Determination of Molybdenum–Oxygen Bond Distances and Bond Orders by Raman Spectroscopy

Franklin D. Hardcastle and Israel E. Wachs

Zettlemoyer Center for Surface Studies, Departments of Chemistry and Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA

A correlation is developed for relating Raman stretching frequencies of molybdenum–oxygen (Mo–O) bonds to their respective bond distances in molybdenum oxide compounds. Mo–O bond orders are also related to stretching frequencies. The Mo–O correlation is expected to offer invaluable insight into the structures of molybdate species in chemical systems which are not amenable to analysis by diffraction or other spectroscopic techniques. In the present study, the correlation is used to predict stretching frequencies for perfect MoO_4 and MoO_6 structures, and to determine Mo–O bond distances of the MoO_6 octahedron in Ba_2CaMoO_6 as well as the dehydrated surface molybdate species in MoO_3/Al_2O_3.

INTRODUCTION

Raman spectroscopy yields much information when applied to the study of structures of transition metal oxides as bulk phases[1,2] and as two-dimensional surface phases.[2,3] This is because the Raman vibrational features depend on the symmetry and the bonding of the transition metal oxide complex and, consequently, can be used to discriminate between alternate molecular structures proposed for a given chemical species. For example, characteristic vibrational bands have been used to determine the tetrahedral coordination of surface rhenium oxide on an alumina support[4] and surface chromium oxide on alumina, titania and silica supports.[5]

Recently, an empirical relation has been derived which relates vanadium–oxygen bond distances to observed Raman stretching frequencies for vanadium oxide reference compounds.[6] The empirical relation is based on the diatomic approximation where each V–O bond is considered as a totally independent oscillator separated from the rest of the molecule or the crystal lattice. According to the diatomic approximation, each distinct metal oxide polyhedron is reduced to an assembly of metal–oxygen diatomic functionalities. Each functionality within the polyhedron is characterized by its interatomic bond distance. A stretching frequency/bond distance correlation may be used to determine bond distances in metal oxides of unknown structures from their measured Raman frequencies.

In the present study, an empirical expression is determined which relates the molybdenum–oxygen crystallographic bond distances to Raman stretching frequencies. Plots are presented showing the behavior of the Mo–O bond distance and bond order as a function of Mo–O stretching frequency. These relationships are expected to offer insight into the structures of molyb-

date species in chemical systems for which diffraction techniques provide incomplete structural information.

EXPERIMENTAL

The Raman spectra of the following molybdate reference compounds were collected in our laboratory: $PbMoO_4$, $CaMoO_4$, β-$Bi_2Mo_2O_9$, $Na_2MoO_4 \cdot 2H_2O$, $Bi_3(FeO_4)(MoO_4)_2$, $(NH_4)_2Mo_2O_7$, $Gd_2(MoO_4)_3$, $MgMoO_4$, $CuMoO_4$, $FeClMoO_4$, α-$Bi_2Mo_3O_{12}$, γ-Bi_2MoO_6, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $CoMoO_4$ and MoO_3. The Raman band positions of α-Te_2MoO_7, α-$MoO_3 \cdot H_2O$ and $MnMoO_4$ were taken from the literature.[7,8] The infrared absorption frequencies for α-$MoO_3 \cdot H_2O$[7] and MoO_3[9] are also literature values.

The Raman spectra were obtained with a Spectra-Physics Ar^+ laser (Model 171) by using about 10–40 mW of the 514.5 nm line for excitation. The laser intensity was monitored at the sample. The scattered radiation from the sample was directed into a Spex Triplemate Spectrometer (Model 1877), where the Raman spectra were detected with an intensified photo-diode array (1024 pixels) via an optical multichannel analyzer (OMA III: Princeton Applied Research, Model 1463). The photodiode array was thermo-electrically 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 was experimentally determined to be better than 2 cm^{-1}. About 100–200 mg of each molybdenum oxide reference compound was pressed into a thin wafer of about 1 mm thickness with a KBr backing for support. Each sample was then mounted onto a spinning sample holder and rotated at ~2000 rpm to avoid local heating effects. A 90° collection geometry was used

to collect the scattered light. Further details concerning the optical arrangement used in the Raman experiments can be found elsewhere.[3]

THEORY

The diatomic approximation

The Raman spectrum of a metal oxide molecule contains detailed structural information because the Raman vibrational modes are determined by the symmetry and bonding of the molecular species.[1] The symmetry and bonding of the molecule may be significantly altered, however, if the environment of the molecule is changed. For example, when the molecule is confined within a crystalline lattice its vibrational spectrum differs from that of the same molecule in free space or in solution because the site symmetry of the metal cation is usually lower in the crystalline state. Furthermore, the confined molecule is an integral part of the entire array of atoms constituting the lattice. In addition to the internal modes of the molecular unit, external modes are expected to occur reflecting the translational and librational nature of the crystalline lattice. A rigorous vibrational mode analysis must account for all atoms constituting the array. Often, however, such an approach is computationally unfeasible and unnecessary. Instead, approximations are made in order to correlate the vibrational spectrum of the molecular unit in the crystal with that of the same molecular unit in the gas or solution phase.

The diatomic approximation allows a straightforward interpretation of the Raman spectrum of a crystalline metal oxide compound. It assumes that each distinct metal–oxygen bond is entirely separated from the crystalline lattice. Such a separation means that there are no vibrational interactions between neighboring metal–oxygen bonds in the lattice. To a first approximation, the Raman spectrum of the crystalline compound is a superposition of stretching frequencies directly reflecting the distinct metal–oxygen bonds constituting the lattice. For any given metal oxide, the diatomic approxiation assumes that each stretching frequency observed in the Raman spectrum is characterized only by the bond length of the metal–oxygen bond it represents.

