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Molecular Prototypes for Simple SiO_2 Potentials

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A popular class of interionic pair potentials for simulation of the properties of condensed-phase SiO_2 uses two calibrations: first-principles electronic structure results for a small cluster and experimental crystalline data. The clusters are argued to be broadly valid prototypes for the local structural and bonding behavior of condensed-phase SiO_2. This approach introduces an issue: the extent to which there is prototypical computed behavior for small silicates irrespective of cluster size, symmetry constraints, methodological refinement, and accuracy of implementation (basis set). By extension, the issue of commonality vs diversity in small silicates arises. We address those issues by comparative study of 12 systems containing one or two Si atoms in combination with H, O, and bare protons. We use several different levels of theoretical refinement and various basis sets. Though some chemical trends are clear, there is no clear single prototype for condensed-phase SiO_2 (including no clear preference to tetrahedral symmetry). We find a wide diversity of bond lengths, bond angles, and interaction energies and significant methodological consequences that go largely ignored in the potential-fitting literature.

Overview

In the molecular dynamics (MD) simulation of condensed-phase properties, the most popular technique is to remove the explict quantum mechanical behavior of the electrons by use of an interionic potential.[1,2] The technologically and scientifically important case of SiO_2 is an example.[3] Among the several widely used parametrized interactions,[4,5] we focus on the so-called TTAM[6] and BKS[7,8] potentials. There are hundreds of citations to use of these potentials, a sign of the extent to which they are viewed in the materials simulation community as successful.[9] This success is intriguing for chemical physics because the BKS and TTAM parametrization schemes share an important assumption at the molecular level, namely, the critical role of properties of a small, terminated Si_mO_n cluster computed from quantum chemical methods.

The issues in potential parametrization are well-summarized by Brenner.[10] For the BKS and TTAM interactions, a pairwise functional form is stipulated. Of course, three-body interactions are known to be important,[5,11,12] but that is not the issue at hand. Rather, our focus is on the molecular inputs to a popular two-body form. The procedure used by both BKS and TTAM is to find parameter sets that fit the potential to Hartree−Fock results for the structure and energetics of a particular terminated Si_mO_n cluster. TTAM and BKS use different terminations of SiO_4. From among those parameter sets, the one that yields the best fit to a selected set of calculated crystalline properties is chosen. Details differ, but this is the essential scheme.

Implicit in this calibration procedure is the assumption that a single, well-chosen, small, terminated cluster is the prototype for the local structural and bonding behavior of condensed-phase SiO_2. The essential reasoning is that tetrahedral behavior dominates. Such reasoning raises questions as to the extent to which there is prototypical computed behavior for small silicates more or less irrespective of cluster size, symmetry constraints, methodological refinement, and accuracy of implementation (basis set). By extension, the issue of commonality vs diversity in small silicates arises.

Elsewhere, we will treat the role of first-principles crystalline calculations in lieu of parametrization to experimental crystalline data[13] and present the MD results for a sample system based on various parametrizations from purely computed inputs.[14] Here we focus exclusively on candidates for prototype molecules and clusters. We study the effects of cluster size, ionicity, termination, choice of approximation [restricted Hartree−Fock (RHF), second-order many-body perturbation theory (MBPT(2)), coupled cluster theory], basis set quality, and other technical choices. In the materials simulation community, the prevailing view seems to be that these technical aspects do not have major significance for the parametrized potential. We show otherwise in quite specific ways. The essential outcome is this: while there are undeniable (and unsurprising) chemical trends in families of clusters, the use of a low-level quantum mechanical treatment of a single small cluster in a small basis is not justifiable as a meaningful prototype.

Potential and Parameters

The published parameters have significant implications for the issue of molecular prototypes. The TTAM and BKS potentials have the same form. For ions i, j with relative displacement $\mathbf{r}_{ij}$ the pairwise potential (in eV) is

$$U_{ij} = \frac{\kappa Q_i Q_j}{r_{ij}} + \alpha_{ij} \exp[-\beta_{ij} r_{ij}] - \frac{\gamma_{ij}}{{r_{ij}}^6} \qquad (1)$$

Because of their forms, these are called Coulomb, Buckingham, and van der Waals terms, respectively. The notation differs deliberately from the original papers to provide a common basis for comparison. κ is the conversion from electrons^2 per Å to eV (≈14.402); hence, the Q_i are in units of electron charge magnitude.

