

trans to the lone pair, thus weakening the trans bond. Similar effects have been seen previously in methylamine³⁵ and trimethylamine.^{33,34} If the methyl C-H peak is split by the methylene group, then the splitting is too small to detect in this experiment. Thus, in terms of overtone spectroscopy, the nitrogen lone pair significantly influences the methylene hydrogens but not the methyl hydrogens. In addition, the anisotropic environment that the methylene group provides for the methyl group apparently does not affect the methyl group absorption. The two-point harmonic frequencies and anharmonicities calculated for these absorptions compare well among analogous bonds in these molecules and with similar modes in other molecules. There are two N-H stretching peaks in the overtone spectrum, one at higher frequency corresponding to the N-H trans to a methylene hydrogen and one at lower frequency corresponding to the N-H trans to the N-C bond. This agrees with earlier results on diethylamine and dimethylamine.³⁵

The large number of C-H bonds in triethylamine makes detailed analysis of its spectra difficult, especially without accompanying data on deuterated analogues. There are at least two C-H peaks in the overtone spectra, the one at higher frequency being a methyl absorption, while the one at lower frequency is a methylene absorption. Data for both of these absorptions were fit to a Birge-Sponer plot and the resulting parameters compare well to the data of Fang et al. for diethylamine.³⁵

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Registry No. Ethylamine-*N,N*-*d*₂, 5852-45-9; ethyl-2,2,2-*d*₃-amine, 6118-19-0; ethylamine, 75-04-7; triethylamine, 121-44-8.

Determination of Vanadium-Oxygen Bond Distances and Bond Orders by Raman Spectroscopy

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An empirical correlation is developed for relating Raman stretching frequencies of vanadium-oxygen (V-O) bonds to their bond lengths in vanadium oxide reference compounds. A least-squares exponential fit of crystallographically determined V-O bond lengths to V-O Raman stretching frequencies is presented along with a relation between V-O bond strengths (in valence units) and Raman stretching frequencies. These empirical correlations lead to a systematic method for determining the coordination and bond lengths of vanadates. This method is illustrated for vanadates of known structure (vanadium *n*-propoxide, BiVO₄, α-Zn₃(VO₄)₂, and Pb₂(VO₄)₃Cl) and unknown structure (AlVO₄ and two-dimensional surface phase in V₂O₅/Al₂O₃). The method is expected to be generally applicable to all vanadates where medium-range order is absent.

I. Introduction

Raman spectroscopy has consistently proven useful in the elucidation of structures of complex transition-metal oxides present as either bulk phases^{1,2} or surface-supported phases.^{2,3} This is because the Raman vibrational spectrum directly probes the structure and bonding of a 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 elucidate the isolated nature of the tetrahedrally coordinated surface rhenium oxide species on an alumina support⁴ as well as the tetrahedral mono- and polychromate species present on alumina, titania, and silica supports.⁵

Vibrational spectroscopy has also proven useful in the characterization of simple diatomic molecules. For many years there has been considerable interest in deriving expressions relating crystallographically determined bond lengths to observed vibrational frequencies for diatomic molecules. The most common empirical expression relating harmonic force constant and interatomic distance for diatomic molecules is Badger's rule,⁶⁻⁸ which has been extended to many families of molecules but does not adequately relate bond distances to force constants in polyatomic molecules. Recently, the diatomic approximation was used to justify the observed relationship between molybdenum-oxygen bond lengths and their Raman stretching frequencies for the molybdenum oxide reference compounds.⁹

In the present study, the diatomic approximation is used to justify the empirical relationship observed between V-O bond lengths and Raman stretching frequencies. A simple exponential function was found to most reasonably describe the empirical dependence between V-O bond length and Raman stretching frequency. The fitting parameters were determined by trial-and-error numerical fits. This correlation is shown to be invaluable as a structural tool because the Raman spectrum of a vanadium oxide compound may be interpreted in terms of V-O bond lengths. The diatomic approach of interpreting Raman spectra differs from previous models¹⁰ because it assumes that vibrational interactions between neighboring chemical bonds in complex transition-metal oxides may be neglected. This assumption suggests that a direct relation exists between a metal-oxygen bond length and its Raman stretching frequency and, therefore, metal-oxygen bond lengths may be directly determined from the measurement of Raman stretching frequencies. This approximation is expected to work

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if the error associated with the experimental observables of interest is comparable to, or less than, the interaction between neighboring metal–oxygen bonds—this is shown to be a valid assumption in all cases. For crystalline vanadium pentoxide, the diatomic approach yields erroneous bond lengths for two of the bridging bonds because of the medium-range order present in the crystal structure.

II. Experimental Section

Raman scattering of the vanadium oxide reference compounds was generated with the 514.5-nm line of a Spectra-Physics Ar⁺ laser (Model 171) by utilizing about 10–40 mW of radiant power as measured at the sample. The scattered radiation from the sample surface was directed into a Spex Triplemate spectrometer (Model 1877), and the Raman signal was detected with an intensified photodiode array and optical-multichannel-analyzer (OMA III: Princeton Applied Research, Model 1463). The photodiode array (990 intensified pixel elements) was thermoelectrically cooled to –35 °C. The spectral resolution and reproducibility was experimentally determined to be better than 2 cm⁻¹. About 100–200 mg of each reference compound was pressed into a thin wafer of about 1-mm thickness.

III. Theory

1. The Diatomic Approximation. Several types of approximations may be made in order to more easily interpret the Raman spectrum of a complex transition-metal oxide species. First, it is commonly assumed that the internal and external modes of the crystal are independent of one another. The internal modes of a molecular unit occur in the high-frequency region and constitute the normal vibrations of the molecular unit. The external modes occur at lower frequency and correspond to translations and librations of the molecular units within the crystal. Such a separation of the internal modes of the molecular unit contained within the crystal from the external modes of the crystalline lattice is an assumption of the site symmetry approximation.¹⁰

The site symmetry approach begins by assigning a high degree of symmetry to each site within a unit cell; usually the actual symmetry at these sites is lower than that assigned. Because the site symmetries within the crystalline lattice must be assigned beforehand, a detailed knowledge of the structure of the crystal is a prerequisite. The site symmetry approach leads to the total number and types of infrared- and Raman-active modes and allows the vibrational spectrum of a confined, distorted molecule within the crystal to be directly compared to that of a similar molecule in free space or in solution. Thus, although the site symmetry approach is useful in allowing the observed Raman bands to be assigned to symmetry species, it does not directly yield structural information about metal oxide species contained within the crystalline lattice.

In the present study, we use another type of approximation called the diatomic approximation. Such an approximation is necessary for justifying the direct relationship observed between metal–oxygen bond lengths and Raman stretching frequencies in transition-metal oxide compounds. Whereas the site symmetry approximation assumes that each metal oxide polyhedron is separated from the crystalline lattice, the diatomic approximation assumes that each distinct metal–oxygen bond is vibrationally independent of the crystalline lattice. Thus, to a first approximation, the Raman spectrum of a crystalline metal oxide is a superposition of the stretching frequencies from an assembly of metal–oxygen diatomic oscillators. Each oscillator has a unique interatomic distance and a unique stretching force constant and exhibits a unique vibrational band. If the metal–oxygen bond is assumed to act like a harmonic oscillator, then the stretching force constant may be found from its square-root dependence on vibrational frequency. In the present study, the diatomic approximation is shown to be justified for vanadium oxide reference compounds within the experimental accuracy afforded by the

measurement of Raman stretching frequencies and crystallographically determined V–O bond lengths.

2. Relating Raman Stretching Frequency to Bond Length. Many empirical and semiempirical formulas are present in the literature of simple diatomic molecules. These formulas relate physical parameters such as bond distances, force constants, and bond valences.^{11–13} Efforts have also been directed at extending force constant/bond distance relationships to polyatomic molecules. Perhaps the most common expression relating bond lengths to force constants in diatomic molecules is Badger's rule.⁸ A general form of Badger's rule is expressed as

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

where k (mdyn/Å) is the force constant for a particular bond, R (angstroms) is the equilibrium bond length, and d_{ij} and a_{ij} are constants (fixed for designated bonds between atoms from rows i and j of the periodic table). Recently, Badger's rule has been used to correlate uranium–oxygen bond lengths with both symmetric and antisymmetric stretching frequencies for dioxo functionalities (UO₂) in uranium oxide compounds.¹⁴

In the course of the present work, it was found that Badger's rule does not adequately correlate bond distances to stretching frequencies or force constants in vanadium oxide crystals. This is because $k^{-1/3}$ is not a linear function of R but exhibits a slight curvature. Herschbach⁸ encountered a similar problem in fitting cubic and quartic anharmonic force constants to internuclear distances for diatomic molecules. Consequently, Herschbach applied an exponential fit to conveniently account for the slight curvature in the data. Trial-and-error numerical fits of the present V–O bond length/stretching frequency data have also led to a simple exponential dependence between Raman stretching frequencies and V–O bond lengths. Thus, in accordance with Herschbach's treatment, an exponential function of the form

$$\nu = A \exp(BR) \quad (1)$$

is applied in the present work as the most expedient method of relating V–O stretching frequencies and bond distances in bulk vanadium oxide reference compounds; ν is the V–O stretching frequency, R is the V–O interatomic distance, and A and B are fitting parameters. If we assume that each V–O bond can be modeled after a harmonic oscillator (this is not an assumption of the diatomic approximation), then the stretching frequency is directly proportional to the square root of the force constant.

