

Si₁₀ and photoabsorption spectra of mid-sized silicon clusters

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Abstract

The photoabsorption spectra of various isomers of Si₁₀, Si₉, Si₁₁ and other silicon clusters are calculated using a tight-binding method. Remarkable similarities between the calculated results and the experimental spectra for mid-sized clusters are noted. It is suggested that the mid-sized clusters are composed of aggregates of smaller clusters.

Recently, Rinnen and Mandich (RM) [1] have presented stunning evidence of great similarities in the photoabsorption spectra of medium-sized clusters Si₁₈–Si₄₁. They report six peaks that recur in the spectra of all species, located at 3.05, 3.27, 3.63, 3.90, 4.94 and 5.25 eV (peaks labelled (1)–(6) in what follows), shown in Fig. 1. In addition, there are peaks at about 1.9 eV and 2.5–2.7 eV that occur in the spectra reproduced in their paper. RM offer three possible explanations, the first being a ‘common bonding network which persists and extends as the cluster grows in size’. The second possibility implies the existence of what might be called a ‘chromophore’, i.e. a group of atoms which has approximately the same structure over an entire range of cluster sizes. The third possibility, rejected by RM and, to our knowledge all other authors, is that the clusters exist as van der Waals aggregates of smaller clusters. We present

evidence in this Letter that RM’s third suggestion may, in fact, be correct ⁴.

Small silicon clusters have been studied at least since the time that Bloomfield, Freeman and Brown observed Si clusters ranging from 2 to 45 atoms [2]. At that time it was suggested that smaller Si clusters are essentially fragments of the crystal lattice [3], i.e. have an open, adamantane-like structure. Since then, the structures of small and medium-sized silicon clusters have been investigated [4]. Experimentally, the conformations cannot be directly determined, but other, indirect but related data, such as abundancies, stabilities, chemical reactivities and various spectra, have been measured ⁵. Theoretical studies of silicon clusters have always assumed that they are well annealed. Indeed, many authors have tried to find some

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⁴ A referee has suggested a fourth possibility, namely that the data are an artifice of the experiment and hence yield no information about the structure of silicon clusters. The idea holds that the overlap between the laser beam profile and the molecular beam is difficult to normalize. We are not competent to judge this point independently, and hence, for the purposes of this Letter, take the evidence presented to us at face value.

⁵ For a review of the experimental literature see Ref. [5].

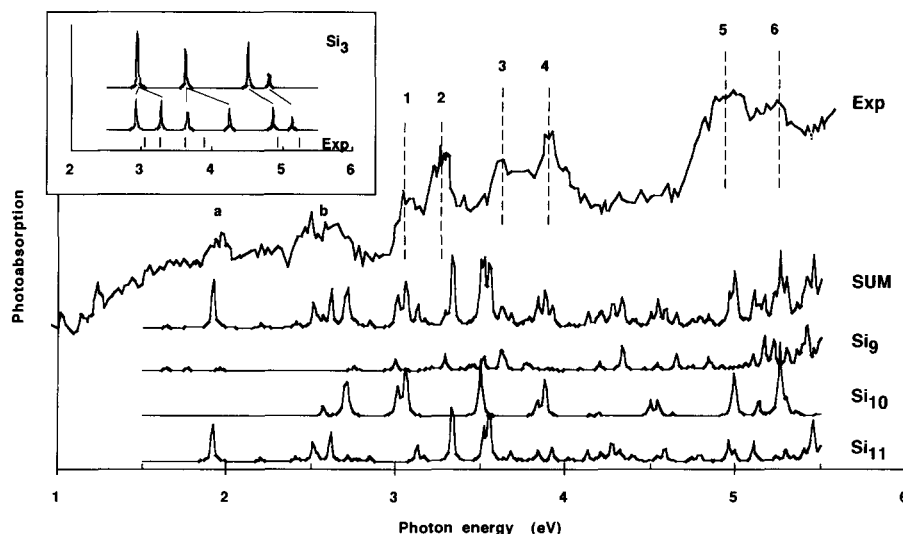


Fig. 1. Calculated photoabsorption spectra of Si_9 , Si_{10} and Si_{11} (all in the TTP or derived ground-state conformations, see Fig. 2) and their superposition compared to one (Si_{31}) of the many similar experimental spectra, reproduced from the experimental data with permission. The spectra of two Si_3 isomers (equilateral at top, isosceles below) are shown in the inset.

common, structural pattern around which various clusters of different sizes can be constructed.

