JOURNAL OF RAMAN SPECTROSCOPY, VOL. 26, 397–405 (1995)

Determination of the Molecular Structures of Tungstates by Raman Spectroscopy

Franklin D. Hardcastle*
Department of Chemistry, Zettlemoyer Center for Surface Studies, Lehigh University, 7 Asa Drive, Bethlehem, Pennsylvania 18015, USA

Israel E. Wachs†
Department of Chemical Engineering, Zettlemoyer Center for Surface Studies, Lehigh University, 7 Asa Drive, Bethlehem, Pennsylvania 18105, USA

An empirical correlation is developed for relating the wavenumbers of (W—O) stretching modes to W—O bond lengths and bond strengths for tungsten oxide reference compounds. A least-squares exponential fit of crystallographically determined W—O bond lengths to the wavenumbers of their Raman stretching modes is presented along with a relation between W—O bond strengths, in valence units, and wavenumbers of Raman stretching modes. The empirical bond length/stretching mode wavenumber/bond strength relationships lead to a unique and effective method of interpreting Raman spectra of tungstate species. This method leads to the W—O bond lengths and coordination of the tungstate species. The utility of the method is illustrated by estimating the wavenumbers of the Raman stretching modes for the ideal WO_4 tetrahedron and WO_6 octahedron, and the bonds lengths and coordinations of the tungstate species in the reference compounds Na_2WO_4, $PbWO_4$, $CaWO_4$ and Bi_2WO_6. In addition, the W—O bond lengths of the WO_6 octahedra in crystalline Ba_2MgWO_6 are reported for the first time. This new approach for evaluating the Raman spectra of tungstate species is expected to be generally applicable to all tungstates, regardless of environment, physical state, or oxidation state.

INTRODUCTION

The Raman spectra of transition metal oxides are generally fairly informative with regard to the structure of metal oxide species. This is true not only for the more common crystalline and solution phases,[1] but also for the exotic two-dimensional surface phases.[2,3] It is well established that the Raman vibrational features of a molecular species depend on its molecular structure and also the nature and strength of its chemical bonding. Different molecular structures generally have different types of bonds, and this leads to different Raman spectral features. Thus, Raman spectroscopy is an effective structural tool because it can be used to discriminate between alternative structures proposed for a chemical species.

The conventional method of ascertaining the molecular structure of a metal oxide species is performed by directly comparing its Raman spectrum with those of reference compounds. This type of approach, commonly referred to as fingerprinting, has proved useful because it identifies similar chemical functionalities and lends insight into the site symmetry and oxygen coordination of the metal cation for symmetric metal oxide species. For example, characteristic Raman bands have been used to determine that the surface rhenium oxide species on a γ-alumina support is tetrahedrally coordinated,[4] and that the surface chromium oxide species on alumina, titania and silica supports is tetrahedrally coordinated and polymeric.[5]

The fingerprint approach of interpreting the Raman spectra of metal oxides, however, is not generally applicable to all molecular geometries because it requires that the molecule of interest exhibits a reasonable degree of point-group symmetry. This is illustrated by considering the surface rhenium and chromium oxide species discussed in the preceding paragraph. Under ambient conditions, with moisture present, the Raman spectra of the surface species are comparable to those of their aqueous solution counterparts. Consequently, the structures of the surface species are determined to be very similar to those present in aqueous solution. Once the moisture is removed from the surface, however, the surface rhenium and chromium oxide species become distorted, and it is no longer possible to ascertain the structure of the metal oxide species by direct comparison with the Raman spectra of reference compounds. Clearly, a more systematic and generally applicable approach is needed to interpret the Raman spectra of metal oxide species.

Recently, a new approach has been developed for interpreting the Raman spectra of transition metal oxides that is systematic and generally applicable. This approach, termed the diatomic approximation, regards each metal–oxygen bond in the metal oxide species or crystalline lattice as vibrationally independent of its surroundings. Naturally, this approach does not lead to a vibrational mode analysis because it neglects nearest-

---

* Present address: Westinghouse Electric Corporation, Bettis Atomic Power Laboratory, West Mifflin, PA 15122, USA

† Author to whom correspondence should be addressed.

CCC 0377–0486/95/060397–09

Received 12 September 1994
Accepted 14 February 1995

neighbor interactions and, consequently, bending/wagging and external modes. Within the limits of experimental error afforded by crystallographic bond length determinations, however, the diatomic approximation is fully justified and may be used to determine metal–oxygen bond lengths from Raman stretching mode wavenumbers because the effect of the interaction force constants on the bond lengths is smaller than the uncertainty associated with most crystallographic bond length determinations. Empirical relationships have already been established for relating molybdenum–,[6] vanadium–[7] and niobium–oxygen[8] bond lengths to Raman stretching mode wavenumbers in bulk transition metal oxide reference compounds.[9]

In this study, an empirical relationship was found between tungsten–oxygen bond lengths and their respective Raman stretching wavenumbers. As in previous studies, trial-and-error numerical fits led to a simple exponential relationship as the most expedient way of describing the bond length–Raman stretching wavenumber relationship for tungsten–oxygen chemical bonds.