The Pauling bond strengths (in valence units), also referred to as bond orders or bond valences, of the V–O bonds and the calculated valence state of the vanadium cation are also useful in discussing the plausibility of proposed structures.¹⁵ The bond valence reflects the relative strength of a chemical bond and shows the distribution of available valence electrons in the chemical bonding of a molecular species. Furthermore, according to Pauling's valence sum rule,¹⁵ there is a conservation of valency associated with the metal cation. Hence, the calculated valence state can be compared to the formal oxidation state of the vanadium cation and serve as a bookkeeping device for the distribution of electrons among the available V–O bonds.

A general relationship has been developed by Brown and Wu¹⁶ that relates the cation–oxygen bond valence s to the interatomic distance R . The empirical expression for relating a V–O bond length to its bond valence is

$$s(\text{V-O}) \approx (R/1.791)^{-5.1} \quad (2)$$

where 1.791 Å is the estimated bond length for a V–O bond of unit valency. The empirical parameters in eq 2, 1.791 and 5.1, were determined based on data from 43 V⁵⁺ environments.¹⁶

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TABLE I: Bond Lengths and Observed Stretching Frequencies for V–O Bonds in Tetrahedrally Coordinated Vanadium Oxide Reference Compounds

compd	ref	R, Å	ν , cm ⁻¹	s	VS	CN
Pb ₃ (VO ₄) ₃ Cl	19	1.72 (2x)	822	1.22		
		1.76	789	1.09		
		1.76	722	1.09	4.6	4
BiVO ₄	20	1.69 (2x)	826	1.34		
		1.77 (2x)	716	1.06	4.8	4
Na ₃ VO ₄	21	1.677	850	1.40		
α -Zn ₃ (VO ₄) ₂	22	1.696 (3x)	823	1.32	5.4	4
		1.67 (2x)	852	1.42		
		1.73	790	1.19		
VOCl ₃	23	1.56	1035	2.02	(5) ^b	4
Cd ₂ V ₂ O ₇	26	1.672	873	1.41		
		1.717 (2x)	815	1.23		
		1.764		1.08	5.0	4
α -Zn ₂ V ₂ O ₇	27	1.658	912	1.47		
		1.704	807	1.28		
		1.728	783	1.20		
NH ₄ VO ₃	29	1.775	719	1.05	5.0	4
		1.65	927	1.51		
		1.67	895	1.42		
α -NaVO ₃	30	1.80 (2x)	645	0.98	4.9	4
		1.631	955	1.60		
		1.653	918	1.49		
		1.801	628	0.97		
		1.805	628	0.96	5.0	4

^a ν : observed V–O Raman stretching frequency. s : V–O bond orders for pentavalent V calculated by $s \approx (R/1.791)^{-5.1}$ (empirical parameters of Brown and Wu.¹⁶ VS: calculated valence state of the V cation ($\sum s_i$); relative error is <5%. ^b Formal oxidation state.

TABLE II: Bond Lengths and Observed Stretching Frequencies for V–O Bonds in Pentacoordinated Vanadium Oxide Reference Compounds^a

compd	ref	R, Å	ν , cm ⁻¹	s	VS	CN
Mg ₂ V ₂ O ₇	28	1.629 (a)	942	1.61		
		1.682 (b)	896	1.37		
		1.702 (a)	838	1.29		
		1.707 (b)	838	1.27		
		1.710 (a)	838	1.26		
		1.744 (b)	726	1.14		
		1.784 (b)	726	1.02		
		1.817 (a)	629	0.93		
		2.440 (b)	200	0.21	5.2 (a)	5
		2.869 (a)	0.09	5.0 (b)	5	
VO(OCH ₂ CH ₂ CH ₃) ₃	31	1.54	1073	2.16		
		1.8 (3x)	618	0.97		
		2	449	0.57	5.6	5

^a ν : observed V–O Raman stretching frequency. s : V–O bond orders for pentavalent V calculated by $s \approx (R/1.791)^{-5.1}$. (empirical parameters of Brown and Wu.¹⁶ VS: calculated valence state of the V cation ($\sum s_i$); relative error is <5%. CN: coordination number of the V cation.

The valence sum rule, as discussed by Brown,¹⁵ is extremely useful in estimating valence states of vanadium cations in vanadate structures. The valence state of a vanadium cation is calculated by adding the contributions from each V–O bond as determined by eq 2. For example, any deviation of a calculated valence state that lies outside 5.0 \pm 0.2 valence units (1 standard deviation from the formal oxidation state, as determined from Tables I–III) suggests a source of error in the bond length data. Common sources of error may be attributed to a misassigned oxidation state or erroneously determined bond lengths.

IV. Results

The vanadium–oxygen bond lengths were obtained from several vanadium oxide reference compounds and correlated with their corresponding Raman stretching frequencies. The reference compounds are listed in Tables I–III along with their crystallographically determined bond lengths, literature references, assigned Raman stretching frequencies, bond strengths (from eq 2), cal-

TABLE III: Bond Lengths and Observed Stretching Frequencies for V–O Bonds in Octahedrally Coordinated Vanadium Oxide Reference Compounds^a

compd	ref	R, Å	ν , cm ⁻¹	s	VS	CN		
PbV ₂ O ₆	32	1.611 (a)	954	1.70				
		1.647 (b)	887	1.52				
		1.666 (b)	887	1.44				
		1.719 (a)	796	1.23				
		1.921 (a2x)	525	0.70				
		1.928 (b2x)	525	0.69				
		2.028 (a)	447	0.54				
		2.063 (b)	397	0.49				
		2.569 (a)	151	0.16	5.0 (a)	6		
		2.732 (b)	113	0.12	5.0 (b)	6		
		V ₂ O ₅	17	1.58	994	1.81		
				1.78	701	1.03		
				1.88 (2x)		0.78		
2.02	481			0.55				
2.78	104			0.11	5.1	6		
Na ₅ V ₁₀ O ₂₈ ·18H ₂ O	33	1.597 (a)	1000	1.78				
		1.611 (b)	966	1.70				
		1.612 (c)	966	1.69				
		1.616 (d)	954	1.67				
		1.689 (e)	830	1.34				
		1.704 (e)	830	1.28				
		1.810 (b)	680	0.95				
		1.816 (d)	680	0.93				
		1.829 (c)	680	0.90				
		1.832 (a)	680	0.89				
		1.838 (d)	592	0.88				
		1.841 (b)	592	0.87				
		1.856 (c)	592	0.84				
		1.885 (a)	592	0.77				
		1.893 (a)	537	0.76				
		1.899 (c)	537	0.75				
		1.908 (e)	537	0.73				
1.946 (e)	537	0.66						
1.996 (b)	452	0.58						
2.003 (d)	452	0.57						
2.010 (d)	452	0.56						
2.015 (a)	452	0.55						
2.017 (b)	452	0.55						
2.048 (c)	452	0.51						
2.114 (e)	365	0.44						
2.117 (e)	365	0.43	5.0 (a)	6				
2.232 (b)	323	0.33	5.0 (b)	6				
2.252 (d)	256	0.32	5.0 (c)	6				
2.310 (c)	256	0.28	4.9 (d)	6				
2.321 (a)	256	0.27	4.9 (e)	6				
VOSO ₄ ·6H ₂ O	34	1.586	1006	1.77				
		2.004		0.52				
		2.021		0.50				
		2.023		0.50				
		2.029		0.49				
		2.160		0.36	4.1	6		
α -VOPO ₄	23	1.580	1041	1.90				
		1.858 (4x)	571	0.83				
		2.853		0.09	5.3	6		

^a ν : observed V–O Raman stretching frequency. s : V–O bond orders for pentavalent V calculated by $s \approx (R/1.791)^{-5.1}$. V–O bond orders for quadrivalent V calculated by $s \approx (R/1.770)^{-5.2}$. (empirical parameters of Brown and Wu.¹⁶ VS: calculated valence state of the V cation ($\sum s_i$); relative error is <5%. CN: coordination number of the V cation.

culated V⁵⁺ valence states (valence sum rule), and coordination numbers of the vanadium cations.

