Dissociation Energies of Silicon Clusters: A Depth Gauge for the Global Minimum on the Potential Energy Surface

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(Received 13 August 1998)

We have modeled the dissociation of Si_n neutrals and cations in the $n \leq 26$ range. The fragmentation pathways up to $n = 26$ and dissociation energies up to $n = 20$ have been calculated assuming a statistical decomposition process. The results for the cations are in good agreement with the measurements. This indicates that our search of configuration space for the silicon clusters in this size range has indeed found the global minima—a family of "stacked Si_9 tricapped trigonal prisms." This is the first time that dissociation energies have been used to test the results of a global optimization. [S0031-9007(98)07726-6]

PACS numbers: 36.40.Qv, 36.40.Wa

Despite a tremendous effort invested for more than a decade, the structural characterization of atomic clusters remains a remarkably refractory problem in molecular physics [1]. Except for the small clusters where the structures are accessible spectroscopically, advances have typically been made by comparison of a geometry-sensitive physical property measured for size-selected species with the predictions of reasonably high-level calculations for a number of plausible morphologies. To reduce the number of geometries to a manageable quantity, it has normally been postulated that free clusters assume their lowest energy geometries. Then the likely candidates can be found rationally, by searching the configuration space. The cluster properties that have been used as structural indicators are ionic mobilities [2,3], ionization potentials [4], polarizabilities [1], and electron affinities [1]. All these are correlated with the cluster geometry only indirectly, so the different isomers are often indistinguishable [3,4]. Further, there is always a possibility that the true lowest energy geometry might be (i) missed by the search procedure or (ii) not produced experimentally for either entropic or kinetic reasons. Thus agreement with the measurements of properties like those listed above is a necessary but not sufficient criterion for accepting the optimized cluster structures. So, in the absence of an unequivocal structural determination such as that accomplished by spectroscopy, it is desirable to compare the cohesive energies calculated for trial geometries with the experimental values. These can be determined by measuring the dissociation energies of size-selected cluster ions [5]. When cluster formation is subject to thermodynamic control, the lowest energy isomers dominate and the experimental cohesive energies should correspond to those calculated for the global minima. If higher energy geometries prevail, the experimental cohesive energies should be short of the calculation. Conversely, a failure of theory to recover the measured depth of the potential well may indicate that the true global minima have not been found. To the best of our knowledge, this tool has never been used to test the results of a global optimization. As there has been enormous interest in the structures of silicon clusters since suggestions that the small ones are not fragments of the bulk silicon tetrahedral lattice [6,7], we chose to use them for a demonstration of the proposed treatment.

The geometries calculated for the smallest ($n \leq 7$) Si_n species have now been confirmed by matrix isolation spectroscopy [8,9] and photoelectron spectroscopy [10,11]. A detailed understanding of the structure in the $n = 8-11$ size range has been derived from extensive global optimizations [7,12,13], but the results have not previously been verified experimentally. The elucidation of the geometries for larger silicon clusters has presented an impressive challenge. Numerous experimental and theoretical efforts to this end have been reviewed elsewhere [4]. We have recently completed an unbiased global search of the configuration space for silicon cluster neutrals in the $n < 21$ range using a genetic algorithm and density functional theory in both the local density approximation (LDA) and a generalized gradient approximation [3,4]. The global minima for Si_n cations in the same size range have also been found [4]. The resulting structures for both neutrals and cations with $n < 19$ can be viewed as stacks of Si_9 tricapped trigonal prisms (TTP) [14]. For $n = 19$ and 20, near-spherical cagelike geometries become competitive. Ionic mobilities calculated for the stacked TTP structures are in good agreement with the values for Si_n cations in helium [3,4].