EXPERIMENTAL

The Raman spectra of the following tungstate reference compounds were collected: $PbWO_4$, $CaWO_4$, K_2WO_4, Na_2WO_4, Li_2WO_4, $Al_2(WO_4)_3$, $NiWO_4$, WO_3, WO_3–H_2O, $CuWO_4$ and $CsLuW_2O_8$. The Raman band positions of $SrWO_4$, $BaWO_4$ and $Na_2W_2O_7$ were taken from the literature.[10,11]

The Raman spectra were collected by using 10–40 mW of 514.5 nm radiation from a Spectra-Physics Model 171 argon ion laser for excitation. The laser beam power was measured at the sample. The diffusely scattered radiation from the sample was collected in a 90° scattering geometry and directed into a Spex Triplemate Model 1877 spectrometer coupled to an intensified photodiode-array detector (900 intensified array elements) and optical multi-channel analyzer (OMA III: Princeton Applied Research, Model 1463). The detector was thermoelectrically cooled to −35 °C. The Raman spectra were collected and recorded using an OMA III (PAR) dedicated computer and software. The spectral resolution and reproducibility were experimentally determined to be better than 2 cm^{-1}. About 100–200 mg of each tungsten oxide reference compound were pressed into a thin wafer about 1 mm thick with a KBr backing for mechanical support. Each sample was mounted on a sample holder (Spex Model 1445A) capable of rotating at about 2000 rpm to avoid local heating effects caused by the focused laser beam.

THEORY

Several levels of approximation may be made in order to interpret more readily the Raman vibrational spectrum of a metal oxide species confined in a crystalline lattice. The most common approximation is to assume that the internal and external modes of the crystal are independent of one another. The internal modes of transition metal oxide molecules within the unit cell of the crystal occur in the medium- and high-wavenumber regions (>200 cm^{-1}) whereas the external modes, including translational and librational modes, occur at lower wavenumbers (<200 cm^{-1}). Next, the site-symmetry approximation[12] or correlation method may be introduced by assuming and assigning a high degree of symmetry to each atom or site within the unit cell. Although the site-symmetry approach leads to the total number and types of infrared and Raman active modes expected from the crystal, a detailed knowledge of the crystal structure is first required in order to perform the analysis. The site-symmetry approximation does allow a direct comparison of the internal modes of a molecular species in the solid state with those of a similar molecule in solution or gas phase and so forms the basis of the fingerprint approach of interpreting Raman spectra. For metal oxides with distorted molecular geometries, where the site-symmetry and fingerprint approaches are not applicable, there is a demonstrated need for a systematic way of determining molecular structures from Raman vibrational bands.

In recent studies, empirical relationships have been found between the metal–oxygen Raman stretching mode wavenumbers and their bond lengths for molybdenum–,[6] vanadium–[7] and niobium–oxygen[8] bonds. The empirical Raman stretching mode wavenumber–bond length relationship was found to follow a simple exponential form:

$$\tilde{\nu} = A \exp(BR) \qquad (1)$$

where A and B are fitting parameters, ν is the Raman stretching mode wavenumber (cm^{-1}) and R is the metal–oxygen bond length (Å). In this study, Eqn (1) was also found to describe adequately the relationship between the Raman stretching mode wavenumbers and bond lengths of tungsten–oxygen bonds that are present in tungsten oxide reference compounds.

The Pauling bond strengths, in valence units, also referred to loosely as bond orders or bond valences, of the metal–oxygen bonds are useful for discussing the plausibility of proposed metal oxide structures.[13] The Pauling bond strength of a bond reflects the relative distribution of available valence electrons throughout the covalent bonds of a metal oxide species. Further, according to the valence sum rule, there is a conservation of valency associated with the metal cation, and so the valence sum rule serves as a bookkeeping device for the valence electrons. Hence the calculated valence state of a proposed structure may be compared with the formal oxidation state of the metal cation as a simple test for the plausibility of that structure.

A generally applicable relationship has been developed by Brown and Wu[14] which relates the cation–oxygen bond valence s to the interatomic distance R. The empirical expression relating a W—O bond length to its bond strength, or valence is

$$s(\text{W–O}) = (R/1.904)^{-6.0} \qquad (2)$$

where 1.904 Å is the estimated bond length of a W—O bond of unit valency. The empirical parameters in Eqn (2), 1.904 and 6.0, were determined from the data for twelve different W^{6+} cation environments.

RESULTS

The tungsten–oxygen bond lengths were obtained from the reported values for several tungsten oxide compounds and assigned to their respective Raman stretching mode wavenumbers. These tungsten oxide reference compounds are listed in Tables 1 and 2 along with their reported W—O bond lengths, assigned Raman stretching mode wavenumbers, calculated bond strengths [from Eqn (2)] and tungsten cation valence states (valence sum rule) and oxygen coordination number of each tungsten cation.

For the tungsten oxide reference compounds listed in Tables 1 and 2, all Raman bands about 400 cm^{-1} are assigned to wavenumbers W—O stretching modes and are assumed to reflect directly the W—O bond lengths present in the tungstate species. The shortest bonds are assigned to the highest Raman stretching mode wavenumbers (>800 cm^{-1}). The W—O bonds of intermediate length (about unit valency) are characteristic of bridging W—O bonds and are assigned to Raman mode stretching wavenumbers in the 600–800 cm^{-1} region. The procedure for assigning the longer W—O bonds (>1.9 Å) to their Raman stretching mode wavenumbers, however, is less certain and depends on extrapolating into the low-wavenumber region (<400 cm^{-1}) with a preliminary exponential fit derived from all other data. This is because the bending/wagging modes also lie in the low-wavenumber region, as do the very intense lattice vibrations characteristic of crystallinity. In contrast, the very long W—O bonds that are expected to give rise to stretching modes below 400 cm^{-1} have lost most of their covalency rendering their Raman band intensities weak. Consequently, the W—O bond length–stretching mode wavenumber relationship is not expected to be reliable for determining W—O bond lengths greater than 2.2 Å because of the unreliability of the band assignments in this region.