In the present study, the diatomic approximation is used to establish the empirical relation between molybdenum–oxygen bond distances and stretching frequencies. The diatomic approximation has recently been used to derive such a relation for vanadium–oxygen bonds,[6] and the relation has been used to estimate V–O bond distances in VO_4 tetrahedra for bismuth vanadate samples of compositional range $1:1 \leqslant Bi:V \leqslant 60:1$.[10] The Mo–O bond order is also related to stretching frequencies by using an empirical relationship from the work of Brown and Wu[11] which relates Mo–O bond distances to bond orders.

Relating stretching frequencies to bond distances

Many empirical and semi-empirical formulae have been developed for simple diatomic molecules.[12–14] These expressions describe interdependencies of physical

parameters such as bond distances, force constants, and bond valences. Recent efforts at relating force constants to bond distances for diatomic molecules have also been extended to polyatomic molecules. Perhaps the most common expression relating bond lengths to force constants in diatomic and polyatomic molecules is Badger's rule.[15] Badger's rule takes the general form

$$k^{-1/3} = (a_{ij} - d_{ij})^{-1}(R - d_{ij}) \qquad (1)$$

where k (mdynes Å^{-1}) is the force constant, R (Å) is the equilibrium bond length, and d_{ij} and a_{ij} are constants which are fixed for designated bonds between atoms from rows i and j of the periodic table. Badger's rule has recently been used to correlate uranium–oxygen bond lengths with symmetric and antisymmetric stretching frequencies of dioxo-functionalities (UO_2) in uranium oxide compounds.[16]

In the course of the present work, it was found that Badger's rule did not adequately correlate Mo–O bond distances to force constants in molybdate reference compounds. In fact, significant curvature from Badger's linear relationship is observed for the several transition metal oxide systems investigated. This deviation from Badger's rule demands application of a more appropriate mathematical form. Herschbach and Laurie[15] found such deviations to be generally present in fitting cubic and quartic vibrational force constants to internuclear distances for diatomic molecules. Consequently, Herschbach and Laurie applied an exponential relationship to account for the curved nature of the data. A similar approach is used in the present study for fitting Mo–O stretching frequencies (force constants) to their respective bond distances. The exponential function used in the present study assumes the general form

$$v = A \exp (BR) \qquad (2)$$

In this function v is the Mo–O stretching frequency, R is the Mo–O bond distance, and A and B are fitting parameters. In the present study, an exponential least-squares fit is performed from the crystallographic and Raman data from several molybdenum oxide reference compounds.

The valence sum rule is a useful concept for discussing the feasibility of a proposed molybdate structure.[17] The sum of the valences, or bond orders, of the individual Mo–O bonds should equal the formal oxidation state of the metal cation. For example, in the case of fully oxidized molybdenum this is 6.0 valence units. The valence or bond order, is a measure of the strength of the chemical bond and shows the distribution of available valence electrons in the chemical bonding of a molecular species. Hence, the Mo–O bond order and calculated valence state of the molybdenum cation serve as a bookkeeping device for valence electrons at a molybdenum cation site as well as a check on the feasibility of a proposed molybdate structure. Brown and Wu[11] developed a generally applicable relationship between the metal–oxygen bond valence s and the bond distance R. The empirical expression relating Mo–O bond distance to bond valence is

$$s(Mo\text{--}O) \approx (R/1.882)^{-6.0} \qquad (3)$$

where 1.882 is the estimated bond length for an Mo–O bond of unit valence. From the calculated valences of the Mo–O bonds of any Mo site, the valence sum rule

can be used to estimate the valence state of the Mo cation.

RESULTS

The Mo–O bond distances were obtained from several molybdenum oxide reference compounds and correlated with their corresponding Raman stretching frequencies.

The reference compounds are listed in Tables 1–3 along with the crystallographically determined Mo–O bond distances, corresponding literature references, assigned Raman stretching frequencies, calculated bond orders from Eqn (3), calculated valence state of the molybdenum cation(s) and coordination number.

The procedure for assigning the Raman stretching frequencies to Mo–O bonds in the molybdate reference compounds is as follows. First, the short Mo–O bonds of the reference compounds were correlated with their

Table 1. Bond distances and observed stretching frequencies for Mo–O bonds in tetrahedrally coordinated molybdenum oxide reference compounds