The fragmentation patterns of both Si_n cations [5, 15–20] and anions [21] are unusual. First, all species with $8 < n \leq 70$ (at least) undergo fission rather than evaporation. That is, both primary dissociation products contain a relatively large number of atoms, one of them always in the 6–11 size range. Second, the preferred fragments are specific to the size and even the charge state (-1 or $+1$) of the original ion. The measured size dependence of the dissociation energies for $\mathrm{Si}_n{}^+$ [5] is also abnormal [22]. Instead of increasing steadily towards the bulk cohesive energy, the dissociation energy loses ~60% of its value between $n = 6$ and $n \sim 20$ and only then starts to increase again for larger sizes. The decay channels for $\mathrm{Si}_n{}^+$, $n \leq 11$ have been qualitatively rationalized [23] by postulating a statistical unimolecular dissociation. In such a process, the lowest energy fragmentation pathway is preferred regardless of the structure of reactant. However, Raghavachari and Rohlfing [23] modeled the decomposition of neutrals rather than cations and assumed octahedron-based geometries for Si_9 (C_s) and Si_{10} (T_d). These geometries are now known not to be the lowest energy isomers for either charge state [3,4, 24–26]. Conversely, other authors have ventured that the larger clusters are assemblies of smaller subunits and that they break into these subunits along "fault lines" when excited [19,21,27–32]. Then the dissociation pattern would directly reveal the structure of the original cluster. For example, the fragmentation of large Si_n species by ejection of Si_6 or Si_{10} has been argued to support silicon clusters being (i) nanocrystals built from the Si_6 chair and Si_{10} adamantane cage blocks of the bulk "diamond" lattice [19], (ii) stacked benzene and naphthalenelike rings [27–29], or (iii) near-spherical objects with tetrahedral [29] or surface-reconstruction-induced geometries [31,32]. The dissociation energies of Si_n cations [5] have never been modeled theoretically. As long as the structures of clusters for $n > 10$ remained obscure, the peculiarity of their fragmentation could not be explained.

The dissociation energy of a Si_n neutral along the channel leading to Si_m and Si_{n-m} is

$$D_{(n,m)} = nE_n - mE_m - (n - m)E_{n-m}\,, \qquad (1)$$

where E_n is the cohesive energy per atom of the Si_n cluster. Using the values of E_n calculated for our optimized geometries [4], we can predict the dissociation energy for any fragmentation pathway of a Si_n neutral. The lowest energy pathways assuming the E_n values by the gradient-corrected Perdew-Wang-Becke 88 (PWB) functional are listed in Table I. In the size range where comparison could be made, our lowest pathways agree with the earlier predictions based on *ab initio* MP4/6-31G* energetics [23], except that we find an alternative channel for $n = 9$, 11, and 12. Since the structures for Si_n with $n > 20$ have not been optimized [3], the $D_{(n,m)}$ for $m \geq 21$ could not be evaluated, and we cannot rigorously prove that the dissociation pathways indicated for $n = 22$–26 are actually lowest in the calculation. The dissociation energies of small ($n \leq 8$) Si_n neutrals have been measured by Gingerich and co-workers [33] using Knudsen effusion mass spectrometry. Our calculated values are in agreement within their data for all sizes.

TABLE I. Fragmentation channels of silicon cluster neutrals and cations.

n (reactant)	Products for neutrals[a]	Products for cations[a]			
		primary		secondary	
		calc[b]	expt	calc[b,c]	expt[d]
3	2	2	2	1	1
4	3	3	3	1	1, 2
5	4	4	4	1	3
6	5	5	5	1, 4	4
7	6	6	6	1	4, 5
8	7	7	7	1, 4, 6	4
9	5, 7	4, 6, 8	6		8
10	6	6	6	4	4
11	6, 7	6	7	4	6
12	6, 7	6	6	7, 11	7
13	7	6	6	7	7
14	7	7	7	8	8
15	10	8	8	9, 11	9
16	10	6	10	9, 10, 11	6
17	10	10, 11	10		11
18	10, 11	11	11	8	No
19	10	9	9	11, 12	12
20	10	10	10	11	No
21	11	11	11	14	No
22	12	12, 15	12		15
23	13	11, 13, 16	13		16
24	14	14	14	17	7, 11
25	15	15	15	18	18
26	16, 19	16	16	19	19

[a] Several fragmentation channels are given if their energies are within 0.12 eV. We report the larger product for neutrals and the ionic product for cations.
[b] Discounting the possibility of channels leading to a product with $m \geq 21$.
[c] In cases with more than one calculated primary pathway no secondary pathway is shown.
[d] "No" means that the relative abundance of secondary products was so minor as to prevent identification (<1%).