Table 1. Tetrahedrally coordinated tungsten oxide reference compounds

Compound	R/Å	ν/cm^{-1} [a]	s/v.u.[b]	Valence/ v.u.	Ref.
$PbWO_4$	1.772 (2×)	902	1.54		19
	1.772	764	1.54		
	1.772	750	1.54	6.2	
$CaWO_4$	1.788 (2×)	910	1.46		19
	1.788	836	1.46		
	1.788	795	1.46	5.8	
$SrWO_4$	1.779 (2×)	919	1.50		19, 22
	1.779	836	1.50		
	1.779	797	1.50	6.0	
$BaWO_4$	1.781 (2×)	922	1.49		19, 22
	1.781	831	1.49		
	1.781	791	1.49	6.0	
K_2WO_4	1.76	926	1.60		23
	1.79	926	1.45		
	1.80 (2×)	853	1.40	5.9	
Na_2WO_4	1.819 (2×)	931	1.31		18, 21
	1.819 (2×)	811	1.31	5.3	
$Na_2W_2O_7$	1.759	940	1.61		18, 24
	1.762	940	1.59		
	1.807 (2×)	835	1.37	5.9	
Li_2WO_4	1.77	963	1.55		25
	1.78	928	1.50		
	1.79	881	1.45		
	1.81	853	1.36	5.8	
$Al_2(WO_4)_3$	1.764 (a)[c]	1060	1.58		26
	1.764 (a)	1030	1.58		
	1.769 (a, 2×)	1002	1.55		
	1.771 (b)	905	1.54		
	1.801 (b)	838	1.40		
	1.804 (b)	838	1.38	(a) 6.3	
	1.825 (b)	810	1.29	(b) 5.6	

[a] ν (cm^{-1}): Assigned W—O Raman stretching mode wavenumber.
[b] s (v.u.): Pauling bond strength in valence units [Eqn 12)].
[c] Designations (a) and (b) represent different tungsten cation sites.

Table 2. Octahedrally coordinated tungsten oxide reference compounds

Compound	R/Å	ν/cm^{-1} [a]	s/v.u.[b]	Valence/ v.u.	Ref.
$NiWO_4$	1.79 (4×)	893	1.45		27
	2.19	415	0.43	6.7	
WO_3	1.80 (a)[c]	808	1.40		28, 29
	1.84 (b)	719	1.23		
	1.84 (b)	719	1.19		
	1.86 (a)	719	1.15		
	1.91 (b)	719	1.01		
	1.92 (b)	719	0.95		
	1.93 (a)	625	0.92		
	1.96 (a)	604	0.84		
	1.97 (ab)	604	0.82		
	1.99 (a)	580	0.77	(a) 5.9	
	2.01 (b)	520	0.72	(b) 5.9	
$WO_3 \cdot H_2O$	1.69	951	2.01		30
	1.83	816	1.27		
	1.83	812	1.27		
	1.93 (2×)	639	0.92		
	2.34		0.29	6.7	
$Na_2W_2O_7$	1.725	957	1.81		18, 24
	1.725	940	1.81		
	1.921	598	0.95		
	1.921	422	0.95		
	2.252 (2×)		0.37	6.2	
$CuWO_4$	1.760	958	1.60		31
	1.816	908	1.33		
	1.845	776	1.21		
	1.988	543	0.77		
	2.028	474	0.68		
	2.208		0.41	6.0	
$CsLuW_2O_8$	1.73	962	1.78		32
	1.80	826	1.40		
	1.88	750	1.08		
	1.89	702	1.05		
	2.04	525	0.66		
	2.42		0.24	6.2	

[a–c] See Table 1.

A range of tungstate structures, spanning both tetrahedral and octahedral geometries, are listed in Tables 1 and 2. The reference compounds containing WO_4 tetrahedra are presented in Table 1 and include $PbWO_4$, $CaWO_4$, $SrWO_4$, $BaWO_4$, K_2WO_4, Na_2WO_4, $Na_2W_2O_7$, Li_2WO_4 and $Al_2(WO_4)_3$. A general conclusion made by comparing the Raman spectra of the tetrahedrally coordinated tungstate species with their molecular structures is that the highest observed wavenumber of the W—O Raman stretching modes of a tungstate species, which is due to the shortest bond in that structure, also reflects the regularity of that structure. That is, for a given coordination type and formal oxidation mode state of the metal cation, a higher Raman stretching mode wavenumber indicates a more distorted structure, whereas a lower Raman stretching mode wavenumber indicates a more regular structure. For this reason, the WO_4 tetrahedra listed in Table 1 are presented in order of increasing highest Raman stretching mode wavenumber. This order also reflects the regularity of these structures so that the shortest W—O bond in the most regular tetrahedron is expected to have the lowest stretching mode wavenumber whereas the most distorted tetrahedron should exhibit the highest stretching mode wavenumber. Accordingly, $PbWO_4$ has the most regular tetrahedron of the reference compounds whereas $Al_2(WO_4)_3$ has the most irregular or distorted tetrahedron.

Tungsten oxide reference compounds containing WO_6 octahedra are listed in Table 2. These tungstate reference compounds include $NiWO_4$, WO_3, WO_3-H_2O, $Na_2W_2O_7$, $CuWO_4$ and $CsLuW_2O_8$. As with the WO_4 tetrahedra in Table 1, the WO_6 octahedra in Table 2 are listed in order of increasing irregularity, and this is reflected in the structure's highest occurring Raman stretching mode wavenumber. Accordingly, $NiWO_4$ has the most regular WO_6 octahedron with four bonds of 1.79 Å and two of 2.19 Å (these reported bond lengths are questionable, however, in view of the extraordinarily high valence state of 6.7 valence units calculated for the W^{6+} cation from these bond length values). The most irregular WO_6 octahedron is found in $CsLuW_2O_8$, which has a very short W—O bond of 1.73 Å, yielding a Raman band at 962 cm^{-1}.

