Structures and Energies of SiO$_2$ Clusters

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We have employed extensive configurational searches for numerical characterization of neutral (SiO$_2$)$_n$ clusters in their mechanically stable forms, i.e., at local potential energy minima. These calculations have used additive pair interactions derived by Tsuneyuki et al., supplemented with small-distance configurational constraints. A nearly complete catalog of structures and energies has been obtained for 1 ≤ $n$ ≤ 4, and we also report the most stable clusters found for 5 ≤ $n$ ≤ 8, as well as $n = 18$. Also a few key sequences of metastable oligomers have been examined. Although the results illustrate the basic tendency toward tetrahedral coordination of silicons by oxygens, none of the stable clusters structurally resemble any of the known crystalline SiO$_2$ polymorphs. The $n = 18$ results suggest that the surfaces of extended crystalline or glassy SiO$_2$ phases may exhibit anomalously coordinated silicons with formal valences +3 and +5.

I. Introduction

Silicon dioxide (principally as quartz) and the related silicate minerals serve as major constituents of our planet.† Furthermore, glasses based on silica have played a prominent role virtually throughout all of recorded history in the rise of commerce, technology, and science.‡ One of the most recent, and technologically demanding, requirements on silica glasses arises from optical fiber communications.

But, despite these important connections, the molecular-level understanding of SiO$_2$ and its fundamental interactions remains rudimentary. On the experimental side this can be attributed to the extremely low volatility of the condensed phases of SiO$_2$ and to the apparent high reactivity of molecular SiO$_2$ and its clusters, particularly with water. As a consequence, rather little theoretical effort thus far has been devoted to the study of the isolated SiO$_2$ molecule and its small gas-phase oligomers, although the present status of computational quantum mechanics makes such investigations quite feasible. An exception to which we allude below is a high-accuracy ab initio survey by Raghavachari.

The present investigation was undertaken to generate a theoretical database of information about gas-phase (SiO$_2$)$_n$ species at a well-defined level of approximation. Specifically we have employed the additive pair interactions that were created by Tsuneyuki et al. (TTAM) to simulate bulk condensed-phase SiO$_2$ phenomena,§ as explained below, it is necessary to append a set of small-distance constraints to these functions to avoid unphysical divergences.

Our motivations for concentrating on the TTAM approximation to the (SiO$_2$)$_n$ potential surfaces include the following:

(a) It has been widely used, and is moderately successful, in simulational studies of crystalline and amorphous condensed phases of silica.¶

(b) It is conceptually simple and computationally straightforward to use.

(c) The existence of a concrete set of results, even for a simple and approximate theoretical model, should have a beneficial stimulating effect, both on experiment and on high-accuracy quantum calculations.

(d) It is important to observe whether structural motifs familiar from the known crystalline SiO$_2$ polymorphs spontaneously appear in the small clusters, and if not, why not.

(e) The cluster geometries may suggest useful new ways to interpret studies of liquid and amorphous glassy SiO$_2$, especially in connection with the “inherent structure” formalism.¶¶

(f) The results for the specific TTAM pairwise additive model considered can be a base from which an improved approximation to the Born–Oppenheimer ground-electronic-state potential surface could be developed, perhaps incorporating explicit three-body interactions or many-body polarization effects.

The following section II recalls and discusses the TTAM pair potential approximation. Section III introduces our procedures for locating potential energy minima and presents our results for the smaller oligomers (SiO$_2$)$_n$, 1 ≤ $n$ ≤ 4, which may include all possibilities in this size range. Section IV presents our results for the larger clusters 5 ≤ $n$ ≤ 8; although it has been infeasible to catalog all clusters in this range, we believe we have identified the most stable clusters (for the model). Section IV also discusses some results for linear and cyclic oligomer sequences. Motivated by a desire to understand how known crystal structures might arise as $n$ increases, we have also devoted effort to the $n = 18$ case, with results reported in section V. The paper concludes, in section VI, with some further discussion of our findings for the TTAM model and their implications.