The procedure used for making assignments of the Raman stretching frequencies to V–O bond lengths for the vanadium oxide reference compounds is straightforward. First, the short V–O bonds of the reference compounds were correlated with their stretching frequencies. The short V–O bonds are typically associated with terminal V=O bonds and vibrate at the highest frequencies, >800 cm⁻¹. Next, the V–O bonds of intermediate length, typical of bridging V–O bonds and having about unit valency, were assigned to Raman stretching frequencies in the 600–800-cm⁻¹ region. The procedure for assigning the longer V–O

TABLE IV: V-O Stretches and Symmetry-Related and Extraneous Raman Bands (cm^{-1}) of Vanadium Oxide Reference Compounds

compd	V-O stretches	sym-related	extraneous
$\text{Pb}_2(\text{VO}_4)_3\text{Cl}$	823, 789, 722	405, 351, 319, 290	
BiVO_4	826, 716	366, 320, 210, 127	
Na_3VO_4	850, 823	393, 364, 355, 332, 259, 239, 227, 215	
$\alpha\text{-Zn}_3(\text{VO}_4)_2$	852, 807, 790, 690	(630) ^b 395, 375, 323, 270, 230, 168	
VOCl_3	1035	165, 129	504, 408, 249 (V-Cl)
$\text{Cd}_2\text{V}_2\text{O}_7$	873, 815	(844) ^b 477, 367, 353, 314, 261	
$\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	912, 807, 783, 719	512, 432, 372, 357, 330, 245, 223	
NH_4VO_3	927, 895, 645	495, 378, 320, 263, 226, 212	
$\alpha\text{-NaVO}_3$	955, 918, 628	(940) ^b 501, 371, 354, 341, 324, 314, 252, 243, 227, 180	
$\text{Mg}_2\text{V}_2\text{O}_7$	942, 896, 838, 726, 629, 200	(867) ^b 617, 566, 440, 411, 379, 358, 334, 316, 306, 283, 268	
<i>n</i> -propoxide ^a	1073, 618, 449	(998) ^b	862, 790, 346 (propoxide)
PbV_2O_6	954, 887, 796, 525, 447, 397, 151, 113	(852, 752, 675) ^b 478, 340, 323, 270, 248, 179	
V_2O_5	994, 701, 481, 104	526, 404, 305, 286, 200, 147	
$\text{Na}_6\text{V}_{10}\text{O}_{28}\cdot 18\text{H}_2\text{O}$	1000, 966, 954, 830, 680, 592, 537, 452, 365, 323, 256	763, 218, 189, 150	
$\text{VOSO}_4\cdot 6\text{H}_2\text{O}$	1006		1078, 1028, 630, 450, 310 (SO_4)
$\alpha\text{-VOPO}_4$	1041, 571		947, 928, 656, 533, 450, 420 (PO_4)

^a $\text{VO}(\text{OCH}_2\text{CH}_2\text{CH}_3)_3$. ^b Due to impurity phases.

bonds ($>1.9 \text{ \AA}$), however, is less certain and depends on extrapolating into the low-wavenumber region with the exponential fit derived from the data for the short and intermediate V-O bonds. Factors limiting the usefulness of the bond length-stretching frequency correlation to the low-frequency region are that the very intense, external modes of the crystal lie in this region as well as the bending and wagging modes of the vanadate species (internal modes resulting from vibrational interactions between neighboring chemical bonds in VO_2 , VO_3 , etc., as well as external modes due to the space-group symmetry of the crystal, do not directly relate to V-O bond lengths by the bond length-stretching frequency correlation). The external modes can generally be distinguished from the V-O stretches because the external modes are typically sharper and intense, but it is difficult to discriminate between the V-O stretches arising from long bonds and the bending/wagging modes. Thus, the assignment of the Raman bands to the long V-O bonds, of greater than $\sim 1.9 \text{ \AA}$ and stretching frequency less than 600 cm^{-1} , is not as reliable as that for shorter V-O bonds.

The simple exponential relationship observed between Raman stretching frequencies and crystallographic bond lengths holds extremely well for ternary vanadium oxides but is not as reliable for the binary oxide of the V^{5+} cation, vanadium pentoxide, or V_2O_5 . Vanadium pentoxide exhibits Raman bands at 994, 701, 526, 481, 404, 304, 283, 200, 146, and 104 cm^{-1} and has V-O bond lengths of 1.58, 1.78, 1.88 ($2\times$), 2.02, and 2.78 \AA .¹⁷ The shortest V-O bond, 1.58 \AA , is assigned to the highest occurring stretching frequency at 994 cm^{-1} . The intermediate bridging V-O bond, 1.78 \AA , is assigned to the next highest stretching frequency at 701 cm^{-1} . The two bridging V-O bonds of length 1.88 \AA , however, are expected to exhibit a Raman stretching mode at about 580 cm^{-1} (based on the exponential relation plotted in Figure 1). Instead, a stretching mode is observed at 526 cm^{-1} . This inconsistency is attributed to the medium-range order present in the three-dimensional, layered structure of the V_2O_5 lattice. In contrast, this medium-range order is not present in ternary vanadium oxides where ortho-, pyro-, or metavanadate structures are present. Extrapolating into the low-frequency region of the Raman spectrum shows that the two long V-O bonds of 2.02 and 2.78 \AA can be assigned to the two Raman stretching frequencies at 481 and 104 cm^{-1} , respectively. The Raman bands at 526, 404, 304, 283, 200, and 146 cm^{-1} cannot be assigned to V-O stretching frequencies and are therefore assigned as symmetry-related Raman modes. Abello¹⁸ assigned the 526-cm^{-1} band to a V-O-V stretching mode, consistent with the present assignment of a bridging V-O stretch due to medium-range order. Abello also

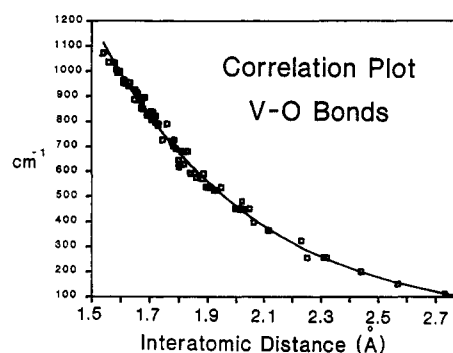


Figure 1. Correlation plot relating V-O bond lengths (\AA) to V-O stretching frequencies. The data points are fit to the exponential function $\nu = 21349 \exp(-1.9176R)$, where R is the V-O bond length in angstroms; ν is in cm^{-1} .

assigned the band at 404 cm^{-1} to a V-O-V stretch, the band at 283 cm^{-1} to a V-O-V bending mode, and the bands at 304, 200, and 146 cm^{-1} to external modes.

Vanadium oxide reference compounds covering a wide range of vanadium oxide structures are presented in Tables I-III. Table I lists nine tetrahedrally coordinated vanadates including orthovanadates, pyrovanadates, and metavanadates. Table II lists the pentacoordinated vanadates, of which only two were found. Table III lists 5 octahedrally coordinated vanadium oxide compounds representing 10 crystallographically distinct vanadium environments.

To make the tabulation of Raman stretching frequencies for the vanadate reference compounds as complete as possible, Table IV is also presented. The first column of Table IV lists the V-O stretching frequencies that have been assigned to bond lengths in Tables I-III. The second column lists modes that do not correspond to simple V-O stretches. These include modes due to bending/wagging, medium-range order (see above), and long-range order (lattice vibrations). Note that the frequencies tabulated in the second column are typically lower than those of the first column. The last column lists those Raman bands identified as extraneous bands or bands associated with chemical functionalities other than vanadates.

Reference compounds containing isolated VO_4 tetrahedra are listed in Table I and include the following: $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$,¹⁹ BiVO_4 ,²⁰ Na_3VO_4 ,²¹ $\alpha\text{-Zn}_3(\text{VO}_4)_2$,²² and the liquid VOCl_3 .²³ The

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most regular tetrahedral structures are present in $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ and BiVO_4 . The Raman spectra of $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ and BiVO_4 are quite similar and exhibit their highest occurring Raman frequencies at 822 and 826 cm^{-1} , respectively. Although the reported V–O bond lengths for $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ are 1.72 and 1.76 Å, these values are not consistent with the Raman data (see Discussion). The actual bond lengths for $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ are probably similar to those reported for BiVO_4 at 1.69 and 1.77 Å because of the similar Raman features displayed by these two compounds. Moreover, the bond lengths of $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ are further suspect because Pauling's valence sum rule leads to a vanadium valence state of 4.6 vu, clearly outside the tolerance of 5.0 ± 0.2 vu estimated from the data of Tables I–III. Nevertheless, the questionable bond lengths of $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ are included as reference compounds in Table I. More distorted VO_4 tetrahedra are present in Na_3VO_4 and $\alpha\text{-Zn}_3(\text{VO}_4)_2$, and these tetrahedra exhibit respective highest occurring Raman bands at 850 and 852 cm^{-1} . The tetrahedron having the shortest V–O bond in Table I but that is clearly not a VO_4 tetrahedron is VOCl_3 , which has a very short V–O bond of only 1.56 Å and a Raman stretching frequency at 1035 cm^{-1} . In summary, the orthovanadates in Table I exhibit their highest Raman frequencies in the 822–852- cm^{-1} region, reflecting their short V–O bond lengths of 1.67–1.72 Å. In contrast, highly distorted orthovanadates may exhibit very high Raman stretching frequencies, and this is exemplified by VOCl_3 , which has a very short bond of 1.56 Å. Another example of a highly distorted tetrahedron is found in AlVO_4 (see Discussion), having the FeVO_4 structure,²⁴ which exhibits its highest Raman stretching mode at 1017 cm^{-1} .²⁵