The data in Tables 1 and 2 consist of 63 points correlating W—O Raman stretching mode wavenumbers to their reported crystallographic bond lengths. The functional form of this correlation is found to be adequately expressed as the simple exponential function Eqn (1). The fitting parameters are determined from a non-linear least-squares treatment of the data. The resulting expression relating W—O bond lengths to Raman stretching mode wavenumbers is

$$\nu/\text{cm}^{-1} = 25\,823 \exp(-1.902R) \qquad (3)$$

Equation (3) is plotted in Fig. 1. The standard deviation of estimating a W—O bond distance from its Raman stretching wavenumber is about 0.034 Å. Conversely, the standard deviation of estimating a Raman stretching wavenumber from an absolute bond length is about 55 cm^{-1}. Also shown in Fig. 1, as dotted lines, are the estimated bond lengths and Raman stretching wavenumbers for the ideal WO_4 and WO_6 structures. These values are estimated in the Discussion section.

A bond valence–stretching wavenumber correlation is also useful for determining the structures of tungstate species because the bond valence, in valence units, is representative of the strength of the chemical bond and denotes the relative number of total valence electrons occupying the bond. According to the valence sum rule, the additive contributions of the valences of each of the W—O bonds per tungsten cation site should equal the formal oxidation state of the tungsten cation, that is, 6.0 valence units for its fully oxidized state. The combined use of the empirical bond valence–bond length relationship of Brown and Wu,[14] Eqn (2), and Eqn (3) yields the following relationship between the Pauling W—O bond strength s (in valence units) and the Raman stretching mode wavenumber:

$$s(\text{W—O}) = \{0.276\,13 \ln[25\,823/\nu\ (\text{cm}^{-1})]\}^{-6.0} \qquad (4)$$

Equation (4) is plotted in Fig. 2. The estimated bond strengths and Raman stretching wavenumbers are shown for the ideal WO_4 tetrahedron and WO_6 octahedron.

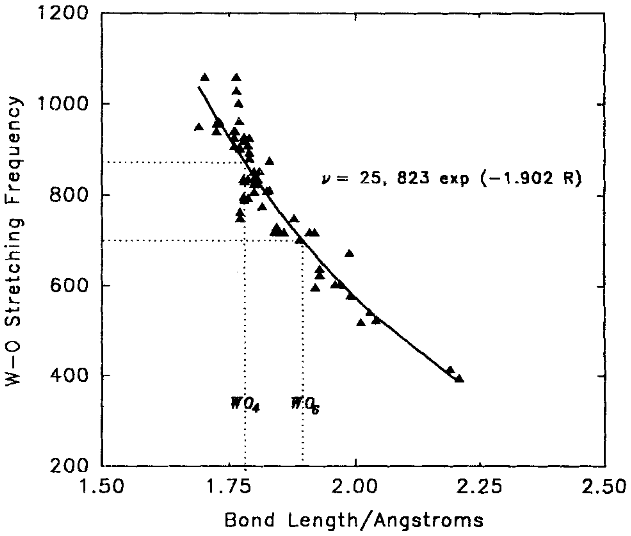

Figure 1. Tungsten–oxygen bond length–stretching mode wavenumber correlation.

DISCUSSION

The general empirical relationship used to relate wavenumbers of Raman stretching modes of metal–oxygen bonds to their associated bond lengths has been previously justified for several transition metal oxides.[6–9] Although vibrational interactions between neighboring metal–oxygen bonds do exist, the net influence of these vibrational interaction force constants on the metal–

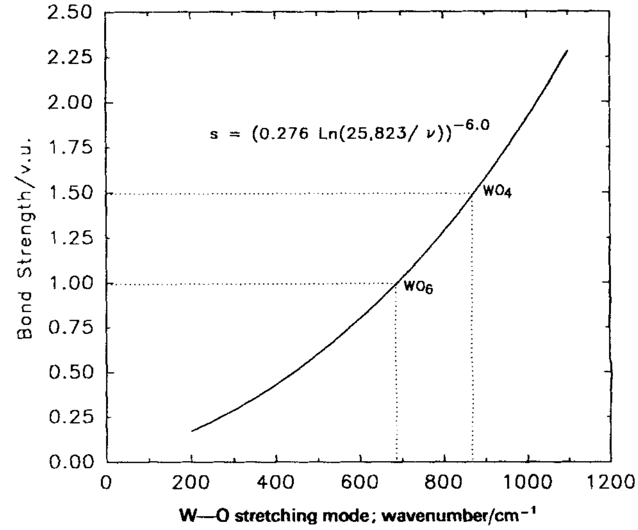

Figure 2. Tungsten–oxygen stretching mode wavenumber–bond strength correlation.

oxygen bond lengths is smaller than the experimental error associated with most bond distance determinations. This means that, to a first approximation, metal–oxygen Raman stretching mode wavenumbers may be directly converted into bond lengths and strengths within a specified precision that is determined by the magnitude of vibrational interactions in metal oxide molecules. This information, generated from the Raman spectrum of a metal oxide species, may be used to deduce possible structures for the tungstate species by using a systemic approach that is illustrated below.

In the following subsections, applications of Eqns (3) and (4) will be illustrated for several tungstate compounds having both known and unknown structures. In order to facilitate in the calculations, a BASIC computer program was written and used to consider all possible combinations of bond strengths consistent with the formal oxidation state of the metal cation within a specified tolerance (the initial tolerance is 0.15 v.u.). Once the program identifies a combination of W—O bond strengths consistent with the formal oxidation state of the tungstate cation (6.0 v.u., $\sigma = 0.15$ v.u.), the coordination, bond strengths and bond lengths of the plausible structure are listed.