II. Pair Potential Approximation

Given a collection of $N$ atoms (or ions) located respectively at positions $r_1$...$r_N$, the Born–Oppenheimer ground-state potential energy surface will be denoted by $\Phi(r_1...r_N)$. This function must satisfy the following conditions:

(1) In the absence of external interactions (e.g., wall forces and gravity) it must exhibit translational and rotational invariance.
The present application has \( N = 3n \), and comprises \( n \) Si particles and \( 2n \) O particles, i.e., the equivalent of \( n \) SiO\(_2\) molecules. For simplicity in the following, we impose the convention that \( r_1 \ldots r_n \) are Si atom (ion) positions and \( r_{n+1} \ldots r_{3n} \) are O atom (ion) positions. The TTAM model\(^5\)\(^6\) approximates \( \Phi \) by a sum of central pair interactions \( \phi_{\text{cpl}} \) for each of the \( 3n(3n - 1)/2 \) pairs of particles present:

\[
\Phi = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \phi_{\text{SiSi}}(r_{ij}) + \sum_{i=1}^{n} \sum_{j=n+1}^{3n} \phi_{\text{SiO}}(r_{ij}) + \sum_{i=n+1}^{3n} \sum_{j=i+1}^{3n} \phi_{\text{OO}}(r_{ij})
\]  

This format automatically satisfies conditions 1 and 2 above.

The TTAM model composes each of the three pair potentials \( \phi_{\text{cpl}}(r) \) out of three kinds of terms, a long-range Coulomb interaction, an \( r^{-6} \) attractive dispersion interaction, and a short-range exponential repulsion. When they are expressed in terms of angstroms and of kilocalories per mole as the length and energy units, respectively, the pair potentials adopt the specific forms\(^5\)\(^6\):

\[
\phi_{\text{SiSi}}(r) = 1913.2812r^{-6} - 537.3214\ln r + 0.06570 \exp[(1.7376 - r)/0.06570] \quad (2.2)
\]

\[
\phi_{\text{SiO}}(r) = -956.6406r^{-6} + 1631.1766\ln r + 0.20851 \exp[(2.9162 - r)/0.20851] \quad (2.3)
\]

\[
\phi_{\text{OO}}(r) = 478.3203r^{-6} - 4951.9369\ln r + 0.35132 \exp[(4.0948 - r)/0.35132] \quad (2.4)
\]

The Coulombic contributions appearing here correspond to fractionally charged particles, 2.4e on Si and \(-1.2e\) on O. Choices 2.2–2.4 cause condition 3 above to be satisfied.

Although the TTAM version of \( \Phi \) vanishes when all \( 3n \) particles are widely separated, this dispersed state has no physical significance on account of the partial charges. However this is a benign artifact that plays no role in the present or previous applications of the TTAM model. Our study focuses on changes in \( \Phi \) associated with changing aggregation patterns of substantially intact SiO\(_2\) units.

Owing to the presence of attractive dispersion contributions \((\propto r^{-6})\), each of the \( \phi_{\text{cpl}} \) diverges strongly to minus infinity as \( r \to 0 \). Consequently condition 4 above on \( \Phi \) is formally violated. However, these violations occur in an unphysical regime and can simply be declared to fall outside the domain of applicability of the TTAM model. We observe that the \( \phi_{\text{cpl}} \) each exhibit unphysical maxima, respectively, at distances (Å)

\[
R_{\text{SiSi}} = 0.0877 \\
R_{\text{SiO}} = 1.0613 \\
R_{\text{OO}} = 1.4760
\]  

We have demanded in our calculations, and have always verified, that no particle pair distance ever falls below its corresponding \( R_{\text{cpl}} \). This amounts to appending physically sensible strong repulsive short-range forces to the TTAM functions \( \phi_{\text{cpl}} \). With this supplementary constraint, condition 4 above is obeyed.

**III. Small Clusters \((n \leq 4)\)**

For each value of the oligomerization degree \( n \), mechanically stable cluster structures and their energies have been extracted from computer searches of the respective potential energy surfaces. Three kinds of minimization routines have been employed: an iterative sequential optimization that proceeds one Cartesian coordinate at a time, a steepest descent optimization, and a variant of the conjugate-gradient method (MINOP). Initial conditions for the configurational searches included both random positions (subject to distance cutoffs (2.5)), as well as those based on known silica structural principles. Completeness, accuracy, and local stability of results were assured by producing cluster structures several times (in most cases) with the different optimization routines and with a variety of initial conditions.