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TABLE 1: Parameters for the TTAM and BKS Potentials for Silica[a]

	α_{ij}	β_{ij}	γ_{ij}
Si−Si TTAM	8.7235×10^8	15.2207	23.30
Si−Si BKS	0	0	0
Si−O TTAM	10721.5	4.7959	70.7343
Si−O BKS	18003.8	4.8738	133.538
O−O TTAM	1756.90	2.8464	214.736
O−O BKS	1388.773	2.760	175.00

[a] α_{ij} is in eV, β_{ij} in Å^{-1}, and γ_{ij} in eV Å^6.

Despite qualitatively different parametrization procedures, both TTAM and BKS arrived at $Q_{\mathrm{Si}} = 2.4$ and $Q_{\mathrm{O}} = -1.2$. (Shell models[15,16] are compelled by their properties to have $Q_{\mathrm{Si}} = 4.0$, which is physically and chemically implausible.) Unlike BKS, all the TTAM parameters are determined atom by atom, so that the TTAM interaction parametrization is additive:

$$\alpha_{ij} = (B_i + B_j)\exp\left[\frac{A_i + A_j}{B_i + B_j}\right]$$
$$\beta_{ij} = \frac{1}{B_i + B_j}$$
$$\gamma_{ij} = C_i C_j \qquad (2)$$

with A_i, B_i, and C_i the atomic parameters for atom i. Immediately, the TTAM Si−Si parameters for the Buckingham and van der Waals terms are nonzero, while in BKS they vanish by design.

Table 1 gives the parameters corresponding to published values for the two potentials. Leaving aside the built-in difference in Si−Si interactions, the Si−O and O−O interactions differ oddly. While the fitted charges Q_{Si} and Q_{O} are identical for the two potentials, the BKS Si−O Buckingham prefactor is 68% larger than the TTAM value, yet the BKS O−O prefactor is smaller than TTAM by 21%. The Si−O van der Waals parameters differ by almost a factor of 2. Taken together, one sees that the two potentials would describe the *same* molecule rather differently.

For clusters of SiO_2 interacting in a simulation, clearly the two potentials are quite close for large intercluster separation. At small Si−Si separations matters are different. The TTAM Si−Si interaction is more repulsive by about 190 eV at 1 Å but *less* repulsive, by about 0.35 eV, at 2 Å. (The artifactual hole at the origin can be ignored; usually it is suppressed in MD without loss of realism by such techniques as adding a highly repulsive, extremely short-ranged interaction such as r^{-24}.)

Appraisal of the BKS Approach

BKS used a hydrogen-terminated cluster: H_4SiO_4. This termination gives a structure that differs dramatically from the TTAM cluster; compare with the next section. Because of the attraction to a neighbor oxygen, BKS found that their cluster had an Si−O−H bond angle of 119.92° in a quasi-cyclic geometry (see Figure 1 in ref 8). In addition, though they allowed D_{2d} distortions (oxygens bent toward one another pairwise), BKS nonetheless arrived at an equilibrium cluster with a tetrahedral core: $\angle$O−Si−O = 109.47°. Both results contradict the findings of a much earlier study of H_4SiO_4 aimed at understanding silica and silicates.[17] That work, at roughly the same level of theoretical refinement except for a lower quality basis set, gave a nontetrahedral SiO_4 core, a bond length 0.025 Å longer than BKS found, and $\angle$Si−O−H = 108.8°. Also note that though BKS designate the tetrahedral O−Si−O configuration as the "optimized geometry" (ref 8, p 5069, Table 1), they also make a somewhat cryptic remark slightly before introducing that table: "We use the optimized geometries of the TO_4 clusters as starting point of the deformations." In this case "T" is Si. But that would not give SiO_4 but SiO_4^{4-}, which is nowhere mentioned in ref 8. A page later those authors also remark that the O−O potential function they were parametrizing "...enforces a tetrahedral arrangement of the oxygen atoms around the central silicon atom." It will be recognized immediately that tetrahedral symmetry for the SiO_4 core is crucial for parametrizing a pairwise potential: if the SiO_4 core is not tetrahedral, then there are two simultaneous optimum O−O distances to be fit by a potential that has only one minimum.