Pyrovanadate reference compounds are represented in Tables I and II by $\text{Cd}_2\text{V}_2\text{O}_7$,²⁶ $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$,²⁷ and $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$.²⁸ In general, the highest occurring Raman stretching frequency reflects the shortest V–O bond in a vanadate structure and is therefore useful as a measure for the relative distortion of a vanadate structure for a given coordination or structure type. From this criterion for distortion, it follows that $\text{Cd}_2\text{V}_2\text{O}_7$ has the most ordered pyrovanadate structure of the reference compounds examined, with the highest stretching frequency at 873 cm^{-1} , and $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ has the most distorted pyrovanadate structure, with its highest stretching frequency at 927 cm^{-1} . The distortion of the pyrovanadate structure in $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ is attributed to the presence of a long fifth V–O bond at each vanadium site (see Table II). Thus, the highest Raman frequency for the pyrovanadates occurs in the 873–912- cm^{-1} region, and this frequency range reflects the shortest V–O bond lengths, of 1.658–1.672 Å, present in these structures.

The metavanadate reference compounds listed in Table I are NH_4VO_3 ²⁹ and $\alpha\text{-NaVO}_3$.³⁰ The VO_4 tetrahedra in these compounds have similar structures: NH_4VO_3 has two terminal bonds of 1.65 and 1.67 Å with two bridging bonds of 1.80 Å, and $\alpha\text{-NaVO}_3$ has two terminal bonds at 1.631 and 1.653 Å with two bridging bonds at 1.801 and 1.805 Å. The highest frequency Raman band for NH_4VO_3 is 927 cm^{-1} , and for $\alpha\text{-NaVO}_3$ it is 955 cm^{-1} . The lower wavenumber of the highest occurring Raman stretching frequency for NH_4VO_3 reflects the lower degree of distortion imposed on this structure relative to $\alpha\text{-NaVO}_3$. These metavanadates exhibit characteristic frequencies in the 927–955- cm^{-1} region due to the Raman stretching frequencies of their shortest V–O bond lengths of 1.63–1.65 Å.

The two pentacoordinated vanadium oxide compounds, $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ ²⁸ and $\text{VO}(\text{OCH}_2\text{CH}_2\text{CH}_3)_3$,³¹ are listed in Table II. $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ is considered to be a distorted pyrovanadate with two

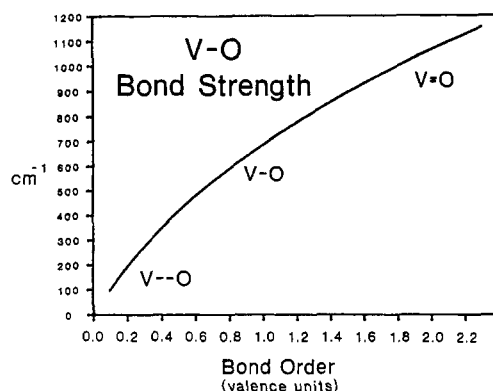


Figure 2. Correlation plot relating vanadium–oxygen bond strength (in valence units) to vanadium–oxygen stretching frequencies, according to eq 4.

crystallographically distinct vanadium environments. Each vanadium site consists of a VO_4 tetrahedron distorted by a fifth oxygen. Consequently, the vanadate species in $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ may be regarded as a V_2O_9 dimer rather than the V_2O_7 dimer characteristic of pyrovanadates. In comparison, $\text{VO}(\text{OCH}_2\text{CH}_2\text{CH}_3)_3$ is a liquid that consists of dimeric structures caused by edge-sharing monomers. The V–O bond lengths in $\text{VO}(\text{OCH}_2\text{CH}_2\text{CH}_3)_3$ were determined by extended X-ray absorption fine-structure experiments (EXAFS) to be 1.54, 1.8, and 2 Å (no error in measurement was reported).³¹

The following octahedrally coordinated vanadium oxide compounds are listed in Table III: PbV_2O_6 ,³² V_2O_5 ,¹⁷ $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$,³³ $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$,³⁴ and $\alpha\text{-VOPO}_4$.²³ PbV_2O_6 contains two distinct VO_6 units that give rise to highest frequency Raman bands at 954 and 887 cm^{-1} . The structure of crystalline V_2O_5 contains chains of highly distorted VO_6 octahedra with one short apical V–O bond at 1.58 Å, an opposing very long V–O bond at 2.78 Å, and four bridging V–O bonds lying roughly in a plane at 1.78, 1.88 (2 \times), and 2.02 Å. Similar types of VO_6 octahedra yield Raman stretching modes as high as 994 cm^{-1} for V_2O_5 , 1000–830 cm^{-1} for the decavanadate ion in $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$, and 1006 cm^{-1} for the VO_6 octahedron in $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$. The remaining five bonds in $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$ are to water molecules, and these are not observed in the Raman spectrum. Furthermore, the formal oxidation state of the vanadium cation in $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$ is +4, consistent with the calculated value of 4.1 vu by the valence sum rule. $\alpha\text{-VOPO}_4$ contains a highly distorted VO_6 octahedron, which is reflected in the very high value for the Raman frequency at 1041 cm^{-1} due to the very short V–O bond of 1.580 Å. In addition, it is noted that all the vanadium oxide reference compounds containing highly distorted VO_6 octahedra, represented by V–O stretching frequencies greater than 994 cm^{-1} in Table III, are monooxo species; that is, possessing only one terminal V=O bond. Thus, the highest Raman frequencies of the octahedrally coordinated vanadate species lie in the 830–1041- cm^{-1} region and reflect the shortest V–O bond lengths, 1.689–1.580 Å, present in these distorted VO_6 structures. Those vanadate species exhibiting Raman stretching frequencies at 994 cm^{-1} or greater are found to be monooxo VO_6 octahedra (this is not a hard-and-fast rule, however, as shown for AlVO_4 ; see Discussion section).

The crystallographic V–O bond lengths and corresponding V–O stretching band positions, from Tables I–III, are correlated in a plot in Figure 1. A least-squares fit of the data to the exponential function, described by eq 1, yields the following expression for the bond length–stretching frequency correlation:

$$\nu = 21349 \exp(-1.9176R) \quad (3)$$

where ν is in cm^{-1} and R is in Å. The precision in the calculation of a V–O bond length R from a measured Raman frequency ν

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using the bond length–stretching frequency correlation is ± 0.019 Å. The standard deviation in the estimate of a Raman stretching frequency from an absolute V–O bond length is ± 23 cm⁻¹.

Bond order–stretching frequency correlations are also useful in the determination of vanadate structures because the V–O bond order is representative of the strength of the chemical bond. The combined use of the empirical relation of Brown and Wu, eq 2, and the above bond length–stretching frequency correlation yields the following relation between the Pauling V–O bond strength (in valence units) and Raman stretching frequency:

$$s(\text{V-O}) = \{0.2912 \ln (21349/\nu)\}^{-5.1} \quad (4)$$

The bond strength–stretching frequency correlation is plotted in Figure 2.

V. Discussion

The bond length–stretching frequency correlation, eq 3, is derived from a least-squares exponential fit of the crystallographically determined bond lengths and measured Raman stretching frequencies. Such a direct relationship is expected from the diatomic approximation because of the assumption that each V–O bond in a vanadate species or crystalline lattice is vibrationally isolated from its surroundings. Thus, for V–O bonds, the Raman stretching frequency is a function of the bond length only. This approach, which assumes that all V–O bonds are vibrationally independent of one another, allows the direct determination of bond lengths from a simple analysis of the Raman vibrational bands.