The SiO\(_2\) monomer in the TTAM model has a symmetric linear form \((D_{\infty h})\), analogous to the CO\(_2\) molecule\(^2\)\(^3\). The Si–O bonds, 180° apart, have length 1.4644 Å. The energy of this triatomic species is found to be

\[
\Phi[\text{SiO}_2] = -1031.567 \text{ kcal/mol} \quad (3.1)
\]

(compared to three widely separated, fractionally charged, TTAM particles).

Unfortunately, direct experimental information on the structure of the isolated SiO\(_2\) molecule does not seem to exist. However there is little reason to doubt the symmetric linear form assigned by the TTAM model. In fact, \textit{ab initio} quantum mechanical calculations support this presumption; Raghavachari\(^4\), for example, finds the \( D_{\infty h} \) structure with bond length 1.48 Å (Hartree–Fock level) or 1.53 Å (Møller–Plesset second-order level).

The TTAM model produces a doubly bridged stable dimer structure. It has \( D_{2h} \) symmetry. Two of the four oxygens in this \((\text{SiO}_2)_2\) cluster form a symmetric double bridge between the silicons, while the other two are external to that rhombus. The dimer energy value is computed to be

\[
\Phi[\text{(SiO}_2)_2] = -2186.497 \text{ kcal/mol} \quad (3.2)
\]

so that comparison with monomer result 3.1 reveals the binding energy of two SiO\(_2\) units to be \(-123.362 \text{ kcal/mol}\). This binding energy may be compared with the value \(-99 \text{ kcal/mol} \) indicated by \textit{ab initio} quantum mechanics at the second-order Møller–Plesset level\(^4\). We stress that these energies strictly refer to static, mechanically stable cluster structures; no account has been taken of nuclear zero-point vibrational motion.

**Figure 1.** Structure of the stable silica dimer in the TTAM model. Bond lengths are in angstroms.
been experimentally characterized itself, the double oxygen bridge between silicons has a precedent. This arrangement has been synthesized in a compound which replaces the two pendant oxygens of \((\text{SiO}_2)_2\) with four mesityl groups.\(^{24}\)

Two distinct structures emerge from our silica trimer calculations. They are both shown in Figure 2. One has a planar ring structure (symmetry \(D_{3h}\)); the other has a pair of double oxygen bridges in perpendicular planes (symmetry \(D_{2d}\)). The former can be viewed as the result of \(\text{SiO}_2\) insertion into the 4-ring of the dimer to form a 6-ring; the latter can be viewed as a repetition of the dimerization process to produce a central silicon with distorted tetrahedral coordination.

The respective energies found for the two \((\text{SiO}_2)_3\) structures are

\[
\Phi[n=3,D_{3h}] = -3357.499 \text{ kcal/mol} \\
\Phi[n=3,D_{2d}] = -3347.602 \text{ kcal/mol} \tag{3.3}
\]

The corresponding binding energies for three isolated \(\text{SiO}_2\) molecules into these trimer structures are

\[
\Delta \Phi[n=3,D_{3h}] = -262.798 \text{ kcal/mol} \\
\Delta \Phi[n=3,D_{2d}] = -252.900 \text{ kcal/mol} \tag{3.4}
\]

Both of the trimeric species are found in the \textit{ab initio} quantum mechanical study, but the order of stability is reversed at the second-order Møller–Plesset level of approximation;\(^{4}\) the predicted binding energies to compare with results 3.4 are \(-189\) kcal/mol for \(D_{3h}\) and \(-212\) kcal/mol for \(D_{2d}\). That the TTAM model apparently overestimates small cluster binding energies and misassigns relative stabilities may not be surprising, since it was created to describe extended condensed phases. We might reasonably expect the TTAM model to perform better in these respects for larger \(n\), the degree of oligomerization.

The geometry of the planar 6-ring shown in Figure 2 for the \(D_{3h}\) trimeric cluster compares reasonably well with that found experimentally for its chemical relative hexamethylcyclotrisiloxane.\(^{25}\) Bond lengths around the ring in this analogue are 1.66(0.04) Å, and the bond angles are 125(5)° for SiOSi and 115(5)° for OSiO.