Our sense of the prevailing view in the MD community is that computational methods used on the parametrizing clusters is believed to have relatively little impact on the eventual MD results. This idea may have been reinforced by the methodological comparison in the second BKS paper.[8] Though BKS studied methodological impacts by comparing Xα (an older, very simple one-parameter DFT approximation), MBPT(2), and RHF, their limited comment downplayed the quite visible differences they found. See their Figure 3 and related discussion. A difficulty they apparently did not notice is that their heteronuclear cluster will not separate properly to its consituent atoms in either RHF or any local or gradient-corrected approximate DFT (including Xα). This flaw is significant for fitting of the $1/r^6$ term in the potential.

Moreover, well before the BKS papers, there was published evidence that procedure does matter.[17−19] The methods used in those papers were similar to BKS (except that the earlier work did not use a pseudopotential). The earlier papers reported equilibrium cluster conformations and dimensions that differed substantially from the BKS results. Though cited in BKS, the disparities apparently went undiscussed until now. Note also that the latter Lasaga and Gibbs paper argues that treatment of electron correlation (i.e., approximations more refined than RHF) is not needed. We find otherwise.

We investigated the impact of (a) degree of inclusion of electron correlation and (b) basis set size upon the optimized geometry and lowest vibrational frequencies for the BKS cluster, H_4SiO_4. The study involved three levels of refinement, RHF (as used by both BKS and TTAM), MBPT(2), which includes some electron correlation, and coupled-cluster single and double excitations plus noniterative (perturbative) triple excitations [CCSD(T)], the most thoroughly correlated calculations. CCSD(T) is essentially the state of the art for accurate computational quantum chemistry today.[20] In all of the correlated calculations the core orbitals were frozen.

BKS[8] used a 6-31G* basis[21] with the core pseudopotential of Barthelat et al.[22] The smallest basis set we used is the 6-31G* set used by BKS. An important distinction is that we did all-electron calculations throughout (no pseudopotentials). We also used two larger basis sets, 6-311G**[23] and, for the coupled cluster calculations, aug-cc-pVDZ.[24] For all these calculations we used the ACES-II code.[25] Table 2 shows H_4SiO_4 equilibrium geometric parameters from the various calculations as compared to the BKS values. We constrained the molecule to have D_{2d} symmetry rather than the T_d symmetry that emerged from the BKS methodology. The equilibrium Si−O bond length ranges over 1.622−1.675 Å as the basis sets and methods are changed, quite a substantial deviation for parametrization of a potential. In particular, for the highest level of theoretical refinement and largest basis set, CCSD(T)/cc-aug-pVDZ, we find a bond length of 1.675 Å compared to their 1.625 Å. The O−Si−O bond

TABLE 2: Dependence of Equilibrium H_4SiO_4 Geometries upon Method and Basis Choice[a]

method/basis	Si−O	O−H	O−Si−O	H−O−Si
RHF/6-31G*	1.631	0.947	103.3 112.6	117.2
RHF/6-311G**	1.622	0.937	103.4 112.6	121.6
MBPT(2)/6-31G*	1.654	0.970	101.8 113.5	114.5
MBPT(2)/6-311G**	1.640	0.956	101.9 112.6	118.8
CCSD(T)/aug-cc-pVDZ	1.675	0.966	100.3 114.2	114.0
BKS	1.625	0.949	109.47	119.92

[a] Bond lengths in Å, angles in deg; D_{2d} symmetry. For comparison, the BKS published values[8] are given.

TABLE 3: Dependence upon Method and Basis Set Choice of Calculated Low-Lying Vibrational Frequencies (cm^{-1}) for D_{2d} Symmetry H_4SiO_4

method/basis	ν_1	ν_2	ν_3
RHF/6-31G*	197	291	315
RHF/6-311G**	241	310	380
MBPT(2)/6-31G*	181	277	316
MBPT(2)/6-311G**	198	291	327
CCSD(T)/aug-cc-pVDZ	163	266	318

angles range over roughly 100°−120°, also a substantial deviation from the tetrahedral value determined by BKS.