Compound	Ref.	R (Å)	v (cm^{-1})[a]	s[b]	Mo VS[c]	CN[d]
PbMoO$_4$	18	1.772	869	1.44	5.8	4
CaMoO$_4$	19	1.775	880	1.42	5.7	4
β-Bi$_2$Mo$_2$O$_9$	20	1.756	887	1.52	6.1	4
Na$_2$MoO$_4$ · 2H$_2$O	21	1.752	897	1.54		
		1.768	843	1.45		
		1.781	836	1.39		
		1.788	805	1.36	5.7	4
Bi$_3$(FeO$_4$)(MoO$_4$)$_2$	22	1.738	897	1.61		
		1.751	883	1.54		
		1.779	866	1.40		
		1.825	750	1.20	5.8	4
(NH$_4$)$_2$Mo$_2$O$_7$	23	(a)[e] 1.714	937	1.75		
		(a) 1.735	910	1.63		
		(a) 1.744	910	1.58		
		(a) 1.822	720	1.21	(a) 6.2	4
MnMoO$_4$	8, 24	(a, x2) 1.724	946	1.69		
		(b, x2) 1.731	936	1.65		
		(a) 1.738	886	1.61		
		(b, x2) 1.795	828	1.33	(a) 6.1	4
		(a) 1.851		1.10	(b) 6.0	4
Gd$_2$(MoO$_4$)$_3$	25	(a) 1.731	959	1.65		
		(b) 1.733	943	1.64		
		(c) 1.743	851	1.58		
		(b) 1.745	851	1.57		
		(a) 1.746	851	1.57		
		(c) 1.750	851	1.55		
		(c) 1.751	845	1.54		
		(a, b) 1.754	845	1.53		
		(c) 1.763	845	1.48	(a) 6.1	4
		(b) 1.799	816	1.31	(b) 6.0	4
		(a) 1.800	795	1.31	(c) 6.2	4
MgMoO$_4$	26	(ab, x2) 1.73	967	1.66		
			955			
			907			
		(b) 1.75	852	1.55		
		(a, x2) 1.80	804	1.31		
			790		(a) 5.9	4
		(b) 1.85	734	1.11	(b) 6.0	4
CuMoO$_4$	27	(a) 1.701	968	1.83		
		(a) 1.703	968	1.82		
		(b) 1.711	949	1.77		
		(c) 1.735	903	1.63		
		(c) 1.761	840	1.49		
		(b) 1.777	804	1.41		
		(bc) 1.781	804	1.39		
		(b) 1.795	804	1.33		
		(c) 1.824	760	1.21	(a) 5.9	4
		(a) 1.837	739	1.16	(b) 5.9	4
		(a) 1.862	702	1.07	(c) 5.7	4
FeClMoO$_4$	28	1.756	975	1.52	6.1	4

[a] v(cm^{-1}) = Assigned Mo–O stretching frequency.
[b] s = Calculated valence of Mo–O bond (Eqn 3).
[c] Mo VS = Calculated valence state of Mo cation; relative error is 2%.
[d] CN = Coordination number of Mo cation.
[e] Letters in parentheses denote crystallographically distinct Mo sites.

Table 2. Bond distances and observed stretching frequencies for Mo–O bonds in penta-coordinated molybdenum oxide reference compounds

Compound	Ref.	R (Å)	v (cm^{-1})[a]	s[b]	Mo VS[c]	CN[d]
α-Bi$_2$Mo$_3$O$_{12}$	29	(a)[f] 1.68	992	1.98		
		(b) 1.69	954	1.91		
		(b, c) 1.72	923	1.72		
		(c) 1.73	899	1.66		
		(a) 1.78	814	1.40		
		(b) 1.85	721	1.11		
		(a, c) 1.86	685 (vw)[e]	1.07		
		(a) 1.87	669	1.04		
		(c) 1.89	669	0.98		
		(b) 1.91	648	0.92		
		(c) 2.13	388	0.48	(a) 5.8	5
		(b) 2.25	311	0.34	(a) 6.0	5
		(a) 2.30	280	0.30	(a) 5.9	5

[a] v (cm^{-1}) = Assigned Mo–O stretching frequency.
[b] s = Calculated valency of Mo–O bond (Eqn 3).
[c] Mo VS = Calculated valence state of Mo cation; relative error is 2%.
[d] CN = Coordination number of Mo cation.
[e] vw = Very weak.
[f] Letters in parentheses denote crystallographically distinct Mo sites.

stretching frequencies. The short Mo–O bonds vibrate at the highest frequencies (>800 cm^{-1}) and are therefore the most obvious to assign. A preliminary least-squares exponential fit of the data for the short Mo–O bonds was performed using Eqn (2). Next, the Mo–O bonds of intermediate length were correlated to their stretching frequencies (~800–400 cm^{-1}) by extrapolating from the short Mo–O bonds using the preliminary exponential fit. This procedure was repeated for the longer Mo–O bonds where the stretching frequencies are in the low-frequency region (<400 cm^{-1}). Once the long Mo–O bonds were correlated to their stretching frequencies a refined Mo–O correlation was determined based on all available data points.

There are two complications which may arise in the assignment of Mo–O bond distances to Raman stretching frequencies. First, not all Raman bands present in the Raman spectrum of a crystalline molybdenum oxide compound are assigned to Mo–O diatomic functionalities because some bands are symmetry related. This is especially evident in the assignment of the intermediate and long Mo–O bonds. The symmetry related bands result from internal or external modes involving groups of three or more atoms present in the crystal, and these modes are not accounted for in the diatomic approximation. For example, internal modes resulting from vibrational interactions between neighboring chemical bonds in chemical functionalities such as MoO$_2$ and MoO$_3$, as well as external modes due to the space-group symmetry of the crystal, do not directly relate to bond distances by the Mo–O correlation. Extrapolating into the lower-wavenumber region with the preliminary Mo–O correlation was used to avoid the symmetry related Raman bands in the intermediate-wavenumber region. After subsequent refining of the correlation, extrapolating into the low-wavenumber region allowed the assignment of the long Mo–O bonds. The second complication which may arise in the assignment of Mo–O stretching modes to bond distances is that not all Mo–O bonds exhibit stretching modes which are observed in the Raman spectrum. This frequently

occurs for long bonds but may also occur for intermediate bonds. Occasionally, these Mo–O stretching modes may be observed in the infrared spectrum.