We have found five distinct tetramers. Two of these possess symmetry \(D_{2h}\) and are illustrated in Figure 3. Two others of roughly comparable stability have symmetries \(D_{4h}\) and \(C_{2v}\), and appear in Figure 4. The last has symmetry \(T_d\) and is by far the least stable of the five; it is shown in Figure 5. The binding energies (relative to four isolated monomers), in increasing order of stability, are found to be

\[
\Delta \Phi(n=4,T_d) = -317.178 \text{ kcal/mol} \\
\Delta \Phi(n=4,D_{2h},\text{bridged cyclic}) = -376.943 \text{ kcal/mol} \\
\Delta \Phi(n=4,D_{2h},\text{linear}) = -382.007 \text{ kcal/mol} \\
\Delta \Phi(n=4,D_{4h}) = -386.096 \text{ kcal/mol} \\
\Delta \Phi(n=4,C_{2v}) = -393.395 \text{ kcal/mol} \tag{3.5}
\]

No \textit{ab initio} quantum mechanical results are available for comparison.

If we leave aside the anomalously high-energy tetramer in Figure 5, all of the other clusters for \(2 \leq n \leq 4\) exhibit structural
characteristics that are useful for anticipating cluster forms for larger \( n \). Although all of the “bonds” shown in Figure 1–4 are indicated by single lines, they can each be chemically classified as single or double bonds: all Si–O bonds to pendant external oxygens are double, while all those within rings are single. With this classification each Si formally has chemical valence +4, and each oxygen, −2. Lengths of double bonds all fall close to 1.49 Å, while single bonds are all approximately 1.64 Å.

IV. Larger Cluster (\( 5 \leq n \leq 8 \))

Although one can confidently expect to discover and analyze all mechanically stable TTAM clusters for small \( n \), this clearly becomes an impractical and physically pointless task for large \( n \). The results presented in the preceding section II for \( n < 5 \) already hint at the proliferation of possible cluster structures as \( n \) increases, and general arguments suggest that in unbounded space the number of distinguishable cluster structures should asymptotically grow with \( n \) as \( \exp(\text{constant} \times n^p) \), \( 1 < p \leq 2 \). Consequently we have focused our search on identifying at least some of the most stable structures in the range 5 \( \leq n \leq 8 \), supplemented by examination of a selected additional set of metastable structures to provide a proper interpretive context. The search through candidate structures was markedly simplified by observing valence, bond length, and (to a lesser degree) bond angle constraints, along with obvious nonoverlap conditions.

Table 1 summarizes our results for the most stable clusters found for the TTAM model. Information presented includes the cluster symmetry, its binding energy \( \Delta \Phi \) relative to isolated monomers, and the binding energy per monomer \( \Delta \Phi/n \). In the large-\( n \) limit this last quantity should converge to a value characteristic of the most stable crystal form of silica at zero pressure and temperature, for the model. Results presented in

\[
\begin{array}{c|ccc}
 n & \text{symmetry} & \Delta \Phi \text{e} & \Delta \Phi/n \text{e} \\
\hline
 1 & D_{2h} & 0.000 & 0.000 \\
 2 & D_{2h} & -123.362 & -61.681 \\
 3 & D_{2h} & -262.798 & -87.599 \\
 4 & D_{4h} & -393.395 & -98.349 \\
 5 & D_{5h} & -533.213 & -106.643 \\
 6 & D_{5h} & -700.606 & -116.768 \\
 7 & C_2 & -830.435 & -118.634 \\
 8 & D_{2h} & -1004.128 & -125.516 \\
 18 & C_1 & -2726.871 & -151.493 \\
\end{array}
\]

\( a \) Total binding energy, and binding per monomer, in kilocalories per mole.

ref 5 indicate similar binding energies for the four silica polymorphs examined: −203.5 kcal/mol for \( \alpha \)-quartz, −199.6 kcal/mol for \( \alpha \)-cristobalite, −205.3 kcal/mol for coesite, and −202.5 kcal/mol for stishovite. In fact, \( \alpha \)-quartz should be the most stable polymorph, and the listed experimental binding energy\(^{26} \) is −216.2 kcal/mol, suggesting that a slight revision of the model parameters might be in order.

The structures of the stable clusters represented in Table 1 are diverse and do not suggest a simple growth principle. The cases for \( n \leq 4 \) discussed in the preceding section III do not uniquely suggest the form of the optimal pentamer. However, our calculations reveal that it contains a pair of equivalent planar 6-rings (alternating Si and O), perpendicular to one another, with a shared Si vertex. This structure exhibits four pendant double-bonded oxygens, two attached to each ring.

