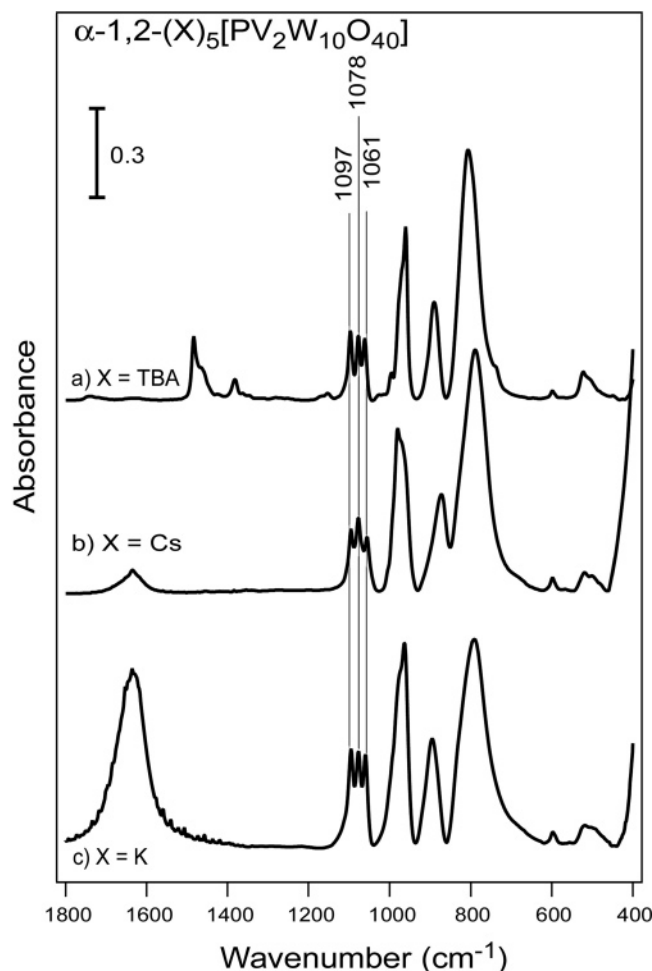


Figure 8. Comparison of the infrared spectra of the $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anion with (a) $(\text{TBA})^+$, (b) Cs^+ , and (c) K^+ as counteranions.

spectra. The absorption features corresponding to the combination of vibrations describing the anions themselves are essentially identical. Consistent with our previous studies of six-coordinate oxotungstates,¹⁹ the presence of water only affects the widths of the absorption bands corresponding to the metal–oxygen vibrations, but not their frequency.

A similar analysis based on the results summarized in Figures 8 and 9 for $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ and $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ anions, respectively, with K^+ , Cs^+ , and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations suggests that the key absorption features in the 1025–1250 cm^{-1} region are not affected significantly by the nature of the counteranion and by the presence of water in the structure. Thus this spectral region can be used unambiguously to identify the presence and quantity of vanadium in mono-, di-, and tri-vanadium-substituted Keggin structure oxotungstates.

The effect of vacuum on the vibrational spectra of vanadium-substituted Keggin-type POMs, and specifically the binding of water in these structures, is addressed in Figure 10. When the bottom two spectra on this figure (corresponding to $\alpha\text{-}((n\text{-C}_4\text{H}_9)_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$ in a KBr pellet and to the same compound under vacuum at room temperature) are compared, the only effect that is clearly observed is the removal of the adventitious water under vacuum, while the rest of the spectrum is not affected significantly. Figure 10 also addresses the effect of temperature on the stability of $\alpha\text{-}((n\text{-C}_4\text{H}_9)_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$. No noticeable changes are observed in the infrared spectrum of this compound for temperatures as high as 1000 K, as compared to the room-temperature spectrum. Only at 1200 K