A special case where both of these complications arise is molybdenum trioxide, MoO$_3$. Molybdenum trioxide exhibits Raman bands at 998, 821, 668, 474, 381, 367, 341, 294, 286, 248, 220 and 200 cm^{-1}, and has Mo–O bond lengths of 1.671, 1.734, 1.948(2×), 2.251 and 2.332 Å. The shortest Mo–O bond at 1.671 Å is assigned to the highest occurring stretching frequency at 998 cm^{-1}. The Raman band at 821 cm^{-1} is very sharp and the most intense Raman band in the spectrum, but is not found to correlate to an Mo–O bond distance by extrapolation. Consequently, the band at 821 cm^{-1} is regarded as a symmetry related vibrational mode because it is not directly related to the Mo–O bond distance and cannot be assigned according to the diatomic approximation. The infrared spectrum of molybdenum trioxide,[9] however, exhibits absorption bands at 860 and 540 cm^{-1} which correlate with Mo–O bonds of 1.734 and 1.948 Å. Extrapolating into the low-frequency region of the Raman spectrum allows the assignment of the two long Mo–O bonds of 2.251 and 2.332 Å to the two stretching bands at 294 and 248 cm^{-1}, respectively. All remaining Raman bands not assigned to Mo–O stretching frequencies are regarded as symmetry related internal and external modes.

A range of molybdate structures which consist of four-, five- and six-fold coordinated Mo are listed in Tables 1–3. Molybdenum oxide reference compounds which contain four-coordinated Mo (MoO$_4$ tetrahedra) are presented in Table 1 and include PbMoO$_4$,[18] CaMoO$_4$,[19] β-Bi$_2$Mo$_2$O$_9$,[20] Na$_2$MoO$_4$ · 2H$_2$O,[21] Bi$_3$(FeO$_4$)(MoO$_4$)$_2$,[22] (NH$_4$)$_2$Mo$_2$O$_7$,[23] MnMoO$_4$,[8,24] Gd$_2$(MoO$_4$)$_3$,[25] MgMoO$_4$,[26] CuMoO$_4$[27] and FeClMoO$_4$.[28] A reference compound which contains five-coordinated Mo, or MoO$_5$ structures, is α-Bi$_2$Mo$_3$O$_{12}$[29] and is presented in Table 2. A general conclusion made from comparing the Raman spectra of complex transition metal oxides is that the lower the stretching frequency for the shortest metal–oxygen

Table 3. Bond distances and observed stretching frequencies for Mo–O bonds in octahedrally coordinated molybdenum oxide reference compounds

Compound	Ref.	R (Å)	ν (cm⁻¹)[a]	s[b]	Mo VS[c]	CN[d]
γ-Bi$_2$MoO$_6$	30	1.75	846	1.55		
		1.77	846	1.44		
		1.85	712	1.11		
		1.86	712	1.07		
		2.22	352	0.37		
		2.28	292	0.32	5.9	6
α-Te$_2$MoO$_7$	7	1.720	913	1.72		
		1.723	913	1.70		
		1.928	550	0.87		
		1.940	550	0.83		
		2.132		0.47		
		2.534		0.17	5.8	6
(NH$_4$)$_2$Mo$_2$O$_7$	23	(b)[f] 1.722	937	1.44		
		(b) 1.734	910	1.63		
		(b) 1.840	720	1.14		
		(b) 2.069	456	0.57		
		(b) 2.166	365	0.43		
		(b) 2.311	291	0.29	(b) 5.5	6
(NH$_4$)$_6$Mo$_7$O$_{24}$ · 4H$_2$O	44	(x4) 1.710	938	1.78		
		(x2) 1.716	938	1.74		
		(x4) 1.728	911	1.67		
		(x2) 1.741	893	1.60		
		(x2) 1.754	863	1.53		
		(x2) 1.903	633	0.94		
		(x4) 1.915	625	0.90		
		(x4) 1.945	570	0.82		
		(x4) 1.966	543	0.77		
		(x2) 2.155	375	0.44		
		(x4) 2.179	363	0.42		
		(x2) 2.264	308	0.33		
		(x2) 2.415	223	0.22	6.2	6
CoMoO$_4$	45	(a, x2) 1.719	941	1.72		
		(b, x2) 1.726	941	1.68		
		(b) 1.891	699	0.97		
		(a, x2) 1.927	627	0.87		
		(b) 1.980	484	0.74		
		(b, x2) 2.313	276	0.29	(a) 5.7	6
		(a, x2) 2.328	276	0.28	(b) 5.6	6
α-MoO$_3$ · H$_2$O	7, 46	1.687	973	1.93		
		1.688	973	1.92		
		1.949	545 (ir)[e]	0.81		
		1.959	545 (ir)	0.79		
		2.277		0.32		
		2.346	260	0.27	6.0	6
MoO$_3$	31, 9	1.671	998	2.04		
		1.734	860 (ir)	1.63		
		(x2) 1.948	540 (ir)	0.81		
		2.251	294	0.34		
		2.332	248	0.28	5.9	6

[a] ν (cm⁻¹) = Assigned Mo–O stretching frequency.
[b] s = Calculated valence of Mo–O bond (Eqn 3).
[c] Mo VS = Calculated valence state of Mo cation; relative error is 2%.
[d] CN = Coordination number of Mo cation.
[e] ir = Mo–O stretching frequency from infrared absorption spectrum.
[f] Letters in parentheses denote crystallographically distinct Mo sites.

bonds, the more regular is the structure. Consequently, the tetrahedrally coordinated molybdate reference compounds in Table 1 are listed in order of increasing highest stretching frequency and reflect the relative regularity of these structures. Thus, the ordering in Table 1 reflects the regularity of the MoO$_4$ tetrahedra in the molybdenum oxide reference compounds. Accordingly, PbMoO$_4$ has the most ordered tetrahedron whilst FeClMoO$_4$ has the most irregular tetrahedron.