Applications

Estimation of wavenumbers of stretching modes for symmetric tungstate units: WO_4 and WO_6. The Raman stretching mode wavenumbers of symmetric metal oxide species can be easily estimated by using Eqns (3) and (4). For highly symmetric species, only one type of metal–oxygen bond is present, one bond length, and therefore only one Raman stretching mode wavenumber should be observed in the high-wavenumber region. However, for the perfect tetrahedron and octahedron both symmetric and antisymmetric stretching modes are expected according to the T_d and O_h character tables. If these two Raman bands were observed, it would indicate two types of metal–oxygen bonds with two different bond lengths, according to the present treatment. For transition metal oxide species, however, the symmetric and antisymmetric modes are expected to be close in wavenumber. In fact, Eqn (3) yields identical bond lengths for both the symmetric and antisymmetric Raman stretching modes within the limits of their standard deviations. This is because the extent of the vibrational interactions between neighboring metal–oxygen bonds corresponds to less than that of the combined error associated with diffraction and Raman measurements.

To test the expectation that the symmetric and antisymmetric modes of a perfect WO_4 tetrahedron or WO_6 octahedron (assuming T_d or O_h point-group symmetry, respectively) would yield identical bond lengths within experimental error requires the experimentally determined Raman spectrum of these ideal structures. Unfortunately, these structures have not been verified to exist. Instead, an example of a metal oxide species that exhibits almost ideal, if not ideal, tetrahedral point-group symmetry is the vanadate species in the sillenite structure of $25Bi_2O_3$–V_2O_5, which exhibits stretching modes at 790 cm^{-1} (intense) and 775 cm^{-1} (weak).[15] Both of these stretching mode wavenumbers, however, yield the same V—O bond length of 1.719 Å, within the standard deviation of 0.019 Å, using a previously derived V—O bond length–stretching wavenumber correlation.[7] This result corroborates the assumption that the vibrational interactions between neighboring metal–oxygen bonds may be neglected in order to derive reasonable bond lengths, bond strengths and coordinations for metal oxide species from observed Raman bands.

Although Eqns (3) and (4) may be used to determine bond lengths and strengths from observed Raman bands, it is also possible to derive wavenumbers of Raman stretching modes from given bond strengths and/or bond lengths. For example, the stretching mode wavenumbers of the ideal WO_4 and WO_6 structures are estimated by first equally dividing the six valence units of available bond strength (assuming W^{6+} cation) between the four equivalent bonds of the tetrahedron and the six equivalent bonds of the octahedron. Equation (2) yields 1.780 Å for the W—O bonds of the tetrahedron and 1.904 Å for those of the octahedron. Substituting these values into Eqn (3) yields Raman stretching mode wavenumbers of 874 cm^{-1} for the ideal WO_4 tetrahedron and 691 cm^{-1} for the ideal WO_6 octahedron. These values are represented in Figs 1 and 2 as dotted lines.

The estimated wavenumbers of stretching modes for the ideal WO_4 and WO_6 structures may be compared with those of the tungstate reference compounds listed in Tables 1 and 2. The most regular tetrahedron in Table 1 can be identified as the one with the lowest Raman stretching mode wavenumber for the shortest W—O bond in its structure. According to these criteria, $PbWO_4$ is identified as having the most regular WO_4 tetrahedron because its shortest W—O bond exhibits a stretching mode at 902 cm^{-1}. This value is 28 cm^{-1}, or half a standard deviation, higher than that predicted for the ideal WO_4 tetrahedron at 874 cm^{-1}, and within the precision of Eqns (3) and (4) the WO_4 structural unit in $PbWO_4$ is consistent with a highly regular, if not ideal, tetrahedron. However, three wavenumbers of the stretching modes are observed for $PbWO_4$ at 902, 764 and 750 cm^{-1} and correspond to 1.76, 1.85 and 1.86 Å, respectively. Within the limits of the standard deviation, 0.034 Å, there are two distinct W—O bond lengths in the $PbWO_4$ structure. Therefore, according to the present treatment, the WO_4 tetrahedron in $PbWO_4$ is not ideal, but consists of at least two sets of unique W—O bond lengths.

It is commonly accepted that the tungstate ion in aqueous solution, $WO^{2-}_{4(aq)}$, possess T_d point-group symmetry. The observed Raman bands for this species appear at 931, 838 and 325 cm^{-1} and have been assigned according to T_d point-group symmetry.[16] The shortest W—O bond in $WO^{2-}_{4(aq)}$, however, exhibits a Raman stretching mode at 931 cm^{-1}, which indicates an irregular tetrahedral structure (if tetrahedral coordination is assumed). In fact, the WO_4^{2-} tetrahedra in $PbWO_4$ (902 cm^{-1}), $CaWO_4$ (910 cm^{-1}), $SrWO_4$ (919 cm^{-1}), $BaWO_4$ (922 cm^{-1}), K_2WO_4 (926 cm^{-1}) and Na_2WO_4 (931 cm^{-1}) are at least as regular as $WO^{2-}_{4(aq)}$. Indeed, it is the authors' contention that the structure of the $WO^{2-}_{4(aq)}$ ion is significantly distorted from the ideal tetrahedron because it is hydroxylated, perhaps as $WO_4H_{2(aq)}$. In the hydroxylated structure, two wavenumbers of W—O Raman stretching modes are