The fundamental assumption of the diatomic approximation is that the vibrational interactions between neighboring chemical bonds are neglected. This assumption is shown to be justified by relating the precision of a bond length determination to that of its force constant. The average experimental precision for metal–oxygen bond lengths, based on a compilation of hundreds of data points,³⁵ is about ± 0.02 Å. According to eq 3, this corresponds to a precision in frequency of 30 cm⁻¹ and a difference in force constant of 0.34 mdyn/Å (assuming a harmonic model). For a highly symmetric vanadate species, for example, the perfect VO₄ tetrahedron, the symmetric and antisymmetric stretching modes appear at 790 and 775 cm⁻¹, respectively.^{35,36} These frequencies correspond to stretching and interaction force constants of 4.46 and 0.47 mdyn/Å, respectively, as determined by a normal-coordinate analysis (GF matrix method). If interactions between the neighboring V–O bonds are neglected, then the stretching frequency at 790 cm⁻¹ is directly converted to a diatomic stretching force constant of 4.48 mdyn/Å, and the band at 775 cm⁻¹ is similarly converted to 4.31 mdyn/Å. The differences between the values for diatomic force constant and those calculated from the normal-coordinate analysis are relatively small at 0.02 and 0.15 mdyn/Å. These values are considerably less than 0.34 mdyn/Å, which is the value reflected in the precision of a typical bond distance determination.

For distorted molecules the diatomic approximation is even more applicable because the interaction force constants are generally less than those of symmetric molecules. For example, Abello¹⁸ determined the interaction force constants of the VO₅ species in crystalline V₂O₅ (assuming C_{2v} site symmetry at the vanadium cation) to be less than or equal to 0.1 mdyn/Å. Thus, the underlying assumption of the diatomic approximation, that interactions between neighboring chemical bonds may be neglected, is justified for relating V–O Raman stretching frequencies to bond lengths in the vanadates.

The advantage of employing the diatomic approximation to arrive at a correlation between V–O bond lengths and stretching frequencies lies in its simplicity. The stretching frequency–bond length correlation immediately provides an excellent determination

of V–O bond lengths directly from their Raman stretching frequencies. The bond lengths generated in this way may be expressed in terms of the bond strengths and evaluated to determine the plausibility of proposed vanadate structures. Conversely, if the bond lengths of a vanadate species are known, then its Raman spectrum above ~ 400 cm⁻¹ may be predicted.

The information tabulated in Tables I–IV may also be used to generate ranges of characteristic frequencies, or group frequencies, with respect to vanadium oxide chemical functionalities. The major shortcoming of the group frequency approach, however, is that it is reliable only for fairly regular structures. While regular vanadate structures may be routinely found in solution and gas phase, vanadates confined to crystalline lattices are distorted. Thus, a great deal of overlap between frequency ranges is expected, and this contributes to the uncertainty in the assignment. According to the group frequency approach, the regular tetrahedral structures in Table I can be grouped as follows: orthovanadates, 822–852 cm⁻¹ (VO₄³⁻(aq), 821 cm⁻¹³⁷); pyrovanadates, 873–912 cm⁻¹ (V₂O₇(aq), 877 cm⁻¹³⁸); and metavanadates, 927–955 cm⁻¹ (VO₃)_nⁿ⁻(aq), 945 cm⁻¹³⁸). In general, however, the group frequency approach is not dependable as a diagnostic tool for the vibrational spectroscopy of inorganic compounds because most inorganic species are distorted, and these distortions give rise to uncharacteristic bands in the Raman spectrum that prevent structures from being discriminated. For example, octahedrally coordinated vanadate species are not symmetric and their Raman bands cannot be used to fingerprint their structures. Clearly, the presence of a Raman stretching band in the 1000–1080-cm⁻¹ region does not guarantee knowledge of the coordination of the vanadate species: VOCl₃ is tetrahedrally coordinated with a band at 1035 cm⁻¹, VO(OCH₂CH₂CH₃)₃ is pentacoordinated with a band at 1073 cm⁻¹, and α-VOPO₄ is octahedrally coordinated with a band at 1041 cm⁻¹. Furthermore, the presence of the highest frequency Raman band in the 790–852-cm⁻¹ region does not guarantee that the vanadate species is a monomeric VO₄ tetrahedron. This is because the highest frequency stretching bands for regular VO₆ octahedra are observed as low as 830 cm⁻¹ for Na₆V₁₀O₂₈·18H₂O, and are estimated to occur as low as 607 cm⁻¹ for the ideal VO₆ octahedron (see discussion below). Thus, for distorted vanadates the Raman band positions are independent of the coordination of the vanadium cation, and this nullifies the application of the group frequency approach as the sole means of assigning structures to distorted vanadate species. As a final note, the group frequency approach should certainly not be used without additional structural knowledge of the vanadate species (as provided from other techniques such as X-ray crystallography, XANES,³¹ and solid-state ⁵¹V NMR^{39,40}).

In summary, the diatomic approximation justifies the direct relationship observed between V–O Raman stretching frequencies and their bond lengths. Naturally, the relationship provides a direct method of ascertaining V–O bond lengths from Raman stretching frequencies. By allowing the determination of V–O bond lengths and the oxygen coordination of vanadate species, this approach enables Raman spectroscopy to be routinely used alongside other structural techniques (crystallography, solid-state ⁵¹V NMR, and XANES) to systematically determine the complete structures of vanadates present in liquid or bulk or as two-dimensional surface oxides.

In the next section, a few applications of the bond length–stretching frequency and bond order–stretching frequency correlations, eqs 3 and 4, are illustrated. These empirical correlations lead to a systematic method for determining the oxygen coordinations and bond lengths of vanadates. This method is illustrated for vanadates of known structure (vanadium *n*-propoxide, BiVO₄, α-Zn₃(VO₄)₂, and Pb₂(VO₄)₃Cl) and unknown structure (AlVO₄ and the two-dimensional surface phase in V₂O₅/Al₂O₃). The

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effects of medium-range order will be demonstrated by determining the V–O bond lengths in crystalline vanadium pentoxide.

Applications. 1. Determining Stretching Frequencies for Symmetric Structures: VO_4 and VO_6 . An interesting application of the bond length–stretching frequency correlation is the prediction of Raman stretching bands for proposed vanadate structures. This is demonstrated in the calculation of the V–O stretching frequency of a regular VO_4 tetrahedron and a regular VO_6 octahedron. These ideal structures have a high degree of point-group symmetry (T_d and O_h , respectively). Consequently, vibrational interactions between bonds are expected to be significant (stretch–stretch interactions are about one-tenth of the stretching force constant). As previously shown, however, these interactions are smaller than the error associated with crystallographic measurements of bond lengths. Equation 3 may therefore be used to provide reasonable estimates of V–O Raman stretching frequencies of proposed vanadate structures.

The V–O Raman stretching frequencies of the symmetric VO_4 and VO_6 structures are estimated by first equally dividing the 5.0 valence units of available bond strength among the four and six V–O bonds, respectively, of the tetrahedron and octahedron. This results in a V–O bond strength of 1.25 vu for all bonds in VO_4 and 0.833 vu for all bonds in VO_6 . In the next step, these bond strengths are converted to bond lengths, by eq 2, for the ideal VO_4 and VO_6 structures of 1.715 and 1.857 Å, respectively. If these bond lengths are considered absolute (without error), then the bond length–stretching frequency correlation, eq 3, yields a stretching frequency of 796 cm^{-1} for the ideal VO_4 tetrahedron and 607 cm^{-1} for the ideal VO_6 octahedron. The calculated value of 796 cm^{-1} is very close to 790 cm^{-1} observed for the symmetric VO_4 tetrahedron present in the sillenite structure of composition $25Bi_2O_3 \cdot V_2O_5$ (containing the most ideal VO_4 tetrahedron yet reported).³⁶ At present, no regular VO_6 octahedral structures have been found. The most regular VO_6 structure in Table III is contained within the decavanadate ion in $Na_6V_{10}O_{28} \cdot 18H_2O$, where the vanadium cation has V–O bond lengths of 1.689, 1.704, 1.908, 1.946, 2.114, and 2.117 Å. The highest stretching frequency from this structure appears at 830 cm^{-1} , which is 223 cm^{-1} higher than the value of 607 cm^{-1} estimated for the ideal octahedron, reflecting the significant degree of distortion still present in this structure.

2. Refinement of Bond Lengths: Vanadium n -Propoxide. The diatomic treatment may also be used to refine or improve upon the V–O bond distances reported from older or unreliable data. In many cases, reported V–O bond lengths have a rather large measurement error, and others tend to be unreliable because of conflicting reports. These inconsistencies are frequently encountered among systems that are not easily examined by diffraction techniques. To refine these bond lengths, the reported bond lengths, although approximate, can be used to assign the stretching frequencies because they are expected to lie at least somewhere on the wing of the correct Raman band. The frequency at the maximum amplitude of each band is located, and this value is subsequently converted to a more accurate and precise bond length value by eq 3.