The most stable hexamer also possesses four pendant double-bonded oxygens. It can be viewed topologically as having come from the pentamer upon replacement of its shared Si vertex with a pair of Si’s that are themselves connected across the cluster by a double oxygen bridge. Figure 6 provides an illustration of this (SiO\(_2\))\(_6\); all atoms are coplanar except for the two oxygens forming the central double bridge.

The optimal heptamer can be obtained structurally from the hexamer in Figure 6 by reacting (as in the basic dimerization process) one of its pendant Si=O units with a monomer. This yields a protruding Si=O unit connected to the remainder with a double oxygen bridge.

Figure 7 shows the most stable octamer discovered in our search. It contains a pair of double oxygen bridges and can be viewed as the next member of a “ladder” sequence of linear polymers containing an even number of SiO\(_2\) molecules. The top portion of Figure 4 and Figure 6 show the first two members of this ladder sequence. Except for the four corner silicons linked to pendant double-bonded oxygens, all of the ladder polymer silicons reside nearly at the centers of vertex and edge-sharing oxygen tetrahedra. These calculations, supplemented by a few others for larger ladder polymers, establish that the...
binding energies rapidly approach a linear asymptote with increasing \( n \). We find that this asymptote is

\[
\Delta\Phi[\text{ladder}] \sim -150.463n + 198.262 \quad (4.1)
\]

when expressed in kilocalories per mole; of course it is only defined for even values of \( n \).

An even simpler sequence of linear polymers is defined for all integers \( n \geq 1 \) and has all silicons collinear. This sequence begins with the monomer, the dimer of Figure 1, the second trimer of Figure 2, and the first tetramer of Figure 3. Once again the binding energies rapidly approach a linear asymptote with increasing \( n \), the form of which is now found to be (kcal/mol)

\[
\Delta\Phi[\text{collinear}] \sim -128.915n + 133.361 \quad (4.2)
\]

The dimer, the first trimer in Figure 2, and the first tetramer of Figure 4 are the leading members of a cyclic polymer sequence. Each of these three is planar. Evidently all subsequent members are nonplanar in the TTAM model. The cyclic pentamer displays a flat ring-distortion potential around the planar configuration but is definitely unstable with respect to buckling of one \( \text{Si}=\text{O} \) unit out of the plane. The mechanically stable form of the cyclic hexamer was found to have alternating up and down directed \( \text{Si}=\text{O} \) units. Because of the multiplicity of the inequivalent ring distortions that are possible for larger cyclic polymers, it is not clear that their binding energies would approach a simple linear asymptote analogous to (4.1) and (4.2).

V. Eighteen-Molecule Clusters

One expects that the most stable structures for very large clusters would be compact and would internally exhibit crystalline order. As mentioned in section IV above, the binding energy per \( \text{SiO}_2 \) unit should be approximately \(-200 \) kcal/mol for the TTAM model;\(^5\) the extended ladder and collinear polymers represented by eqs 4.1 and 4.2 do not come close to fulfilling this requirement.

Even before internal crystallinity dominates the surface effects in the optimally stable clusters, as \( n \) increases, it is reasonable to expect that crystalline order might make an appearance among metastable cluster forms. It was under this presumption that we decided to focus attention on \( n = 18 \), knowing that a more exhaustive search over a wider \( n \) range was impractical. The specific case \( n = 18 \) offers the opportunity to examine the behavior of a recognizable fragment of tridymite, a well-known silica polymorph,\(^1\) with surface valences appropriately satisfied.

Figure 8 shows a tridymite-like configuration for \((\text{SiO}_2)_{18}\) that was created to serve as a starting point for relaxation to a potential energy minimum. Notice the characteristic stacked hexagons, each consisting of 12 alternating Si and O, with 3 interhexagon links consisting of additional O’s. Three additional chains also link Si vertices of the 2 hexagons, to preserve formal valence rules.

We found it impossible to stabilize this tridymite-like structure. Instead, application of the optimization routines caused it invariably to collapse to a grossly different form. This was true even after minor readjustments of the configuration of Figure 8 to generate alternative starting configurations for optimization. Figure 9 shows the final result of one of these trials, which in fact is the most stable structure found from tridymite-like initial configurations.