Table 3. Na_2WO_4: structure determination by Raman spectroscopy

Observed Raman Bands		W—O stretches 931, 811 cm^{-1} Bending/external 371, 309 cm^{-1}			
		$\tilde{\nu}$/cm^{-1}	s/v.u.		R/Å
W—O bond types	A	931	1.676		1.747
	B	811	1.313		1.819
		Coordination	A	B	Valence
Possible structure		4	2	2	5.979
		This study (Raman)			Reported
		2 × A	2 × 1.747 (34) Å		4 × 1.819 Å
		2 × B	2 × 1.819 (34) Å		

expected: one due to terminal W═O bonds and one due to W—OH bonds. The terminal W═O bonds have a strength of about 1.676 v.u. each, leaving about 1.324 v.u. for each of the W—OH bonds. This bond strength for the W—OH bond translates to a stretching mode wavenumber of 815 cm^{-1} by Eqn (4), which is very close to that observed at 838 cm^{-1}. The only tungstate structure that can generate W—O stretching mode wavenumbers at 931 and 838 cm^{-1} (using the BASIC program previously discussed to determine all possibilities systematically) is a WO_4 tetrahedron with two bonds of 1.75 Å and two of 1.80 Å (the calculated W^{6+} valence is 6.1 v.u.). These bond lengths are consistent with the postulated $H_2WO_{4(aq)}$ unit.

The most regular tungstate octahedron currently known is the slightly distorted WO_6 unit in the perovskite Ba_2MgWO_6. This compound is not included as a reference compound in Table 2 because its bond lengths are not known. The Raman stretching mode wavenumber of the shortest W—O bond in Ba_2MgWO_6 is reported to occur at 817 cm^{-1}.[17] This value is 126 cm^{-1} higher (two standard deviations) than that estimated for the perfect WO_6 octahedron, suggesting that the WO_6 octahedron in Ba_2MgWO_6 is not ideal, but is significantly distorted.

Crystalline compounds of known structure: Na_2WO_4, $PbWO_4$, $CaWO_4$ and Bi_2WO_6. Table 3 illustrates the systematic procedure for determining the coordinations and bond lengths of the tungstate species in Na_2WO_4. This compound exhibits two Raman stretching mode wavenumbers above 400 cm^{-1}, at 931 and 811 cm^{-1}, and two wavenumbers below 400 cm^{-1}, at 371 and 309 cm^{-1}, attributed to bending/wagging or external modes. The two stretching mode wavenumbers at 931 and 811 cm^{-1} are each initially assumed to be representative of unique W—O bond types, shown in Table 3 as A and B. These two wavenumbers are entered into a computer program and the bond strengths and lengths determined by Eqns (3) and (4), respectively. The program then determines every possible combination of wavenumbers consistent with the formal oxidation state of the tungsten cation, or 6.0 v.u. with a tolerance of 0.15 v.u. As Table 3 shows, only one structure is possible, and it is tetrahedrally coordinated with two bonds at 1.75 Å and two of 1.82 Å (calculated valence of 6.0 v.u. for the tungsten cation). Single-crystal x-ray diffraction measurements on Na_2WO_4 show all four W—O bonds at 1.819 Å[18] (yielding a calculated valence of 5.3 v.u.).

Table 4 shows the identical procedure performed on $PbWO_4$ and $CaWO_4$, both having the scheelite crystal structure. $PbWO_4$ exhibits three W—O stretching wavenumbers at 902, 764 and 750 cm^{-1}. As Table 4 shows, five structures are possible for $PbWO_4$, but only two structures, (a) and (b), use the highest stretching mode wavenumber at 902 cm^{-1}. Because both (a) and (b) are equally probable, a hybrid structure is formed having three bonds of 1.76 Å and one bond of 1.86 Å. Diffraction measurements show all four bonds at 1.772 Å for $PbWO_4$.[19] For $CaWO_4$, the observed stretching mode wavenumbers at 910, 830 and 795 cm^{-1} yield three possible structures, but only (c) uses all three stretching wavenumbers. This tetrahedron has two W—O bonds of 1.76 Å, one of 1.80 Å, and one longer bond of 1.83 Å. Diffraction measurements show all four W—O bonds of $CaWO_4$ at 1.788 Å.[19]

Thus, Eqns (3) and (4) provide a great deal of information about tetrahedral tungstate species in the solid state. Of the possible structures generated, most can be rejected by choosing only those structures using the highest occurring Raman band. This is because the shortest W—O bond always results in the Raman band of highest wavenumber for tungstate species. The second criterion for rejecting possible structures is to maximize the number of observed Raman stretching mode wavenumbers because of the underlying assumption that each observed Raman stretching mode wavenumber represents a unique bond type. For $PbWO_4$ (Table 3), however, only two of the three observed Raman bands were used by each possible structure. This may indicate a stronger degree of vibrational coupling between neighboring W—O bonds in the $PbWO_4$ structure. This conflict was resolved, however, by necessarily forming a hybrid structure of possibilities (a) and (b) from Table 3. A third criterion for rejecting possible structures is to choose metal cation valences that most closely match those of its formal oxidation state; in the case of W^{6+} this value is 6.0 v.u. As a final criterion, structures may be rejected based on information provided by chemical arguments or other experimental techniques. For example, if tetrahedral coordination is known for a chemical species, then five- and six-coordinated possibilities may be immediately rejected. The possibility of impurity phases must also be considered because the Raman bands due to these extra-

Table 4. Scheelites PbWO$_4$ and CaWO$_4$: structure determination by Raman spectroscopy