A possible reason for the discrepancy in H_4SiO_4 equilibrium geometries is that BKS used a pseudopotential. This speculation is consistent with the discrepancy between their results and an earlier all-electron RHF/STO-3G calculation.[17] We did not pursue the matter except to do an all-electron calculation at about the same level of approximation as BKS, RHF with a 6-31G* basis set. The result is $\angle$O−Si−O = 103.3°, still substantially away from the BKS value but closer to the RHF/STO-3G 107.1°.[17] Again, for the highest quality approximation and largest basis set, we get 100.3° (the smaller angle) and cannot find a way, except for outright constraint, to get 109.47°. The shift from equilibrium to tetrahedral O−Si−O bond angle introduces a spurious strain energy of 2.9 eV. Such a large shift obviously is a substantive issue for parametrization of any potential.

Another measure of the appropriateness of a given potential is to examine the restoring forces for small deviations from equilibrium. We use the first few vibrational frequencies of the molecule to assess this fundamental effect. Table 3 shows the dependence of those frequencies upon changes in basis sets and methods. Again, there is substantial variation with respect to basis set and method, a factor of 1.48. This factor corresponds to reference force constants differing by more than a factor of 2, a variation that would be reflected in the resulting BKS-like parametrization. Note that these variations from what BKS found are irrespective of the additional dependence upon choice of a pseudopotential, something neither we nor they tested. Also, note that we find generally lower frequencies than the RHF/STO-3G value[17] for this cluster.

TABLE 4: RHF Mulliken and Natural Bond Orbital Populations for the BKS Cluster H_4SiO_4 Calculated at the Equilibrium Geometry from RHF/6-31G* Geometry in C_1 Symmetry (R(Si−O) = 1.629 Å)

basis	Si (NBO)	Si (Mulliken)	O (NBO)	O (Mulliken)
6-31G*	2.600 65	1.487 98	−1.170 43	−0.848 04
6-311G**	2.519 63	1.607 99	−1.127 09	−0.709 11
aug-cc-pVDZ	2.673 67	3.106 65	−1.188 34	−0.914 38

The fact that no combination of level of theoretical refinement and basis set gives a tetrahedral geometry led us to consider a “tetrahedrally constrained” BKS cluster. “Tetrahedrally constrained” is shorthand for two constraints: (i) the SiO_4 core is required to have $\angle$O−Si−O = 109.47°; (ii) the terminating Hs are required to lie in the quasi-cyclic pattern used by BKS. The Si−O−H angle was not constrained to the BKS value ($\angle$Si−O−H = 119.92°) but optimized. The result is 113.5°. Under these conditions, we still find a significant difference between the small basis RHF results of BKS and the present large basis, highly correlated calculations [CCSD(T)]. The main point is that the BKS value of the Si−O bond length is substantially too short: 1.63 Å vs 1.6806 Å for the tetrahedrally constrained system (and almost as short with respect to 1.6753 Å for the unconstrained case).

Appraisal of the TTAM Approach

TTAM used a $SiO_4^{4-} + 4e^+$ cluster (an SiO_4^{4-} neutralized by four point positive charges, each a distance 1.65 Å radially outside the corresponding oxygen). No basis functions were centered on the point charges. TTAM attempted to motivate the choice as having a geometry common to both silica and its melt. The bare charges pose a technical problem for the most refined approximation, CCSD(T). We did treat the T_d deformation (uniform expansion or contraction of the Si−O bond length) near the equilibrium structure for the TTAM cluster and their basis set within the RHF and MBPT(2) approximations using the Q-Chem code.[26] The MBPT(2) value for the equilibrium Si−O bond length is 1.64 Å. TTAM do not quote their result for the equilibrium Si−O bond length, but it appears to be about 1.63 Å. Just as with BKS, the differences between the TTAM values and the present ones occur mostly for two reasons: our use of more refined methods and our allowing for full geometry optimization.