In the present example, the refinement procedure is used to determine more accurate V–O bond lengths for the liquid vanadium n -propoxide, $VO(OCH_2CH_2CH_3)_3$. The structure of $VO(OCH_2CH_2CH_3)_3$ is that of a dimer with each five-coordinated vanadium cation having one terminal V=O bond, two V–OR propoxy bonds, and two V–OR–V propoxy bridges forming a dipropoxy bridge between vanadium cations. The V–O bond lengths in $VO(OCH_2CH_2CH_3)_3$ were determined by EXAFS to be 1.54 Å (terminal vanadyl V=O), 1.8 Å (V–O propoxy bonds), and 2 Å (bridging V–O–V bonds).³¹ The error associated with the EXAFS fitting procedure was not reported. These reported bond lengths are converted to Pauling bond strengths by eq 2, and the sum of the individual bond strengths is equal to a calculated valence state of 5.6 vu for the vanadium cation (see Table II). The calculated valency lies outside the acceptable range of 5.0 ± 0.2 vu allowed by eq 2 (see Tables I–III), showing that the calculated valence state is not consistent with the formal oxidation state of V^{5+} in vanadium n -propoxide. This inconsistency indicates

TABLE V: Vanadium n -Propoxide Structure Determination by Raman Spectroscopy

		Observed Raman Bands, cm^{-1}			
V–O		1073, 618, 449			
propoxide		862, 790, 346			
$V_2O_5 \cdot nH_2O$ gel		998			
V–O Bond Types					
	cm^{-1}	s , vu	R , Å		
A	1073	2.0255	1.5595		
B	618	0.8541	1.8472		
C	449	0.5499	2.0138		
Possible Structures					
coord no.	no. of bonds			valence	
	A	B	C		
a	3	2	1	0	4.905
b	4	2	0	2	5.151
c	5	1	3	1	5.138
d	5	1	2	2	4.833
e	6	1	1	4	5.079
f	6	0	6	0	5.125
g	6	0	5	1	4.821
guidelines				acceptable structures	
(1) highest occurring frequency must be used				a, b, c, d, e	
(2) maximize the number of frequencies used (3)				c, d, e	
(3) coordination known (CN = 5)				c, d	
(4) most consistent valence				c	
Acceptable Structure					
		reported ^a			
c	1×A	1× 1.560	1× 1.54		
	3×B	3× 1.847	3× 1.8		
	1×C	1× 2.014	1× 2		

^aReference 31.

that the V–O bond lengths reported for $VO(OCH_2CH_2CH_3)_3$ are not correct.

The bond lengths provided by the EXAFS experiment for $VO(OCH_2CH_2CH_3)_3$ may be used to arrive at refined V–O bond lengths. The three reported bond lengths may be converted to V–O stretching frequencies, and these stretching frequencies overlap with the bands at 1073, 618, and 449 cm^{-1} . With use of eq 3, these Raman bands lead to refined bond lengths of 1×1.560 , 3×1.847 , and 1×2.014 Å (± 0.019 Å). These bond lengths may also be determined by following a systematic procedure for determining vanadate structures by Raman spectroscopy. In the following paragraph, this systematic method is followed for determining the structure of the vanadate structure in the $VO(OCH_2CH_2CH_3)_3$ molecule from an examination of its Raman spectrum.

The procedure for determining the structure of the vanadate species in the vanadium n -propoxide molecule is outlined in Table V. The approximate bond lengths of vanadium n -propoxide reported from the EXAFS data allowed the assignment of the measured V–O Raman stretching frequencies for the terminal V=O bond, V–O propoxy bond, and bridging V–O–V bond at 1073, 618, and 449 cm^{-1} , respectively. The remaining Raman bands are attributed to the n -propoxide structure and a vanadium pentoxide gel present as the hydrolysis–condensation product. The three V–O stretches represent three bond types designated A–C. Equations 3 and 4 are used to find the corresponding bond strengths and lengths of the V–O bond types. At this point a computer program (written in QuickBasic) is used to systematically consider every possible combination of V–O bond strengths consistent with the experimentally determined valence of the V^{5+} cation of 5.0 ± 0.2 vu. The resulting seven possible structures, a–g, are tabulated in Table V along with the types of bonds making up each structure and calculated valences.

The next step involves reducing the number of possible structures to one possible structure by using a set of guidelines or “rules

TABLE VI: BiVO_4 Structure Determination by Raman Spectroscopy

Observed Raman Bands, cm^{-1}				
V-O	826, 716			
bending/ext	366, 320, 210, 127			
V-O Bond Types				
	cm^{-1}	s, vu	$R, \text{\AA}$	
A	826	1.3206	1.6960	
B	716	1.0605	1.7705	
Possible Structures				
coord no.	no. of bonds			valence
	A	B		
a	4	3	1	5.022
Acceptable Structure				
a	$3 \times \text{A}$	3×1.696	2×1.69	
	$1 \times \text{B}$	1×1.770	2×1.77	

^aReference 20.

of thumb". The first guideline is that the shortest bond of a metal oxide species always exhibits the highest occurring Raman stretching frequency. Consequently, all structures not having the A-type bond may be eliminated (f and g). The second most important guideline is to maximize the number of frequencies used. This follows from the assumption that every covalent bond in a metal oxide species gives rise to a Raman stretching frequency, and every Raman band occurring above about 450 cm^{-1} is due to the stretch of a metal-oxygen bond (except when medium-range order is present; for example, V_2O_5). Three structures—c, d, and e—use all three bond types. If we assume the coordination to be 5-fold and choose the structure having the most consistent calculated valence, then only structure c remains. The bond lengths of structure c compare favorably with those of the reported values,³¹ as shown at the bottom of Table V, and are identical with those determined from the refinement procedure in the preceding paragraph.

3. *Crystalline Compounds of Known Structure: BiVO_4 , $\alpha\text{-Zn}_3(\text{VO}_4)_2$, and $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$.* Tables VI–VIII illustrate how the V–O bond lengths and coordinations are determined for BiVO_4 , $\alpha\text{-Zn}_3(\text{VO}_4)_2$, and $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$, respectively. BiVO_4 exhibits two Raman bands above 450 cm^{-1} , at 826 and 716 cm^{-1} , and these are assumed to represent two different bond types, A and B. Using the same procedure described for vanadium *n*-propoxide, the frequencies are converted to bond strengths and lengths by eqs 3 and 4, and all possible structures consistent with the valence of the V^{5+} cation are determined. As Table VI shows, only one structure is possible, and it is tetrahedrally coordinated. The bond lengths, shown at the bottom of Table VI, are very similar to those reported from single-crystal diffraction measurements.²⁰

In some cases it is not possible to eliminate all but one of the possible structures. For the case of $\alpha\text{-Zn}_3(\text{VO}_4)_2$ and $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$, for example, two possible structures remain in each case as shown in Tables VII and VIII, respectively. Consequently, a hybrid or average structure is formed by averaging each set of bond lengths from the two structures. It is interesting to note that all of the possible structures are tetrahedrally coordinated. The bond lengths of $\alpha\text{-Zn}_3(\text{VO}_4)_2$ determined from the Raman spectrum closely match those determined from diffraction measurements,²² whereas the bond lengths of $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$ represent refined values because of the uncertainty in the reported diffraction measurements.¹⁹

4. *Determining the Structure of an Unknown Metal Oxide: AlVO_4 .* The diatomic treatment may be used to generate viable structures for metal oxide species of unknown structure. This is demonstrated for aluminum vanadate, AlVO_4 , for which the complete structure is unknown. AlVO_4 has been determined by X-ray powder diffraction to be isomorphous with FeVO_4 , although infrared spectra show that the VO_4 tetrahedra in AlVO_4 are more distorted than those in FeVO_4 ;²⁴ FeVO_4 belongs to the triclinic

TABLE VII: $\alpha\text{-Zn}_3(\text{VO}_4)_2$ Structure Determination by Raman Spectroscopy

Observed Raman Bands, cm^{-1}					
V-O	852, 807, 790, 690				
bending/ext	395, 375, 323, 270, 230, 168				
pyrovanadate	911, 512 (vw) ^a				
metavanadate	968, 630 (vw)				
V-O Bond Types					
	cm^{-1}	s, vu	$R, \text{\AA}$		
A	852	1.3867	1.6798		
B	807	1.2734	1.7081		
C	790	1.2321	1.7192		
D	690	1.0035	1.7898		
Possible Structures					
coord no.	no. of bonds				valence
	A	B	C	D	
a	4	3	0	0	5.164
b	4	2	1	0	5.050
c	4	2	0	1	5.006
d	4	1	2	0	4.937
e	4	1	1	1	4.896
f	4	1	1	2	5.124
g	4	1	0	2	4.854
h	4	1	0	3	5.083
guidelines					
(1) maximize the number of frequencies used (3 or 4)				b, c, d, e, f, g	
(2) most consistent valence				b, c	
Acceptable Structure					
b, c	$2 \times \text{A}$	2×1.680	2×1.67		
	$1 \times \text{BC}$	1×1.71	1×1.73		
	$1 \times \text{C}$	1×1.790	1×1.79		

^avw = very weak. ^bReference 22.TABLE VIII: $\text{Pb}_2(\text{VO}_4)_3\text{Cl}$ Structure Determination by Raman Spectroscopy

Observed Raman Bands, cm^{-1}					
V-O	823, 789, 722				
bending/ext	405, 351, 319, 290				
V-O Bond Types					
	cm^{-1}	s, vu	$R, \text{\AA}$		
A	823	1.3131	1.6979		
B	789	1.2296	1.7199		
C	722	1.0739	1.7661		
Possible Structures					
coord no.	no. of bonds			valence	
	A	B	C		
a	4	3	1	0	5.169
b	4	3	0	1	5.013
c	4	2	2	0	5.085
d	4	2	1	1	4.930
e	4	1	3	0	5.002
f	4	1	2	1	4.846
g	4	0	4	0	4.919
guidelines					
(1) maximize the number of frequencies used (3)				d, f	
(2) most consistent valence				d, f	
Acceptable Structure					
d, f	$1 \times \text{A}$	1×1.698	2×1.72		
	$1 \times \text{AB}$	1×1.709			
	$1 \times \text{B}$	1×1.720	2×1.76		
	$1 \times \text{C}$	1×1.766			

^aReference 19.