		PbWO$_4$				
Observed Raman Bands		W—O stretches 902, 764, 750 cm^{-1} Bending/external 356, 327, 190, 176 cm^{-1}				
		$\tilde{\nu}$/cm^{-1}	s/v.u.			R/Å
W—O bond types	A	902	1.584			1.764
	B	764	1.185			1.851
	C	750	1.148			1.861
		Coordination	A	B	C	Valence
Possible structures	(a)	4	3	1	—	5.936
	(b)	4	3	—	1	5.9000
	(c)	5	—	5	—	5.926
	(d)	5	—	4	1	5.890
	(e)	5	—	3	2	5.852
		This study (Raman)				Reported
Reasonable structure	(ab)	3 × A 1 × BC	2 × 1.764 (34) Å 1 × 1.856 (38) Å			4 × 1.772 Å
		CaWO$_4$				
Observed Raman Bands		W—O stretches 910, 836, 795 cm^{-1} Bending/external 395, 330, 213, 112 cm^{-1}				
		$\tilde{\nu}$/cm^{-1}	s/v.u.			R/Å
W—O bond types	A	910	1.609			1.759
	B	836	1.385			1.804
	C	795	1.269			1.830
		Coordination	A	B	C	Valence
Possible structures	(a)	4	3	—	1	6.096
	(b)	4	2	2	—	5.987
	(c)	4	2	1	1	5.871
		This study (Raman)				Reported
Reasonable structure	(a)	2 × A 1 × B 1 × C	2 × 1.759 (34) Å 1 × 1.803 (34) Å 1 × 1.830 (34) Å			4 × 1.788 Å

neous phases, although generally weaker in intensity, would disconcert the analysis. For a multi-phase system, then, it follows that all the observed Raman bands must be assigned to their respective phases before beginning the analysis. These criteria, used in conjunction with Eqns (3) and (4), provide a systematic procedure for determining the oxygen coordination and tungsten–oxygen bond lengths of a tungstate molecular species.

A more slightly complicated example is provided by Bi$_2$WO$_6$, and the procedure for determining the structure of its tungstate species is presented in Table 5. Five bands are observed above 400 cm^{-1} in the Raman spectrum of Bi$_2$WO$_6$ and all of these are assumed to represent five unique W—O bond types in its structure. Within the tolerance of 0.15 v.u., sixteen possibilities arise. Only structure (o), however, uses all five of the wavenumbers and is therefore determined to be the only viable structure. The bond lengths of structure (o) are listed at the bottom of Table 5. The shortest and longest bonds of the WO$_6$ octahedron add to 3.86 Å, which is a reasonable length for this WO$_6$ structural unit considering a mono-oxo length of 3.98 Å and a di-oxo length of 3.80 Å (from Table 2). The single-crystal x-ray diffraction results yielded two bonds of 1.69 Å, two of 1.82 Å and two of 2.30 Å for the WO$_6$ unit in Bi$_2$WO$_6$[20] [these reported bond lengths yield a calculated valence of 7.4 v.u. for the W^{6+} cation by Eqn (2)].

Crystalline compounds of unknown structure: Ba$_2$MgWO$_6$ and HgWO$_4$. Table 6 outlines the procedure for determining the tungstate structure in Ba$_2$MgWO$_6$ from the Raman spectrum. Ba$_2$MgWO$_6$ exhibits three Raman bands above 400 cm^{-1} at 817, 680 and 444 cm^{-1}. As Table 6 shows, only three possibilities arise with structures (b) and (c) using all three wavenumbers. Consequently, a hybrid structure is formulated from both of these possibilities, and the bond lengths of the WO$_6$ octahedron present in the Ba$_2$MgWO$_6$ structure are listed at the bottom of Table 6.

CONCLUSION

Empirical expressions were presented for relating tungsten–oxygen bond lengths, Raman stretching mode wavenumbers and Pauling bond strengths (in valence

Table 5. Bi_2WO_6: **structure determination by Raman spectroscopy**

Observed Raman Bands	W—O stretches 829, 792, 712, 597, 520 cm^{-1} Bending/external 416, 326, 304, 280, 259, 224, 210, 185, 155 cm^{-1}

		$\tilde{\nu}$/cm^{-1}	s/v.u.	R/Å
W—O bond types	A	829	1.364	1.808
	B	792	1.260	1.832
	C	712	1.052	1.888
	D	597	0.790	1.980
	E	520	0.636	2.053

		Coordination	A	B	C	D	E	Valence
Possible structures	(a)	5	4	—	—	—	1	6.094
	(b)	5	3	1	—	—	1	5.990
	(c)	5	3	1	—	1	—	6.143
	(d)	5	3	—	1	1	—	5.935
	(e)	5	2	2	—	—	1	5.886
	(f)	5	2	2	—	1	—	6.039
	(g)	6	3	—	—	—	3	6.001
	(h)	6	2	1	—	1	2	6.051
	(i)	6	2	1	—	—	3	5.898
	(j)	6	2	—	2	—	2	6.105
	(k)	6	2	—	1	2	1	5.996
	(l)	6	2	—	1	3	—	6.149
	(m)	6	1	2	—	2	1	6.100
	(n)	6	1	2	—	1	2	5.947
	(o)	6	1	1	1	2	1	5.892
	(p)	6	1	1	1	3	—	6.046

		This study (Raman)		Reported
Reasonable structure	(o)	1 × A	1 × 1.808 (34) Å	2 × 1.69 Å
		1 × B	1 × 1.832 (34) Å	2 × 1.82 Å
		1 × C	1 × 1.888 (34) Å	2 × 2.30 Å
		2 × D	2 × 1.981 (34) Å	
		1 × E	1 × 2.053 (34) Å	

units). These empirical relationships provide an easily used method of directly determining W—O bond lengths and coordinates from observed Raman spectra. This method of interpreting the Raman spectra of tungsten oxide compounds (based on a simple diatomic approach) was illustrated for crystalline tungstate compounds of known structure (Na_2WO_4, $PbWO_4$, $CaWO_4$ and Bi_2WO_6) and unknown structure (Ba_2MgWO_6) where bond lengths and coordinates were determined. The Raman stretching mode wavenumbers of the perfect WO_4 tetrahedron and WO_6 octahedron were estimated to be 874 and 691 cm^{-1}, respectively. A re-evaluation of the Raman spectrum of the tungstate species in basic, aqueous solution, $WO^{2-}_{4(aq)}$, suggested a