Turning to basis sets, TTAM[6] used a Si (12s8p2d)/[5s3p2d] basis and a (9s6p)/[3s,3p] basis for O.[27] Using their basis set (in the Q-Chem code[26]), we obtain a frequency of 2565 and 2608 cm^{-1} for the frequency of tetrahedral deformation mode from RHF and MBPT(2) calculations, respectively. With the somewhat larger 6-311G** basis set, these shift to 2789 and 2762 cm^{-1}, respectively. Again it is apparent that changes in the vibrational frequency of this magnitude would correspond to considerable variation in the parametrization.

Determination of Effective Ionic Charge

Regarding effective charges, BKS rationalized $Q_{Si} = 2.4$ from the fact that a fit of the potential to their cluster results alone gives a value of 2.2 “in reasonable agreement with the Mulliken value” (they found 1.8). TTAM also appealed to Mulliken populations in their determination of Q_{Si}. There are two problems with this rationalization. Mulliken population analyses are notoriously sensitive to basis set effects (noted by TTAM as one reason for choosing a non-Mulliken value of Q_{Si}). Second, different clusters have different populations. The latter issue is so obvious that we have not bothered to study it.

To test for basis set effects on calculated charges, we adopted the equilibrium geometry for the BKS and TTAM clusters as determined by the richer basis RHF calculations. We then did RHF calculations for all three basis sets and used the results as input to both Mulliken and natural bond orbital[28] (NBO) population analyses. The NBO procedure is that implemented in Q-Chem.[26] Tables 4 and 5 show the results for the BKS and TTAM clusters, respectively. The aforementioned sensitivity of Mulliken populations to basis set selection is confirmed. By

TABLE 5: RHF Mulliken and Natural Bond Orbital Populations for the TTAM Cluster $SiO_4^{4-} + 4e^+$ at the 6-31G* Geometry

basis	Si (NBO)	Si (Mulliken)	O (NBO)	O (Mulliken)
6-31G*	2.601 2	1.650 70	−1.650 3	−1.412 67
6-311G**	2.555 28	2.013 68	−1.638 82	−1.503 42
aug-cc-pVDZ	2.742 87	2.718 38	−1.685 72	−1.679 60

TABLE 6: Mulliken Population as a Function of Si−O Distance for the TTAM Cluster $SiO_4^{4-} + 4e^+$

method	1.58 Å	1.60 Å	1.62 Å	1.64 Å	1.66 Å	1.68 Å	1.70 Å
RHF/Q_{Si}	2.24	2.27	2.29	2.31	2.33	2.35	2.36
RHF/Q_O	−1.56	−1.57	−1.57	−1.58	−1.58	−1.59	−1.59
MBPT(2)/Q_{Si}	2.24	2.27	2.29	2.31	2.33	2.35	2.36
MBPT(2)/Q_O	−1.56	−1.57	−1.57	−1.58	−1.58	−1.59	−1.59

TABLE 7: Calculated Bond Lengths (Å) and Angles (deg) for Various Si_mO_n and $H_qSi_mO_n$ Clusters[a]

cluster	Si−O	Si−Si	O−O	O−Si−O	Si−O−Si
SiO	1.563				
SiO_2	1.557				
Si_2O_2 (D_{2h})	1.748	2.534	2.408	87.1	92.9
Si_2O_4 (D_{2h})	1.716	2.442	2.410	89.2	136.8
Si_3O_3 (D_{3h})	1.721	3.200	2.697	103.2	
H_3SiOH	1.707				
H_2SiO	1.570				
$OSi(OH)_2$	1.659				
$H_4Si_2O_6$	1.714			89.0	91.0
$H_6Si_2O_7$ (C_{2v})	1.651			111.5	138.8
	1.678				
H_4SiO_4	1.675			100.3	
$SiO_4^{4-} + 4e^+$	1.640			109.47	

[a] CCSD(T) results with the aug-cc-pVDZ basis except for $SiO_4^{4-} + 4e^+$ which is from MBPT(2)/6-311G** and $H_6Si_2O_7$ which is from CCSD(T)/cc-pVDZ. Some symmetries are shown. For $H_6Si_2O_7$, the first Si−O distance is for terminal Os and the second is for the bridge. For details, see text.