In addition to the tridymite-like initial configurations, a variety of alternative starting points for optimization were also used. Some of these were based on the standard valence rules; others were not. The former included nearby pairs of smaller clusters that could interact and combine under the optimization routines. Final binding energies for the 13 distinct cluster forms examined ranged from approximately \(-2727\) to \(-1908 \) kcal/mol.

Figure 10 presents the structure of the lowest-energy cluster found for \( n = 18 \). It contains outward-pointing doubly-bonded oxygens on its surface and an internal oxygen with no bonds shorter than the 1.80 Å cutoff to any silicons (but at least two bonds stretched just beyond this cutoff). This optimal \((\text{SiO}_2)_{18}\) is relatively compact and contains closed circuits of \( \text{Si}=\text{O} \) bonds passing through sets of 8, 10, and 12 distinct atoms.

Examination of Figure 10, with simple bond counting, reveals a striking feature shared by the Figure 9 structure, and several of the other lower-energy \((\text{SiO}_2)_{18}\) clusters. Specifically several of the silicons appear to deviate from the formal valence +4 that was always observed in the optimal clusters for smaller \( n \).
Seven of these anomalous silicons are only singly bonded to three oxygens (which themselves connect to other silicons) and thus have formal valence +3; five other anomalous silicons are also singly bonded to three oxygens but also doubly bond to a pendant oxygen and so must be assigned a formal valence of +5. Note that no change in the 1.80-Å bond criterion used in preparation of Figures 1–10 could have the effect of restoring all silicons in Figures 9 and 10 to valence +4. We cannot guarantee that the cluster shown in Figure 10 is the most stable form for \( n = 18 \) or that formal silicon valences +3 and +5 actually occur in that most stable form. However, our search was biased toward producing compact forms as one expects the optimal cluster to possess, and formal valence anomalies may be a way for the system to reduce partially the high energy cost associated with pendant doubly-bonded oxygens. We suspect that indeed valence anomalies are an intrinsic characteristic of the surface of large aggregates in the TTAM model.

VI. Discussion

In the very large cluster regime, binding energies should be dominated by a bulk contribution proportional to \( n \), with surface corrections proportional to \( n^{2/3} \). This suggests that the following expression might be a reasonable choice for approximating binding energies of the most stable clusters for all values of \( n \):

\[
\Delta \Phi(n) \approx A(n - 1) + B(n^{2/3} - 1) + C(n^{1/3} - 1)
\]  

(6.1)

Here \( A \)–\( C \) are suitable numerical constants, and the coefficient of \( n^{2/3} \) has been chosen to enforce the obvious condition that the binding energy of the monomer vanishes. The \( n^{1/3} \) term may be interpreted roughly as a curvature correction to the surface energy.

Form 6.1 has been fitted to the \( \Delta \Phi \) values in Table 1 by minimizing the squared error. One finds

\[
A = -218.9 \text{ kcal/mol}
\]

\[
B = 154.0 \text{ kcal/mol}
\]

\[
C = 59.1 \text{ kcal/mol}
\]  

(6.2)

The fit is not perfect, because the \( \Delta \Phi \) values in Table 1 do not display quite the smooth pattern that eq 6.1 requires; the root mean square error is 11.14 kcal/mol. Nevertheless the results of (6.2) seem reasonable, particularly when \( A \) is compared with bulk condensed-phase binding energies, as discussed in section IV above. Furthermore, the surface energy term \( Bn^{2/3} \) is positive as expected, and for large spherical clusters with internal density equal to that of α-quartz this surface energy amounts to 1677 dyn/cm. If our tentative identification of the binding energy of the most stable \((\text{SiO}_2)_{18}\) cluster were grossly erroneous, these reasonable fitting values would have been deleteriously affected.

Our observation of formal silicon valences +3 and +5 from elementary bond counting in the lowest-energy \((\text{SiO}_2)_{18}\) raises the possibility of similar occurrences at the surfaces of glassy and crystalline macroscopic silica phases. It seems likely that surface reconstruction simulations using the TTAM model would encounter significant surface concentrations of these species, whose identification would be facilitated by mapping positive-temperature system configurations onto inherent structures.

Possibly these anomalous valences are an artifact of the simple TTAM model, so it is important in the future to check for their occurrence with accurate quantum mechanical calculations.

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References and Notes