Table 6. Ba_2MgWO_6: **structure determination by Raman spectroscopy**

Observed Raman Bands	W—O stretches 817, 680, 444 cm^{-1}

		$\tilde{\nu}$/cm^{-1}	s/v.u.	R/Å
W—O bond types	A	817	1.330	1.816
	B	680	0.975	1.912
	C	444	0.501	2.136

		Coordination	A	B	C	Valence
Possible structures	(a)	5	3	2	—	5.940
	(b)	6	3	1	2	5.968
	(c)	6	2	3	1	6.086

		This study (Raman)		Reported
Reasonable structure	(bc)	2 × A	2 × 1.816 (34) Å	Unknown
		1 × AB	1 × 864 (82) Å	
		1 × B	1 × 1.912 (34) Å	
		1 × BC	1 × 2.024 (34) Å	
		1 × C	1 × 2.136 (34) Å	

hydroxylated species, $WO_4H_{2(aq)}$, with two W—O terminal bonds of 1.75 Å and two W—OH bonds of 1.80 Å. As demonstrated, the method developed in this study for determining the structures of tungsten oxide species from their Raman spectra provides much insight into the structures of materials that cannot be routinely examined by diffraction methods.

Acknowledgements

The following are gratefully acknowledged for providing tungsten oxide reference compounds: Professor Sir John Thomas (Davy Faraday Research Laboratory, The Royal Institution) for providing Bi_2WO_6 and A. W. Sleight (E. I. du Pont de Nemours) for providing $PbWO_4$ and $CsLuW_2O_8$.

REFERENCES

1. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed. Wiley, New York (1978).
2. L. Dixit, D. L. Gerrard and H. J. Bowley, *Appl. Spectrosc. Rev.* **22**, 189 (1986).
3. I. E. Wachs, F. D. Hardcastle and S. S. Chan, *Spectroscopy* **1**, 30 (1986).
4. F. D. Hardcastle, I. E. Wachs, J. A. Horsley and G. H. Via, *J. Mol. Catal.* **46**, 15 (1988).
5. F. D. Hardcastle and I. E. Wachs, *J. Mol. Catal.* **46**, 173 (1988).
6. F. D. Hardcastle and I. E. Wachs, *J. Raman Spectrosc.* **27**, 683 (1990).
7. F. D. Hardcastle and I. E. Wachs, *J. Phys. Chem.* **95**, 5031 (1991).
8. F. D. Hardcastle and I. E. Wachs, *Solid State Ionics* **45**, 201 (1991).
9. F. D. Hardcastle, Dissertation, Lehigh University, Bethlehem, PA; University Microfilms International, Ann Arbor, MI (1990).
10. E. Gurmen, E. Daniels and J. S. King, *J. Chem. Phys.* **55**, 1093 (1971).
11. F. Knee and R. A. Condrate, *J. Phys. Chem. Solids* **40**, 1145 (1979).
12. W. G. Fateley, F. R. Dollish, N. T. McDevitt and F. F. Bentley, *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: the Correlation Method*. Wiley-Interscience, New York (1972).
13. I. D. Brown, *Chem. Soc.* Rev. **7**, 359 (1978).
14. I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B* **32**, 1957 (1976).
15. F. D. Hardcastle, I. E. Wachs, H. Eckert and D. A. Jefferson, *J. Solid State Chem.* **90**, 194 (1991).
16. N. Weinstock, H. Schulze and A. Muller, *J. Chem. Phys.* **59**, 5063 (1973).
17. A. F. Corsmit, H. E. Hoefdraad and G. Blasse, *J. Inorg. Nucl. Chem.* **34**, 3401 (1972).
18. K. Okada, H. Morikawa, F. Marumo and S. Iwai, *Acta Crystallogr., Sect. B.* **30**, 1872 (1974).
19. E. Gurmen, E. Daniels and J. S. King, *J. Chem. Phys.* **55**, 1093 (1971).
20. R. W. Wolfe, R. E. Newnahm and M. I. Kay, *Solid State Commun.* **7**, 1797 (1969).
21. K. Okada, H. Morikawa, F. Marumo and S. Iwai, *Acta Crystallogr.*, Sect. B **30**, 1872 (1974).
22. M. Liegeois-Duyckaerts and P. Tarte, *Spectrochim. Acta, Part A* **28**, 2037 (1972).
23. A. S. Koster, F. X. N. M. Kools and G. D. Rieck, *Acta Crystallogr., Sect. B* **25**, 1704 (1969).
24. F. Knee and R. A. Condrate, *J. Phys. Chem. Solids* **40**, 1145 (1979).
25. W. H. Zachariasen and H. A. Plettinger, *Acta Crystallogr.* **14**, 229 (1961).
26. D. C. Craig and N. C. Stephenson, *Acta Crystallogr., Sect. B* **24**, 1250 (1968).
27. O. Keeling, Jr, *Acta Crystallogr.* **10**, 209 (1957).
28. R. Mattes and F. Schroder, *Z. Naturforsch., Teil B* **24**, 1095 (1969).
29. S. Tanisaki, *J. Phys. Soc. Jpn.* **15**, 573 (1960).
30. J. T. Szymanski and A. C. Roberts, *Can. Mineral.* **22**, 681 (1984).
31. L. Kihlborg and E. Gebert, *Acta Crystallogr., Sect. B* **26**, 1020 (1970).
32. C. C. Torardi, C. Page, L. H. Brixner, G. Blasse and G. J. Dirksen, *J. Solid State Chem.* **69**, 171 (1987).