TABLE 8: Calculated Lowest Three Vibrational Frequencies (cm^{-1}) for Various Si_mO_n and $H_qSi_mO_n$ Clusters[a]

cluster	ν_1	ν_2	ν_3
SiO	1140		
SiO_2	274	1337	
Si_2O_2 (D_{2h})	130	554	644
Si_2O_2 (C_1)	204	528	534
Si_2O_4 (D_{2h})	116	227	291
Si_3O_3 (D_{3h})	73	73	186
H_3SiOH	198	683	715
$H_6Si_2O_7$ (C_{2v})	46	66	213
$H_6Si_2O_7$ (C_s)	46	66	213
H_2SiO	671	673	978
$OSi(OH)_2$	300	315	362
H_4SiO_4 (C_1)	163	266	318

[a] Symmetries shown explicitly where relevant. All CCSD(T) with aug-cc-pVDZ basis except $SiO_4^{4-} + 4e^+$ and $H_6Si_2O_7$; see Table 7. See text also.

comparison, the NBO approach gives a value that is stable within about 4% for Q_{Si}. It is notable that the small basis sets used by both TTAM and BKS do not characterize Q_{Si} and Q_O adequately.

We also investigated the TTAM cluster $SiO_4 + 4e^+$ and its T_d deformations at the SCF and MBPT(2) levels of method refinement with the basis set used by TTAM. Table 6 displays the change in the Mulliken population as a function of the Si−O distance. Note that, even for the rather small range of Si−O distances explored, 0.12 Å, the Si population varies by 0.12 electron, yet the Q_{Si} value used by TTAM does not occur in that range.

Effects of Cluster Selection

With methodological effects clarified, we explored cluster selection effects by studying a set of small Si_mO_n and $H_qSi_mO_n$ clusters. These were picked on the basis of chemical plausibility for relevance to the local environment in silica, either ordered or disordered. The central outcome is that, treated at the highest level of refinement [CCSD(T) with a large basis set (aug-cc-pVDZ)], a moderately sized suite of physically plausible small clusters gives a significant range of Si−O, Si−Si, and O−O equilibrium bond lengths, bond angles, and low-lying vibrational frequencies.

Table 7 shows the calculated equilbrium Si−O bond lengths and O−Si−O bond angles. All are from CCSD(T) calculations except for the TTAM cluster, discussed already, and $H_6Si_2O_7$, discussed below. We find bond lengths from 1.563 to 1.748 Å. Calculated O−Si−O bond angles range over 87.1°−103.2° for the optimized geometries. This variation illustrates clearly the arbitrariness in determining even a large range of fitted parameters from only one cluster.

As noted already, a crucial part of the energy surface for potential fitting obviously is the neighborhood of the minimum. That region is characterized by the lowest few harmonic vibrational frequencies for each cluster. Table 8 shows that these also vary widely between clusters. The lowest vibrational frequencies go from 73 to 1140 cm^{-1} with several in the 70−300 cm^{-1} range. Even that more restricted range corresponds to an order-of-magnitude difference in harmonic restoring forces, that is, qualitatively different behavior around the bottom of the potential well.

One subtlety in these results is the equilibrium structure of $H_6Si_2O_7$, namely the central Si−O−Si angle. As far back as Newton and Gibbs,[29] it had been recognized that the energy barrier of the linear structure relative to bent (in the vicinity of 145°) is quite small, about 0.05 eV/atom or 1.25 kcal/mol. Figure 2 of Ross and Meagher[30] or Figure 2b of Watanabe et al.[11] gives nice plots of the situation. The Si−O bond stretch has a comparatively deep well, a good feature for parametrization. Because the early results all were from small basis set RHF calculations, while the Watanabe et al. data were from MBPT(2), we restudied the system with high-level correlated calculations. We find that the difference between linear (C_s) and bent (C_{2v}) configurations is of the reported size.