As the larger neutral clusters could not be size selected, their dissociation energies and pathways are not directly measurable. However, experimental information is available for the fragmentation pathways and energies of the cations. The dissociation energies of $\mathrm{Si}_n{}^+$ into $\mathrm{Si}_m{}^+$ and Si_{n-m} could be similarly evaluated using Eq. (1) with the cohesive energies calculated for the cations. Substituting the PWB values [4] for $n, m \leq 20$, we have calculated the dissociation energies for all channels with $m < 21$ for $\mathrm{Si}_n{}^+$, $n = 2$–26. The lowest energy fragmentation pathways remain the same as those calculated for neutrals, except for $n = 9$ (which changes from $m = 5$, 7 into $m = 4$, 6, and 8) and $n = 15$ (which changes from $m = 10$ into $m = 8$); see Table I. Other competitive pathways open for $\mathrm{Si}_{17}{}^+$ ($m = 11$), $\mathrm{Si}_{22}{}^+$ ($m = 15$), and $\mathrm{Si}_{23}{}^+$ ($m = 11$, 16). These changes are caused by the low adiabatic ionization potentials (AIPs) of $m = 4$, 6, 8, 11, and 16 compared to their neighbors [4], which renders these cations relatively more stable than the respective neutrals, and the relatively high AIP of $m = 12$. Alternative fragmentation pathways close for $\mathrm{Si}_{11}{}^+$ and $\mathrm{Si}_{12}{}^+$

(both $m = 7$), $Si_{18}{}^+$ ($m = 10$), and $Si_{26}{}^+$ ($m = 19$), because of the relatively high AIPs of Si_7, Si_{10}, and Si_{19}.

We now compare the fragmentation patterns calculated for cations with the measurements. The products of collision-induced dissociation [5,20] (CID) and photodissociation [15–19] in the $n < 27$ size range are quite similar overall. Yet, for most clusters, the photodissociation studies report a larger variety of fragments with lower yield of each, and hence correspond to a higher excitation energy [20]. So the CID results are more indicative of the lowest energy fragmentation channels, and these are used for comparison in Table I, except for $n = 3$–5 where no CID measurements were reported. The primary pathways agree for all sizes except $n = 11$ and 16. Even for these sizes, the main pathways are only ~0.3 eV above the lowest ones in our calculations, while the lowest ones in our calculations are the second most important pathways in the experiments [19,20]. In both cases, these pathways are significant, with an intensity that is 20–30% of the total. In the photodissociation study [16], the $m = 6$ and 7 channels were nearly equally intense for $n = 11$. For $n = 16$, our error is in placing the charge on Si_6 rather than on Si_{10}. Thus the primary dissociation pathways calculated for all *new* $Si_n{}^+$ geometries found [10] for $n = 11$–26 are in a perfect agreement with the measurements. This is an extremely stringent test, because *both* the cohesive energies of the neutrals and adiabatic ionization potentials must be correct for *all potential* products. It actually verifies that our optimized geometries are, at least, very close in energy to the true global minima. For instance, the existence of isomers lower than those we discovered [4] for any of the cations with $m = 12$, 15–18 by just 0.1–0.4 eV would have induced $Si_{m+7}{}^+$ to eliminate Si_7 rather than Si_{10}. For $Si_{20}{}^+$ or $Si_{21}{}^+$, this would have happened if, respectively, $Si_{13}{}^+$ or $Si_{14}{}^+$ had isomers 0.6–0.7 eV below our geometries. Likewise, the existence of a structure for $Si_{11}{}^+$ lower than ours by only 0.1 eV would have caused the dissociation of $Si_{15}{}^+$, $Si_{17}{}^+$, and $Si_{23}{}^+$ to switch into a wrong channel. Note that 0.1 eV amounts to just ~0.25% of the atomization energy for Si_{11}. The agreement with experiment would not have been secured either had the stacked TTP geometries [3,4] not been found and some other, higher energy isomers accepted as the ground states. For example, had the search for any of the $Si_m{}^+$ with $m = 12$–16 stopped just 0.1–0.4 eV short of our structures, the wrong primary dissociation pathway would have been predicted for the $Si_{m+10}{}^+$ cluster. In particular, this would have happened for the previously accepted $Si_{13}{}^+$ geometry, the C_{3v} capped trigonal antiprism [25,34]. Similarly, the Si_{19} cation would rather dissociate into $Si_{12}{}^+$ and Si_7 were the global minimum for $Si_9{}^+$ either the C_s distorted tricapped octahedron [7] or the C_{2v} distorted tricapped trigonal prism [24]. A striking illustration of the extraordinary sensitivity of the fragmentation pattern to the accuracy of the energies for the potential products is provided by Si_{10}. With the T_d tetracapped octahedron [7] assumed for Si_{10} and $Si_{10}{}^+$ instead of the C_{3v} tetracapped trigonal prism, none of the primary dissociation pathways for $n = 16$, 17, 19, 20, 22–26 could be reproduced.