Molybdenum oxide reference compounds containing MoO$_6$ octahedra are listed in Table 3. The least distorted MoO$_6$ octahedron occurs in γ-Bi$_2$MoO$_6$[30] which has two short Mo–O bonds at 1.75 and 1.77 Å, two intermediate bonds at 1.85 and 1.86 Å, and two long bonds at 2.22 and 2.28 Å. The regularity of the octahedron in γ-Bi$_2$MoO$_6$ is reflected in the low Mo–O stretching frequency at 846 cm⁻¹ due to the two shortest Mo–O bonds. As with Table 1, the compounds in Table 3 are also listed in order of increasing stretching
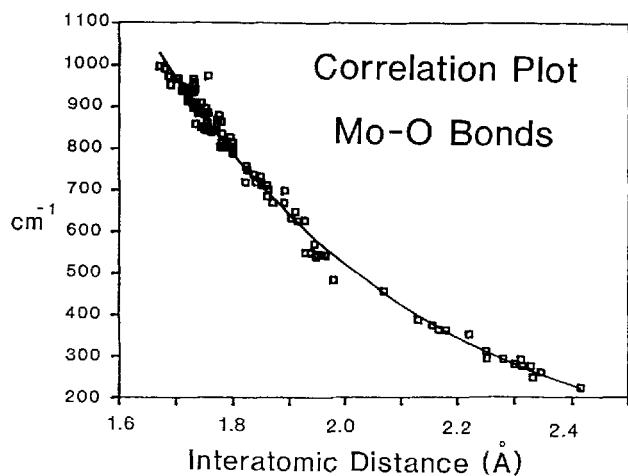
Figure 1. Mo–O correlation plot relating bond distance (Å) to stretching frequency (cm^{-1}). The 108 data points are fit to the exponential function v (cm^{-1}) = 32895 exp ($-2.073R$), where R is the bond distance in ångströms.

frequency for the shortest Mo–O bonds and reflects the relative degree of distortion for the MoO$_6$ octahedra. Thus, the most distorted MoO$_6$ octahedron listed in Table 2 is present in MoO$_3$.[31] Most of the stretching frequencies tabulated in Table 3 are from Raman spectra, but a few infrared absorption bands are also included for α-MoO$_3 \cdot$ H$_2$O [7] and MoO$_3$.[9]

The data from Tables 1–3 consist of 108 data points correlating Mo–O stretching frequencies to crystallographic Mo–O bond distances from the literature. The Mo–O correlation, resulting from a least-squares exponential fit of the data, is found to be

$$v \text{ (cm}^{-1}) = 32895 \exp(-2.073R) \qquad (4)$$

The precision in estimating an Mo–O bond distance from the Mo–O correlation, given an absolute stretching frequency, is ± 0.016 Å. The standard deviation associated with the calculation of a stretching frequency from an Mo–O bond distance is ± 25 cm^{-1}. The data points and the above Mo–O correlation [Eqn (4)] are plotted in Fig. 1. Bond order/stretching frequency correlations are also useful in the determination of molybdate structures because the Mo–O bond order is

Figure 2. Correlation plot relating Mo–O bond order (valence units) to Mo–O stretching frequency (cm^{-1}).

representative of the strength of the chemical bond. For this reason, a plot showing the relationship between Mo–O bond order and stretching frequency is presented in Fig. 2 (calculated from Eqn (3) and the Mo–O correlation).

DISCUSSION

The Mo–O correlation is derived from a least-squares exponential fit of the crystallographically determined bond distances and observed Raman stretching frequencies. Such a direct relationship between these two experimental observables is justified under the assumptions of the diatomic approximation. The basic assumption behind the Mo–O correlation is that each distinct Mo–O bond is entirely separated from its crystalline lattice. Such a separation means that there are no vibrational interactions between neighbouring Mo–O bonds in the lattice. Each isolated Mo–O bond exhibits a stretching frequency which is characteristic of its bond length. To a first approximation, the Raman spectrum of the molybdate compound is a superposition of Mo–O stretching frequencies. Raman bands appearing in the spectrum which cannot be correlated to Mo–O bond lengths are due to symmetry related modes.

The reasoning behind the diatomic approximation is very different from that of the site symmetry approximation.[6] The site symmetry approximation assumes that a high degree of symmetry is present at the Mo cation site, usually more than is actually present. The diatomic approximation, because it assumes that all Mo–O oscillators are vibrationally independent, disregards the site symmetry at the Mo cation site. Thus, both of these approaches begin with an assumption concerning the site symmetry of the Mo cation: the diatomic approximation assumes no site symmetry whilst the site symmetry approximation assumes high symmetry. Certainly, if possible, both approaches should be used in order to attain a thorough understanding of the vibrational spectrum in terms of the complete structure of the molybdenum oxide compound.