Specifically, CCSD(T) calculations with the cc-pVDZ data set (the most accurate calculations affordable) yield an optimized configuration that is bent (Si−O−Si angle 138.8°, Si−O distance of 1.6506 Å) and lies 1.7 kcal/mol (0.074 eV/particle) below the linear configuration. This is slightly more advantageous energetically than the CCSD/cc-pVDZ result (1.4 kcal/mol = 0.061 eV/particle below, 140.8° angle, 1.647 Å Si−O distance) and indistinguishable from the MBPT(2) results in the same basis (1.7 kcal/mol = 0.074 eV/particle below, 138.6°, 1.6508 Å). Moreover, we also find that either the bent or linear configurations can be made to be favored energetically by using less extensive basis sets and/or less-refined approximations. An illustration of how low the barrier is between bent and linear is provided by the lowest three vibrational frequencies: they are the same. When it comes to parametrization of a potential therefore, we are free to parametrize to the Si−O stretch in the linear configuration. The same choice, for the same reasons, was made by both Wong-Ng et al.[31] and Lindsay et al.[32] However, we note that they reported much larger bent vs linear energy differences, about 4 kcal/mol (0.17 eV/particle).

Discussion

The Si−O bond in the TTAM cluster plays an unusual and subtle role in the TTAM parametrization. In particular, it is involved with the determination of reasonable $\gamma_{\mathrm{Si-Si}}$ and $\gamma_{\mathrm{O-O}}$ values. In the BKS parametrization $\gamma_{\mathrm{Si-Si}} = 0$, and $\gamma_{\mathrm{O-O}}$ was obtained from the crystalline part of their fitting procedure ($\gamma_{\mathrm{O-O}}$ was set to zero in their cluster fitting). However, for the TTAM parametrization $\gamma_{\mathrm{Si-Si}} \neq 0$, even though it comes in part from a cluster with only one Si. This happens because in TTAM $\gamma_{ij} = C_iC_j$; recall eq 2. The initial range of C_{Si} comes from the cluster Si−O interaction, while the final value is pinned down from the crystal. But the RHF separated atom limit for a heteronuclear bond is well-known to be wrong because of spurious ionicity. Therefore, the crystalline calibration of C_{Si} is forced to choose among values all of which represent spurious behavior. A related problem (spurious ionicity from a common Fermi level) causes DFT calculations to be too attractive at large bond lengths. This behavior helps explain why BKS found (see their Figure 3) the HF and Xα Si−O separation energetics to be close, which apparently helped convince them, incorrectly, of the unimportance of method.

The variation of calculated Q_{Si} and vibrational frequencies ν_i with cluster constitution, method, and basis set is so large that there seems no obvious way to fit the BKS−TTAM potential form to all the systems. The difficulty in fact was foretold in Table 1. TTAM and BKS get the same Q_{Si} (hence also Q_{O}), yet their other parameter values differ markedly despite their being only two clusters involved. Even the procedure of choosing Q_{Si} and then requiring $Q_{\mathrm{O}} = -Q_{\mathrm{Si}}/2$ is arbitrary, since starting with the cluster oxygen population and requiring $Q_{\mathrm{Si}} = -2Q_{\mathrm{O}}$ would lead to a different set of values for the *same* cluster calculation. For example, from Table 4 for the BKS cluster, $Q_{\mathrm{Si}} = 2.67$ directly, while evaluation as $Q_{\mathrm{Si}} = -2Q_{\mathrm{O}}$ gives 2.38.

The spread in the results also undercuts rather severely the claim by TTAM that the use of a single cluster plus the experimental configuration of the zero-pressure crystal constitutes an “ab initio” procedure. More generally, there is no evidence from this study that a single cluster can be considered a prototype. Without regard to details of local behavior in condensed-phase SiO$_2$, a prototype cluster for potential fitting at least ought to have computed properties that are robust with respect to methodological changes and basis set choices. This study shows that not even that minimalist requirement is met by the clusters that are chemically obvious candidates for the role of prototype. A more rational procedure might be to use a family of clusters, all calculated at a high level of theoretical refinement. However, this approach would introduce the question of relative weighting of the clusters, not a matter for discussion here.

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