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Titanium-Oxygen Bond Length -Bond Valence Relationship

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Abstract

A bond length–bond valence correlation is a simple method of checking and evaluating molecular structures and is of great interest in chemistry, biology, geology, and material science. Recently, we used quantum-mechanical arguments to derive Pauling’s bond length–valence relationship and to define the adjustable fitting parameter b in terms of atomic-orbital exponents. Improved orbital exponents were generated for elements 1–103 using published atomic radii and single-bond covalent radii as well as a continuous function for effective principal quantum number. In this study, we use orbital exponents for titanium (Ti) and oxygen (O) to generate a bond length–valence relationship for Ti–O bonds. Recent crystallographic Ti–O bond lengths from 32 environments were collected and converted to Ti–O bond valences to check the reliability of the bond length–valence relationship where R_o was found (bond length of unit valence). This relationship is expected to apply to any Ti–O bond regardless of environment, physical state, or oxidation number.

Introduction

Linus Pauling developed five basic rules of chemical bonding in 1929 (Pauling 1929). Perhaps the most important, for the present study, is Pauling’s second rule, which states that the principle of local charge neutrality, where the negative charge of each anion is neutralized by the neighboring positive charges of the cations, and the cationic charges are neutralized by neighboring anions. In simpler terms, the sum of the bond valences around each cation is compensated by the valence of its surrounding anions and has been generalized as the valence sum rule.

Pauling’s bond length – valence relationship (Pauling 1947, Zachariasen 1954, Brown 2009) is

$$s = \exp\left(\frac{R_o - R}{b}\right) \quad (1)$$

where s is the bond valence (bond order) or number of shared electron pairs involved in the bond, R is bond length, R_o is the bond length of a chemical bond having unit valence, and b is an empirical fitting parameter. In practice, the b and R_o parameters are found by minimizing the difference between the bond valence sums and the atomic valence of the central cation. Although values of b have been found to range between 0.25 to 0.65 Å (Hardcastle and Laffoon 2012), it is commonly assumed to be a universal constant at 0.37 Å – this strategy was proposed by Brown and Altermatt (1987). This assumption decreases the reliability of the relationship for very short and very long bonds, but makes Equation (1) easier to use because there is now only one adjustable fitting parameter, R_o .

Bond length–valence relationships using the valence sum rule have a wide range of applications, including use in evaluating proposed molecular structures and checking crystal structures. It can also be used to determine the oxidation states of cations and anions, and determine coordination numbers for organo-metallic complexes. The application of this relationship is not limited to the system or environment.

Theory

The “ b ” Parameter

The recent derivation of Pauling’s bond length–valence relationship (Hardcastle 2013) resulted in the following expression for the b parameter

$$b = \frac{ea_o}{(\xi_{cation} + \xi_{anion})} \quad (2)$$

where e is Euler’s constant (2.718282), a_o is the Bohr radius (0.529 Å), and ξ is the atomic-orbital exponent. The value of b calculated using Equation (2) can then be substituted into Pauling’s relationship, Equation (1). If the sum of the orbital exponents is large, for example, then the b parameter is small, making the change in bond order more sensitive to bond length according to

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Equation (1).

Results and Discussion

Atomic-orbital exponents for titanium and oxygen have been calculated using self-consistent field methods at 1.2042 and 2.2266, respectively (Clementi and Raimondi 1963), and also by Ghosh at 0.8514 and 2.275, respectively (Ghosh and Biswas 2002). The recently determined atomic-orbital exponents for titanium and oxygen are 1.3710 and 1.9535, respectively (Hardcastle 2013). Substituting these values into Equation (2) yields a b parameter of 0.4327 Å, significantly different from the “universal” constant of 0.37 Å proposed by Brown and Altermatt (1987). Using the values of Clementi and Ghosh gives respective b parameters of 0.4193 Å and 0.4601 Å; it is interesting to note that our value of 0.4327 Å is the average of those calculated from the orbital exponents of Clementi and Ghosh.