There are both advantages and disadvantages of using the diatomic approximation to arrive at a correlation between Mo–O bond distances and stretching frequencies. The advantage of the technique lies in its simplicity. Within the limits of experimental error, the diatomic approximation immediately provides a very good estimate of Mo–O bond distances from observed stretching frequencies. These spectroscopically determined bond distances can be expressed in terms of bond valences and evaluated to determine the plausibility of proposed structures. Conversely, if the bond distances of a metal oxide are already known, then the stretching frequencies corresponding to these bonds may be predicted. The disadvantage of the diatomic approximation $vs.$ the site symmetry approximation, is that the diatomic approximation, by itself, does not lead to an assignment of the symmetry species of the Raman vibrational modes.

Cotton and Wing[32] have previously shown Mo–O plots of force constant $vs.$ bond distance, bond order $vs.$ bond distance, and bond order $vs.$ force constant; these
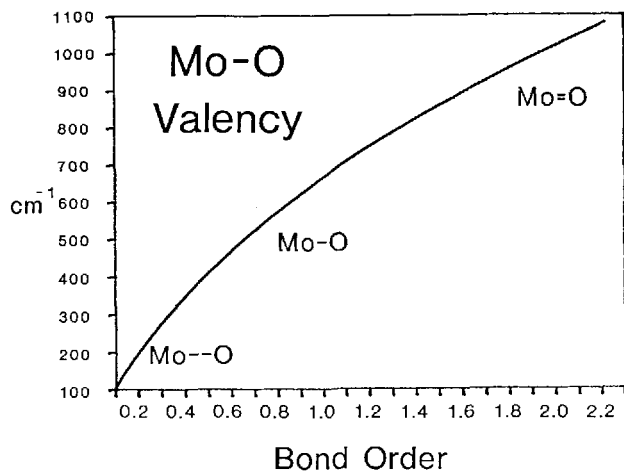
plots are here compared to the empirical correlation established in the present work. The force constant/bond distance plot of Cotton and Wing consists of a hand-drawn best fit curve through a set of seven data points of Mo–O bond lengths and symmetric stretching force constants selected from five molybdenum oxide reference compounds. These reference compounds contain a wide range of molybdate functionalities including MoO, MoO_2, Mo–O–Mo, and MoO_4 groups which are considered in a simple group-theoretical approach for determining symmetric stretching force constants. The data points derived in the Cotton and Wing study for the force constant/bond distance relation are shown in Fig. 3 along with the present Mo–O correlation [Eqn (4)] to demonstrate the strong agreement between these two studies.

The Mo–O bond order plots of Cotton and Wing,[32] however, are not consistent with the empirical correlation established in the present study. This is because Cotton and Wing assumed an Mo–O bond order of 3 for their mono-oxo reference compounds (only one terminal Mo–O bond), a bond order of 2.5 for bonds of the dioxo species (two terminal Mo–O bonds) and a bond order of 2 for bonds of the trioxo species. These bond order assignments, however, are arbitrary and lead to Mo–O bond orders which are typically higher than those of Brown and Wu by ~0.5 valence units. In comparison, the expression of Brown and Wu [Eqn (3)] is not based on arbitrarily assigned data, but on empirical data from 50 Mo environments.[11] Furthermore, Eqn (3) has been shown to be quite reliable and evaluated to perform as well, or better, than other bond order/bond distance expressions.[33]

Applications

Determining stretching frequencies for ideal structures: MoO_4 and MoO_6.

An interesting application of the Mo–O correlation is the prediction of Raman stretching frequencies for proposed molybdate structures. The stretching frequencies for the perfect MoO_4 tetrahedron and MoO_6 octahedron can be estimated from the Mo–O correlation. These ideal structures have a high

Figure 3. Correlation plot relating Mo–O bond distance (Å) to Mo–O force constant (mdynes Å^{-1}). The seven plotted data points are from the correlation of Cotton and Wing (1965).[32]

degree of point-group symmetry (T_d and O_h, respectively). Consequently, vibrational interactions between bonds are expected to be significant. For example, stretch–stretch interaction constants are roughly one-tenth of the stretching force constant.[34] In spite of the significant vibrational interactions, the diatomic approximation may be used to provide an excellent estimate of the frequency of the totally symmetric Mo–O stretching mode for each of these structures. This is because the magnitude of the vibrational interaction constants between neighboring Mo–O bonds is of the same order of magnitude as the error associated with the experimental measurements of crystallographic Mo–O bond distances and Raman stretching frequencies. The stretching frequencies of the regular MoO_4 and MoO_6 structures are estimated by first equally dividing the six valence units of bond order between the four bonds of the tetrahedron and the six bonds of the octahedron. This results in Mo–O bond lengths of 1.759 and 1.882 Å for the MoO_4 and MoO_6 structures, respectively, by Eqn (3). If these bond distances are considered absolute (without error), then the Mo–O correlation [Eqn (4)] yields symmetric stretching frequencies of 858 cm^{-1} for the perfect MoO_4 tetrahedron and 665 cm^{-1} for the perfect MoO_6 octahedron. The predicted stretching frequencies have a standard deviation of ± 25 cm^{-1} reflected in the overall precision of Eqn (4), but in the high-frequency region the error is only ± 12 cm^{-1}. Thus, we expect 858 and 665 cm^{-1} to be excellent estimates of the stretching frequencies for the perfect MoO_4 and MoO_6 structures, respectively.