Furthermore, for all sizes where more than one dissociation pathway has been observed in the CID measurements [20], we successfully predict the second most important channel too (Table I), except for $n = 7$ and 24. Again, even in these two cases the second most abundant products are in the third place in calculations and are higher in energy than those in the second place by only 0.3–0.4 eV. The measured fractional yields of secondary products are strongly correlated with the calculated energy differences between the lowest and second lowest fragmentation pathways. That is, for seven out of 20 sizes in the range of $n = 6$–25, this difference is over 0.3 eV. Six out of these seven clusters dissociate cleanly, with one dominant channel having the relative intensity of over 90% [20]. Of the other 13 sizes, only two dissociate in this way.

While the fragmentation patterns are useful in checking the relative cohesive energies of selected cluster ions as described above, a systematic verification of the absolute values requires investigating the binding energies. The values computed using PWB for the lowest dissociation pathways listed in Table I are compared with the measurements [5] in Fig. 1. (For $n = 19$ and 20, the prolate isomers [4] were assumed.) For $n \leq 18$, our calculation clearly agrees with the experiment very well, except possibly for a kink at $n = 13$. The overall trend is reproduced for $n = 19$ and 20, but the value calculated for $n = 19$ is somewhat low. This suggests that our prolate $Si_{19}{}^+$ geometry is not a true global minimum, hardly surprising since it had been "constructed" rather than obtained

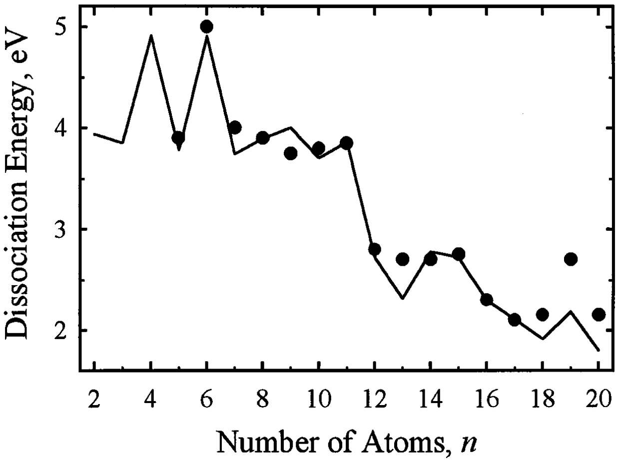

FIG. 1. Dissociation energies of Si_n cations. Circles are the experimental values [5]. The line shows the energies calculated employing the Perdew-Wang-Becke 88 gradient-corrected density functional.

by an extensive search [3,4]. The dissociation energies determined using LDA exhibit the same size-dependent trends, but the absolute values are overestimated, as expected [4,25].

In summary, thermodynamic calculations assuming no barriers along the dissociation asymptotes successfully reproduce both primary and secondary pathways for the fragmentation of silicon cluster cations containing up to 26 atoms. The computed dissociation energies are also in excellent agreement with experiment, possibly except for $n = 19$. Thus mobilities [4], ionization potentials [4], fragmentation pathways and their energies calculated for our stacked TTP geometries all agree with the measurements. That such a wide range of experimental data is consistent with these geometries found by an unbiased global search [3] is compelling evidence for that the prolate Si clusters are indeed the stacks of tricapped trigonal prisms. We have also shown that the dissociation of silicon clusters is statistical and independent of reactant structure. For other systems where this is the case, dissociation studies could be employed to directly test the performance of a global optimization.

This research was supported by NSF, the Army Research Office, and the Office of Basic Energy Sciences.

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