Using our value of $b=0.4327$ Å, a best fit to the Ti-O crystallographic bond lengths from 32 different environments resulted in a Ti-O unit bond valence length of $R_o=1.787$ Å, which is slightly less than 1.815 Å proposed by Brese (Brese and O’Keefe 1991). The optimized valence for the titanium was 3.96, less than its full valence of 4.00. The difference of 0.04 valence units is consistent with about 1% of the valence electron density, on average, due to Ti bonding beyond the first coordination sphere (bonds greater than 3 Å). The resulting expression relating Ti-O bond valence s to bond length R is

$$s = \exp\left(\frac{1.787 - R}{0.4327}\right) \quad (3)$$

For the fully oxidized titanium cation, the oxidation state is 4, so Equation (3) may be used in conjunction with Pauling’s valence sum rule

$$\sum_j s_{ij} = 4.000 \quad (4)$$

because the sum of the Ti-O bond valences given by Equation (3) must equal the total valence of the titanium cation, Equation (4). The valence calculation results are tabulated in Table 1, which lists Ti-O bond lengths reported in the literature; Ti-O bond valences, calculated from Equation (3); and valence sums using Equation (4).

The bond valence – length relationship is expected to hold regardless of environment, physical state, or oxidation state. In addition to verifying the validity of

this approach for Ti-O bonds, our group has recently verified this approach for Si-O bonding in silicates (Laffoon 2013) using orbital exponents of 1.484 and 1.9535 for Si and O, respectively; the Si-O unit bond valence length of $R_o=1.605$ Å is less than 1.624 Å proposed by Brese (1991), but is identical to that found from structural studies of silicates (Laffoon et al. 2013). Furthermore, orbital exponents for carbon, nitrogen, phosphorus, chromium, molybdenum, tungsten and rhenium were also tested by combining data from metal-metal bonding, published bond lengths for diatomic gas phase molecules (Huber 1979), published b parameters, and best fits to crystallographic data (Hardcastle, unpublished results).

Conclusions

Bond length-bond valence empirical correlations have wide applicability in evaluation of molecular structures and checking crystal structures, and these relationships seem to be independent of chemical state or environment. Recently, Pauling’s bond length-valence relationship was derived, and the adjustable fitting parameter b was defined in terms of atomic-orbital exponents. In the present study, we verified this model for Ti-O bonds by converting crystallographic Ti-O bond lengths from 32 titanate environments to bond valences and using Pauling’s valence sum rule.

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Table 1. Selected crystallographic Ti-O bond lengths, bond valences, and valence sums for titanates.