A comparison of the predicted stretching frequencies for the perfect MoO_4 and MoO_6 structures with those of existing molybdate compounds suggests that the perfect MoO_4 tetrahedron may exist, whilst the perfect MoO_6 octahedron may not exist. The most perfect MoO_4 tetrahedron listed in Table 1 is present in $PbMoO_4$ which has a stretching mode at 869 cm^{-1}. This value is only 11 cm^{-1} higher than 858 cm^{-1} predicted for the perfect tetrahedron and lies within the standard deviation. Thus, the MoO_4 tetrahedron present in $PbMoO_4$ probably contains a perfect MoO_4 tetrahedron. The MoO_4^{2-}(aq) anion is believed to have T_d point-group symmetry, but displays a somewhat high symmetric stretch at 897 cm^{-1} [35] which indicates an irregular structure. In fact, the distorted MoO_4 structures in $CaMoO_4$ (880 cm^{-1}), β-$Bi_2Mo_2O_9$ (887 cm^{-1}), $Na_2MoO_4 \cdot 2H_2O$ (897 cm^{-1}) and $Bi_3(FeO_4)(MoO_4)_2$ (897 cm^{-1}) are at least as regular as that in MoO_4^{2-}(aq). Indeed, it is the authors contention that the average structure of the aqueous molybdate ion is not representative of a perfect tetrahedron. Instead, a strong case may be made for the presence of hydroxylated molybdate tetrahedra: MoO_4H_2 is estimated to have a terminal Mo=O stretch at ~980 cm^{-1} (Mo—(OH) stretch at ~800 cm^{-1}).[36] Consequently, an observed stretching frequency at 897 cm^{-1} may reflect an equilibrium between the ideal tetrahedron (858 cm^{-1}) and varying degrees of hydroxylation for the aqueous molybdate species.

The most regular molybdate octahedron currently known is the slightly distorted MoO_6 unit in the perovskite Ba_2CaMoO_6. The Raman stretching frequency of the shortest Mo–O bond is reported to occur at 813 cm^{-1}.[37,38] This value is 33 cm^{-1} lower than that of
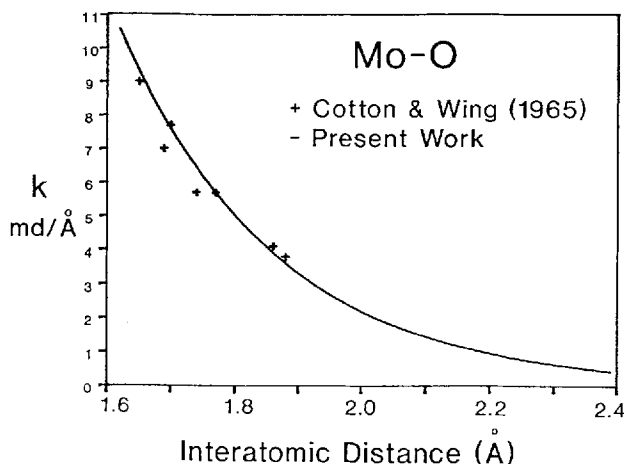
γ-Bi_2MoO_6, which is the most regular of the octahedral structures listed in Table 3, and 147 cm^{-1} higher than that expected for the ideal MoO_6 octahedron at 665 cm^{-1}. Although the Mo–O bond distances in Ba_2CaMoO_6 have not yet been determined, the Raman band positions suggest a distortion less than that of γ-Bi_2MoO_6, but greater than that of the ideal MoO_6 octahedron.

Determining the structure of bulk metal oxides: Ba_2CaMoO_6. The Mo–O correlation [Eqn (4)] may be used to determine the structure of an unknown molybdate species present in the bulk phase. For example, the structure of the molybdate species in the bulk compound Ba_2CaMoO_6, discussed in the preceeding section, can be determined. This compound is an ordered perovskite (fcc lattice) with Ba in twelve-fold coordination, Ca and Mo in six-fold coordination, and all octahedra are corner-sharing. Although a single crystal structure determination of Ba_2CaMoO_6 has not been reported, it has been the subject of electronic and vibrational spectroscopic studies.[37,38] The determination of the Mo–O bond lengths in the MoO_6 octahedron of Ba_2CaMoO_6 is demonstrated using reported vibrational frequencies and the diatomic approximation.

In the previous section, the structure of the MoO_6 octahedron in Ba_2CaMoO_6 was determined to be less distorted than that of γ-Bi_2MoO_6, but more distorted than that of the perfect MoO_6 octahedron. The Mo–O bond lengths of γ-Bi_2MoO_6 range from 1.75 to 2.28 Å,[30] and it is assumed that those of Ba_2CaMoO_6 have a smaller range of bond distances because the MoO_6 octahedron of Ba_2CaMoO_6 is less distorted than that of γ-Bi_2MoO_6. The Raman spectrum of Ba_2CaMoO_6 shows three bands at 813, 651 and 417 cm^{-1}, and the infrared spectrum shows two bands at 600 and 358 cm^{-1}.[37,38] These frequencies are converted to bond orders by Eqns (3) and (4): 1.374, 0.972, 0.508, 0.854 and 0.413 valence units respectively. The only combination of bond orders consistent with the formal oxidation state of the Mo^{6+} cation, within 6.0 ± 0.1 valence units, is $1.374(1\times)$, $0.972(3\times)$ and $0.854(2\times)$ valence units. The Mo–O bond orders reflect the two Raman bands at 813 and 651 cm^{-1} and the infrared band at 600 cm^{-1}. These stretching frequencies, by Eqn (4), are converted to Mo–O bond lengths (and precision) of 1.785(16), $1.891(16)\times 3$ and $1.932(16)\times 2$ Å. Consistent with our expectations, these bond lengths have a smaller range of values than those of γ-Bi_2MoO_6 and reflect the smaller degree of distortation of the MoO_6 octahedron in Ba_2CaMoO_6. The MoO_6 unit in Ba_2MoO_6 can be described as a slightly distorted octahedron with the Mo cation displaced slightly toward one oxygen. This displacement results in one short bond of 1.785(16) Å and two opposing long bonds of 1.932(16) Å. The three equidistant bonds at 1.891(16) Å are assumed to be more or less normal to the axis of the displacement.