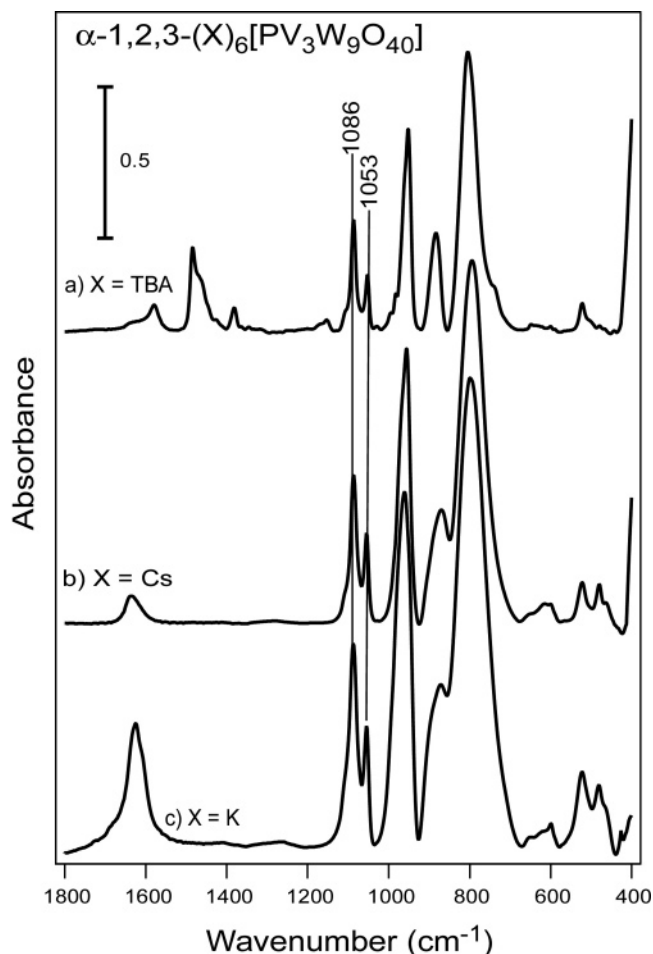


Figure 9. Comparison of the infrared spectra of the $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ anion with $(\text{TBA})^+$, Cs^+ , and K^+ as counteranions.

do the spectral features change, which indicates decomposition. The absorption bands corresponding to TBA are decreased significantly, indicating that, at that temperature, TBA starts leaving the sample and likely partially decomposing. It is possible that both structural changes caused by this process and chemical changes in the POM salts lead to the decomposition of the salt, although the exact mechanism of this process cannot be confirmed solely on the basis of the results of this study. A similar effect is observed for other POMs with water incorporated in their structures. Only a small amount of adventitious water is removed by simple evacuating; the rest is quite stable up to the temperatures of at least 900 K.

Thus, vanadium-substituted POM salts of Keggin structure are very stable with respect to elevated temperatures and could potentially be used in high-temperature devices or catalytic processes.

4. Conclusions

The infrared spectroscopy, as supported by computational investigation, was shown to be a unique and unambiguous probe of the presence and the number of vanadium atoms in mono-, di-, and tri-vanadium-“crown”-substituted Keggin-structure oxotungstates. The spectral region of 1025–1250 cm^{-1} provides a set of benchmark absorption features that can be used to identify the above-named compounds, regardless of the counteranion and the presence of water in the structure. These spectral features are not affected by vacuum, and the vanadium-substituted Keggin POMs exhibited a remarkable thermal stability up to

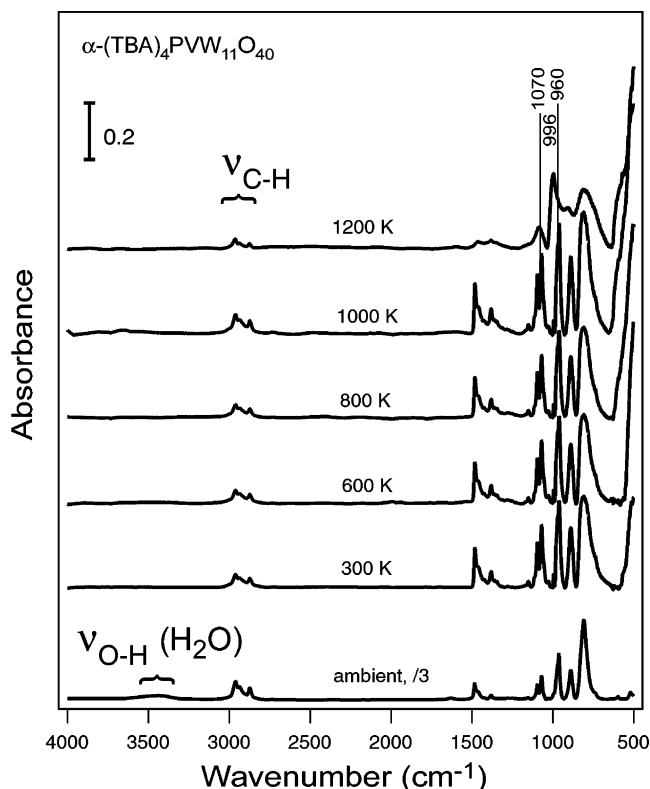


Figure 10. Infrared studies of thermal stability of $(\text{TBA})_4[\text{PW}_{11}\text{O}_{40}]$ under vacuum.

the temperature of 1000 K, which proves that high-temperature catalytic processes can be run using these compounds.

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Supporting Information Available: Total energies, Cartesian coordinates, and IR frequencies (Word; PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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