TABLE IX: AlVO_4 Structure Determination by Raman Spectroscopy

		Observed Raman Bands, cm^{-1}					
V–O bending/ext		1017, 988, 949, 919, 899, 850, 557, 510 371, 319, 279, 215, 133					
		V–O Bond Types					
	cm^{-1}	s, vu	$R, \text{\AA}$		cm^{-1}	s, vu	$R, \text{\AA}$
A1	1017	1.8500	1.5875	C	899	1.5108	1.6518
A2	988	1.7629	1.6026	D	850	1.3816	1.6810
A3	949	1.6496	1.6236	E	557	0.7370	1.9014
B	919	1.5655	1.6403	F	510	0.6525	1.9474

Possible Structures for Three Distorted, Monooxo Tetrahedra											
	coord no.	no. of bonds								valence	
		A1	A2	A3	B	C	D	E	F		
a	4	1	0	0	1	0	0	1	1	4.805	
b	4	1	0	0	1	0	0	2	0	4.890	
c	4	1	0	0	0	1	0	2	0	4.835	
d	4	0	1	0	0	0	2	0	1	5.178	
e	4	0	1	0	1	0	0	2	0	4.802	
f	4	0	0	1	0	1	1	0	1	5.194	
g	4	0	0	1	0	0	2	0	1	5.065	
h	4	0	0	1	0	0	2	1	0	5.150	

guidelines						acceptable structures					
(1) maximize frequencies used by all three tetrahedra						ceg, cef, bdf, bef					
(2) determine number of occurrences of individual structures						f, e > b, c > d, g					
(3) find most probable set of structures from (2)						cef, bef					
(4) combine to form hybrid structure						(bc) ef					

Acceptable Structures											
bc	1×A	1×	1.587	e	1×A	1×	1.603	f	1×A	1×	1.624
	1×B	1×	1.646		1×B	1×	1.640		1×C	1×	1.652
	2×E	2×	1.901		2×E	2×	1.901		1×D	1×	1.681
									1×F	1×	1.947

space group $P\bar{1}$ and consists of three isolated and crystallographically distinct VO_4 tetrahedra.⁴¹ Recent ^{51}V MAS NMR studies have verified the presence of three unique vanadium environments in AlVO_4 with the isotropic chemical shifts of the three species occurring at -661 , -745 , and -775 ppm (with respect to VOCl_3).^{39,40} The NMR experiments further confirm that the vanadium sites are in highly distorted tetrahedral coordination with oxygen and that these VO_4 tetrahedra are isolated from one another.

The Raman spectrum of AlVO_4 also shows the presence of three distinct and highly distorted vanadate species because of three very sharp Raman bands appearing at 1017 , 988 , and 949 cm^{-1} ,⁴² each representing the shortest $\text{V}=\text{O}$ bond of each of the distorted VO_4 tetrahedra. The remaining dominant Raman bands occur at 919 , 899 , 850 , 557 , and 510 cm^{-1} . The highest frequency bands at 1017 , 988 , and 949 cm^{-1} are each assigned to the shortest $\text{V}=\text{O}$ bond of each of the three distorted VO_4 tetrahedra. These three frequencies are labeled as A1, A2, and A3, respectively, with the remaining bands labeled as B–F.

Table IX illustrates the structure determination of AlVO_4 by Raman spectroscopy. Because of the data provided by NMR and XRD, only the four-coordinated, monooxo possibilities are listed in Table IX as possible structures. There are four different combinations of structures utilizing all the observed Raman bands. The most probable combination was selected on the basis of the number of times the individual structures appeared in the analysis. After the analysis, two structures remained from which a hybrid structure was formed. The resulting bond lengths of the three tetrahedra in AlVO_4 are presented at the bottom of Table IX. In Table X these bond lengths are compared with those determined crystallographically for the isostructural FeVO_4 .⁴¹ Although the bond lengths reported here for the VO_4 tetrahedra in AlVO_4 are tentative, they depict the strong distortion that occurs to the VO_4

TABLE X: Comparison of V–O Bond Lengths of the VO_4 Tetrahedra in AlVO_4 and FeVO_4

	AlVO_4^a (± 0.02 \AA)	FeVO_4^b (± 0.007 \AA)
V(1)–O	1.59	1.649
–O	1.65	1.662
–O	1.90	1.783
–O	1.90	1.785
V(2)–O	1.60	1.660
–O	1.64	1.683
–O	1.90	1.780
–O	1.90	1.786
V(3)–O	1.62	1.679
–O	1.65	1.680
–O	1.68	1.713
–O	1.95	1.806

^aDetermined from Raman stretching frequencies. ^bReference 41.

tetrahedra by substituting the Al^{3+} cation for the Fe^{3+} cation in the FeVO_4 lattice.

5. *Complications due to Medium-Range Order: V_2O_5 .* As already noted, the empirical relation between the V–O Raman stretching frequencies and crystallographic bond lengths holds for ternary vanadium oxides but is not as reliable for vanadium pentoxide, V_2O_5 . The shortest V–O bond in V_2O_5 , 1.58 \AA , is assigned to the highest occurring stretching frequency at 994 cm^{-1} , and the intermediate bridging V–O bond of 1.78 \AA is assigned to the next highest stretching frequency at 701 cm^{-1} . The two bridging V–O bonds of length 1.88 \AA , however, with an expected band at about 580 cm^{-1} , instead exhibit a band at 526 cm^{-1} . This inconsistency is attributed to the medium-range order present in the three-dimensional, layered structure of the V_2O_5 lattice. Deviations from the diatomic treatment due to the presence of medium-range order have also been observed in other binary metal oxides such as Nb_2O_5 , MoO_3 , and WO_3 but not in their corresponding ternary metal oxides.³⁵ The medium-range order is believed to result in nonlocalized interactions between the chemical bonds responsible for the medium-range order. The nonlocalized

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TABLE XI: V_2O_5 Structure Determination by Raman Spectroscopy

Observed Raman Bands, cm^{-1}		V-O Bond Types				R, Å
V-O bending/ext	994, 701, 526, 481 404, 305, 286, 200, 147, 104	cm^{-1}	s, vu			
A	994	1.7807			1.5994	
B	701	1.0274			1.7815	
C	526	0.6807			1.9313	
D	481	0.6027			1.9779	

Possible Structures						
coord no.	no. of bonds				valence	
	A	B	C	D		
a	4	2	1	0	1	5.192
b	4	2	0	1	1	4.844
c	4	2	0	2	0	4.923
d	4	1	3	0	0	4.863
e	5	1	2	1	1	5.119
f	5	1	2	0	2	5.041
g	6	1	0	4	1	5.106
h	6	1	0	3	2	5.028
i	6	1	0	2	3	4.950
j	5	0	5	0	0	5.137
k	6	0	3	1	2	4.968
l	6	0	3	0	3	4.968

guidelines	acceptable structures
(1) eliminate structures not using highest frequency	a, b, c, d, e, f, g, h, i
(2) maximize the number of frequencies used (3 or 4)	a, b, e, f, g, h, i
(3) assumption: structure is not 4-coord	e, f, g, h, i
(4) distorted, monooxo octahedron (eliminates 6-coord)	e, f
(5) maximize the number of frequencies used (4)	e

Acceptable Structure			
			reported ^a
e	1×A	1× 1.599	1× 1.58
	2×B	2× 1.782	1× 1.78
	1×C	1× 1.931	2× 1.88
	1×D	1× 1.978	1× 2.02
	1×	1× ~2.5	1× 2.78

^aReference 17.

interactions act to displace the metal-oxygen stretching frequencies from those predicted from the diatomic model, thereby giving erroneous bond lengths.