Ti-O Valence			Ti-O Valence			Ti-O Valence			Ti-O Valence			Ti-O Valence		
Wang et al. 2010			Indrakanti et al. 2007			Veith et al. 1997			Braunbarth et al. 2000			Aguilo et al. 2003		
O1	1.832	0.901	O1	2.229	0.360	O1	2.129	0.454	O31	1.956	0.677	O1	2.123	0.460
O2	1.833	0.899	O2	1.834	0.897	O2	2.186	0.398	O32	1.956	0.677	O2	1.963	0.666
O3	1.809	0.950	O3	1.840	0.885	O3	2.019	0.585	O33	1.956	0.677	O5	2.083	0.505
O4	1.82	0.927	O4	2.080	0.508	O4	2.006	0.603	O34	1.956	0.677	O6	2.013	0.593
		3.677	O5	1.808	0.953	O5	1.784	1.007	O41	1.957	0.675	OT1	1.926	0.725
O1	1.841	0.883	O6	2.313	0.297	O6	1.775	1.028	O42	1.957	0.675	OT2	1.751	1.087
O2	1.801	0.968			3.899			4.074			4.057			4.035
O3	1.841	0.883	O1	2.095	0.491	O1	2.204	0.381	Guo et al. 2001			O1	2.15	0.43
O4	1.813	0.942	O2	1.852	0.861	O2	2.207	0.379	O1	1.831	0.903	O2	1.96	0.67
		3.675	O3	2.27	0.327	O3	2.057	0.536	O6	1.851	0.863	O5	2.15	0.43
O1	1.802	0.966	O4	2.256	0.338	O7	1.994	0.620	O2	1.985	0.633	O6	1.97	0.66
O2	1.852	0.861	O5	1.808	0.953	O8	1.769	1.042	O5	1.990	0.626	OT1	1.95	0.69
O3	1.795	0.982	O6	1.852	0.861	O9	1.743	1.107	O4	2.043	0.553	OT2	1.74	1.12
O3	1.852	0.861			3.830			4.065	O3	2.061	0.531			3.99
		3.669	O1	2.021	0.582	O1	2.088	0.499			4.108	Ma et al. 2011		
O1	1.833	0.899	O2	1.830	0.905	O2	2.155	0.427	Kuang et al. 2002			O1	1.954	0.680
O2	1.832	0.901	O3	2.335	0.282	O3	2.066	0.525	O3	1.923	0.730	O2	1.954	0.680
O3	1.820	0.927	O4	1.981	0.639	O4	1.981	0.639	O32	1.923	0.730	O3	1.954	0.680
O4	1.809	0.950	O5	2.006	0.603	O5	1.777	1.023	O33	1.923	0.730	O4	1.954	0.680
		3.677	O6	1.830	0.905	O6	1.790	0.993	O4	2.016	0.589	O5	1.997	0.615
O1	1.812	0.944			3.916			4.106	O42	2.016	0.589	O6	1.997	0.615
O2	1.812	0.944	O1	1.880	0.807	O1	2.155	0.427	O43	2.016	0.589			3.950
O3	1.815	0.937	O2	1.798	0.975	O2	2.098	0.487			3.958	Zhou and Gong 2008		
O4	1.815	0.937	O3	1.797	0.977	O3	2.087	0.500	Nyman et al. 2001			O1	2.025	0.577
		3.762	O4	2.064	0.527	O7	1.983	0.636	O1	1.99	0.63	O2	2.025	0.577
Thorogood et al. 2011			O5	2.040	0.557	O8	1.772	1.035	O10	1.96	0.67	O3	2.010	0.597
O1	1.913	0.747			3.843	O9	1.783	1.009	O12	1.91	0.75	O4	2.010	0.597
O1a	1.930	0.719	O1	2.248	0.345			4.095	O13	2.01	0.60	O5	1.602	1.534
O2	1.982	0.637	O2	1.810	0.948	O10	1.79	0.993	O14	1.89	0.79			3.882
O2a	1.995	0.618	O3	1.809	0.950	O11	1.793	0.986	O15	1.97	0.66	Nair et al. 2001		
O2'	2.110	0.474	O4	1.790	0.993	O5	1.937	0.707			4.09	O31	1.976	0.646
O4	1.864	0.837	O5	2.023	0.580	O7	2.057	0.536	O1	1.96	0.67	O32	1.976	0.646
		4.032			3.816	O2	2.154	0.428	O10	1.95	0.69	O33	1.976	0.646
O1	1.98	0.64	Nyman et al. 2000			O1	2.156	0.426	O12	1.91	0.75	O34	1.976	0.646
O2	1.98	0.64	O1	1.97	0.66			4.077	O13	2	0.61	O41	1.937	0.707
O3	1.98	0.64	O10	1.84	0.89	O9	1.786	1.002	O14	1.96	0.67	O42	1.937	0.707
O4	1.98	0.64	O12	1.92	0.75	O6	1.796	0.979	O15	1.96	0.67			3.998
O5	1.93	0.72	O13	2.02	0.58	O4	1.931	0.717			4.06	O31	1.982	0.637
O6	1.93	0.72	O14	1.95	0.69	O7	2.052	0.542				O32	1.982	0.637
		4.00	O15	2.08	0.51	O2	2.148	0.434				O33	1.982	0.637
					4.05	O1	2.169	0.414				O34	1.982	0.637
								4.088				O41	1.925	0.727
												O42	1.925	0.727
														4.003

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