Determining the structure of surface metal oxides: MoO_3/Al_2O_3. The determination of bond distances from Raman stretching frequencies is of most benefit when diffraction techniques are unable to detect oxygen positions because of the absence of long-range order. Such is the case for supported metal oxides which are present as two-dimensional metal oxide overlayers on

high surface-area oxide substrates. Consequently, diffraction techniques are not suitable for studying the structures of surface metal oxides. One example of a surface metal oxide is the dehydrated surface molybdate species supported on alumina, MoO_3/Al_2O_3, which has been the subject of several Raman investigations.[39–42]

The Raman spectra reported for the dehydrated MoO_3/Al_2O_3 system show two weak and broad bands at 872 and 950 cm^{-1}, and a very sharp and intense band at 1012 cm^{-1}.[39] These stretching frequencies reveal the presence of at least three types of surface molybdate species. The weak bands at 872 and 950 cm^{-1} are unaffected by moisture and may be due to microcrystalline molybdates formed from small amounts of cationic impurities (such as K^+, Na^+, Ca^{2+}, Sr^{2+} and Ba^{2+}). The band at 950 cm^{-1} is not observed at lower molybdate loadings.[40–42] The band at 872 cm^{-1} is consistent only with a regular MoO_4 tetrahedron. The band at 950 cm^{-1}, along with the bending mode at 320 cm^{-1} and diagnostic Mo—O—Mo bending modes at 210 cm^{-1}, is due to a polymolybdate species. The structure of this polymolybdate species cannot be determined from the Raman spectrum. The intense band at 1012 cm^{-1} is not accompanied by other vibrational features because as dehydration occurs, and the broad band due to the hydrated molybdate species at 959 cm^{-1} sharpens and shifts to 1012 cm^{-1} under dehydration, there is no observable sharpening of other Raman bands in the spectrum. This observation is consistent only with a mono-oxo molybdate species, having only one terminal Mo=O bond, because a molybdate functionality having two or more equivalent neighboring bonds would yield at least three vibrational features (symmetric stretch, antisymmetric stretch and bending mode).[1] Two or more inequivalent terminal Mo–O bonds would exhibit two or more Mo–O stretching frequencies. Eqn (4) converts this terminal Mo=O bond to a bond length of 1.681(16) Å. The mono-oxo functionality for the surface molybdate species is consistent with octahedral coordination for the Mo^{6+} cation because, whereas mono-oxo species for MoO_6 octahedra are quite common (for example, MoO_3), there are no known tetrahedral mono-oxo molybdate species. Even for highly distorted MoO_4 tetrahedra as, for example, in $Al_2(MoO_4)_3$ the tetrahedra possess at least two short Mo=O bonds.[43]

The fact that no additional Raman features are associated with the 1012 cm^{-1} band of the dehydrated surface molybdate species indicates that all oxygens which bridge the Mo cation to the support are intimately coupled to the support. In other words, the bridging oxygens lie in the first oxide layer of the alumina support and have at least three-centre bonds with one bond to Mo and, presumably, at least two bonds at Al atoms. Speculation concerning the structure of this molybdate species is tempting. For example, four Mo–O bonds to the first oxide layer of alumina at ~ 1.89 Å and an opposing oxygen to the second oxide layer at more than 2.2 Å, but additional data is needed to determine the structure more accurately.

The Mo–O correlation [Eqn (4)] provides a powerful tool in the interpretation of Raman spectra of molybdate species whose structures are distorted by a crystalline lattice or by a surface. In cases where diffraction techniques fall short of providing oxygen positions,

Raman spectroscopy may be used to determine Mo–O bond distances for the molybdate species. Knowledge of the bond distances of a molybdate species can lead to information concerning its coordination and structure. Such an approach should popularize Raman spectroscopy as a complementary technique to diffraction methods in the structural studies of complex transition metal oxide systems.

CONCLUSIONS

A Mo–O correlation between observed molybdenum–oxygen Raman stretching frequencies and bond distances was developed. The Mo–O correlation was plotted as stretching frequencies *vs.* bond distances. A plot was also presented for Mo–O bond orders *vs.* stretching frequencies. These empirically derived relationships are expected to provide insight into the structures of molybdate species, especially for those chemical systems which are not amenable to analysis by diffraction or other spectroscopic techniques. In the present study, Raman stretching frequencies were predicted for the perfect MoO_4 and MoO_6 structures. The Mo–O bond distances of the MoO_6 octahedron in the perovskite Ba_2CaMoO_6 were determined as well as the bond distance of the Mo=O bond for the dehydrated surface molybdate species in the MoO_3/Al_2O_3 system. The Mo–O correlation is expected to aid in the determination of the structure of dehydrated surface molybdate species on various oxide supports (γ-Al_2O_3, TiO_2, SiO_2 etc.) which are heterogeneous catalysts for many industrially important reactions.

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