To illustrate the effect of medium-range order on a structure determination by Raman spectroscopy, Table XI shows the structure determination of vanadium pentoxide. It is assumed that all Raman stretching frequencies above 450 cm^{-1} are due to V-O stretches. The four observed bands at 994, 701, 526, and 481 cm^{-1} each represent a different V-O bond type, A-D, respectively. These values give rise to a total of 12 possible structures for the vanadate molecule in V_2O_5 . The last three structures (j, k, l) are rejected because the highest observed frequency, at 994 cm^{-1} , is not used. Structures c and d are rejected because only two of four frequencies are used; this leaves five possible vanadate structures using three or four frequencies. If it is assumed that the vanadate structure consists of a highly distorted monooxo (one terminal V=O bond), octahedrally coordinated species, then the five-coordinated structures, e and f, remain. Maximizing the number of frequencies used leaves structure e as the only possibility. The average size of an octahedrally coordinated, monooxo vanadate molecule is 4.079 Å (as determined by averaging values in Table III) indicating that the very long V-O bond opposing the short V=O terminal bond is about 2.5 Å in length and would therefore vibrate at a much lower frequency than 450 cm^{-1} . The V-O bond lengths of structure e, shown at the bottom of Table

XI, compare moderately well with the reported values.¹⁷ The notable difference, however, is that the two bridging V-O bonds of length 1.88 Å appear as 1.782 and 1.931 Å according to the Raman spectrum. This discrepancy is due to the medium-range order present in the vanadium pentoxide crystalline lattice.

6. *Determining the Structure of Surface Metal Oxides: V_2O_5/Al_2O_3 .* The determination of bond lengths 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. Surface metal oxides lack long-range order because they are dispersed onto a metal oxide substrate at monolayer or submonolayer coverages. A very important type of surface metal oxide system is the dehydrated surface vanadate species supported on alumina, V_2O_5/Al_2O_3 , which has recently been the subject of ^{51}V NMR^{39,40,43} and Raman investigations.⁴³⁻⁴⁵ The Raman results for the V_2O_5/Al_2O_3 system identify two general types of surface vanadate species: one that is regular and one that is highly distorted. The highly distorted vanadate species displays a ^{51}V NMR chemical shift consistent with that of a VO_4 tetrahedron at around -650 ppm .⁴⁰ In addition, wide-line ^{51}V NMR experiments show this tetrahedron to possess cylindrical symmetry. The Raman spectrum of this highly distorted vanadate species exhibits a stretching band at 1026 cm^{-1} ,⁴³⁻⁴⁵ which corresponds to a V-O bond length of $1.583(19)\text{ Å}$ according to the bond length-stretching frequency correlation, eq 3. The bond strength of the terminal V=O bond is determined by eq 2 to be about 1.9 vu. Only one Raman band is observed for this surface species, and this indicates that the surface vanadate species is monooxo (one terminal V=O bond). In contrast, a dioxo species would result in two stretching bands if there were at least two inequivalent (as for $AlVO_4$ and $FeVO_4$; see Table V) or equivalent V=O bonds.¹ Further evidence for a monooxovanadate species is provided by infrared spectroscopy where a single absorption band is observed at $\sim 1035\text{ cm}^{-1}$,⁴⁶ consistent with the Raman band observed at 1026 cm^{-1} . The discrepancy of 9 cm^{-1} between the infrared and Raman data is insignificant as errors associated with instrumentation (calibration, resolution) and the uncertainty in the true peak position of the very broad infrared band must be considered. Furthermore, symmetric and antisymmetric stretching frequencies are generally separated by $20\text{--}100\text{ cm}^{-1}$ for dioxo functionalities in the gas phase,¹ much greater than the apparent 9 cm^{-1} difference. Therefore, the coincidence between the infrared and Raman band positions is consistent only with a monooxo species and not a dioxo species.

The combined data from the Raman and NMR techniques allow the determination of the bond lengths of the dehydrated surface vanadate species on alumina. For a monooxo VO_4 surface vanadate species with cylindrical symmetry, as the Raman and NMR results show, the remaining three bonds of this species would necessarily be equivalent and presumably form V-O-Al linkages to the alumina surface. The bond strengths of the three surface bonds are each about 1.0 vu (for a total valence state of 5.0 valence units for the V^{5+} cation). The V-O single bond is converted to a length of $1.78 \pm 0.09\text{ Å}$ (relative error is less than 5%) by eq 2. Thus, the V-O bond lengths of the dehydrated surface vanadate species on alumina are $1.583(19)$ (apical bond) and $1.78(9)$ Å (three bridging bonds). The absence of an expected stretching band near 700 cm^{-1} (or anywhere in the spectrum) for the bridging V-O bonds, in spite of the overwhelming intensity and sharpness of the V=O stretch at 1026 cm^{-1} , indicates that the bridging oxygen in each V-O-Al linkage is intimately coupled to the alumina support. In fact, the V-O bonds to the alumina may be delocalized over the alumina surface. It is of interest to note that a similar situation is observed for the VO_6 octahedron in $VOS-O_4 \cdot 6H_2O$ ³⁴ (see Table III), which exhibits only a terminal V=O stretch at 1006 cm^{-1} ; its remaining five bonds, consisting of five

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ligands to water molecules, are not observed in the Raman spectrum.

VI. Conclusions

The diatomic approach to interpreting the Raman spectra of vanadium oxide compounds (the diatomic approximation) was used to justify the correlation observed between vanadium-oxygen Raman stretching frequencies and their bond lengths. Empirical relations were presented for relating vanadium-oxygen bond lengths and stretching frequencies as well as bond strengths (in valence units) and stretching frequencies. These relationships provide an excellent method of directly determining V-O bond lengths from Raman stretching frequencies for vanadium oxide compounds and may conceivably lead to the complete structure of the vanadate species. The correlations are of greatest benefit

when used to determine structural information about vanadates that cannot be examined by diffraction or other spectroscopic techniques. Applications of the empirical relations were discussed for vanadate species present in the liquid phase, in bulk crystalline compounds, and as a two-dimensional surface oxide. In fact, the diatomic treatment has already been used to evaluate vanadate structures in the multiphasic bismuth vanadates ($1:1 \leq \text{Bi:V} \leq 60:1$).^{35,36}

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Nucleophilic Substitution Reactions in Molecular Clusters following Photoionization

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Substitution reactions in mixed van der Waals aggregates consisting of halobenzenes and polar molecules are studied by resonant two-photon ionization (R2PI). Spectroscopic fingerprints in the ion yield curves of the product ions allow their neutral precursors to be assigned. Intracuster ipso substitution reactions have been found, depending both on the number and type of solvent molecules and on the halogen present. They are discussed in terms of an addition-elimination mechanism. Electron transfer is found to play an important role both in the reaction mechanism and in the size-dependent switching between redox and substitution reactions.

1. Introduction

Recently, molecular clusters have attracted considerable attention in chemical physics as microscopic model systems for studying the transition from isolated to solvated molecules.¹⁻³ By characterizing the size and composition of the neutral clusters, the size dependence of their energetics and dynamics after electronic excitation or ionization may be investigated. Among the various properties of clusters, the physical chemist is particularly interested in their reaction behavior, as it reflects the influence of solvation on reaction dynamics.

In the past much valuable information on the energetics of solvated ions at equilibrium conditions has been deduced from ion-molecule reactions studied by mass spectrometry in high-pressure or ion cyclotron resonance cells^{4,5} or in flowing afterglows.⁶ Reactions in molecular clusters following electron impact or photoionization however have been investigated only recently.^{1,7,8,10} The specific information that can be derived from ionizing clusters may be summarized as follows. Cluster ions may be considered as models for transition states in ion-molecule reactions in the sense that their fragmentation represents the "half-collision" analogue of the latter. However one difference should be pointed

out. The intracuster reacting particles are often trapped by electrostatic forces and hence exhibit only a limited range of trajectories as compared with the corresponding bimolecular reaction. For the same reason they often interact for a much longer time period than in "normal" collisions. This aspect turns out to be particularly important with regard to charge-transfer processes. In addition, the molecules surrounding a primary formed ion may serve as a heat bath. Clusters, with the exception of dimers, always have an incorporated third body which is crucial in termolecular processes depending on dissipative energy transfer like association and deexcitation reactions.

The ionization of weakly bound van der Waals (vdW) clusters, however, poses a serious problem. Fragmentation very often takes place already in the vicinity of the ionization threshold due to energy released as the clusters change from their neutral to their ionic equilibrium structure. Thereby neutral subunits may be evaporated,^{11,12} a process we call "vdW fragmentation" (vFR) in the following. Hence the size distribution in the mass spectrum does not represent that of the neutral beam, making the characterization of the size of the precursor clusters a difficult task. The characterization of their structure is an even more challenging problem which generally can only be solved with spectroscopic methods.

Here we report on the chemical behavior of ionized molecular clusters studied by resonant two-photon ionization (R2PI). This method allows in contrast to conventional photoionization an "optical mass spectrometry",^{13,14} by which the neutral precursor

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