One of the open questions has been the conformation of the stable and abundant Si_{10} . Tománek and Schlüter found that close-packed structures were considerably more stable than the open sort [6–8] and suggested a tetracapped octahedron (TO), a prediction verified by some other calculations [9,10]. We tried to answer this question using a tight-binding model [11,12] and found a new preferred geometry, a distorted bicapped tetragonal antiprism (DBTA). We also found that the tetracapped triangular prism (TTP) conformation, suggested by other workers as the lowest-energy structure [13], has under tight-binding a cohesion energy only 0.07 eV less than DBTA. This is consistent with the evidence that multiple isomers of Si_{10} exist in equilibrium [14]. We have also published predictions of the photoabsorption spectra of the three most promising candidates of Si_{10} [12], data which appear to be useful in the interpretation of recent experimental observations for mid-sized silicon. Because the tight-binding model is empirically fit to the band structure of the bulk, it is a potentially very powerful method for investigating the optical properties of silicon clusters. As will be detailed in what follows, it is found that the calculated spectrum of TTP and related 9- and 11-atom

species duplicate RM's data with surprising accuracy.

The spectrum of a particular cluster, assuming only silicon atoms, depends essentially on two properties: the symmetry of the cluster and the size of the cluster. We can think of no way in which all clusters from 18 to 41 atoms can share the same symmetry. The notion of chromophore, an analogy with organic chemistry, is misleading in this context: organic chromophores depend crucially on the presence of heteroatoms, and further, the organic molecules so described almost always consist of the smallest elements on the periodic table, so that all electrons are tightly held and in localized orbitals. Neither of these criteria applies to silicon clusters. Similarly, a common bonding network may very well apply to large clusters, approaching bulk size, but can hardly account for the great similarity in the spectra of small clusters, which are very probably close-packed, molecular species. Thus we conclude that none of the suggested models for medium-sized silicon clusters, whether based on bulk fragments, reconstructed surfaces or close-packed molecular structures, serves to explain the evidence presented by RM.

This leaves RM's third suggestion as a possible explanation, which is that they are observing van der Waals aggregates of smaller silicon fragments, notably TTP-like 9-, 10- and 11-atom clusters. The van

der Waals nature of these species would perturb but largely preserve the spectra native to the smaller cluster, and these spectra would thus persist over a wide range of cluster sizes. There is no reason that the larger aggregates consist exclusively of TTP-like pieces, but only that such species predominate in the spectra. RM discount this idea since it supposes that a hot van der Waals cluster remains bound over a long time period. There has been much discussion about the problem of cluster annealing [15,16], and this suggests that the production of mid-sized, covalently bound silicon clusters is probably not a simple matter. Indeed, given the relative stability of Si_{10} , perhaps it is more accurate to consider the larger species as clusters of Si_{10} molecules, held together by what are fairly strong dispersion forces and dipole interactions. It is also possible that the aggregate of clusters is itself the lowest energy configuration. At least for the ionic species detected by mass spectrometry, it can be argued that such aggregates may well be lower in energy than molecular species.

It is thus necessary to estimate the energy of inter-cluster interactions. TTP has a dipole moment and is readily polarizable. The tight-binding model is fit to the band structure, and as shown in Ref. [8], the dipole moment and polarizabilities may be accurately calculated. Considering Si_{20} as an aggregate of two TTP Si_{10} clusters, the interaction due to the dipole moment can be calculated to be between 0.1 and 0.3 eV, depending on orientation, while the van der Waals potential derived from the polarizability is found to be 0.3 eV. Thus the aggregation energy can be estimated to be about 0.5 eV. Thus there is a discrepancy with the data reported by Jarrold and Honea [17], who report the dissociation energy of larger clusters into Si_{10} fragments to be in the range of 2–4 eV.

There are at least three possible resolutions of this discrepancy. In the first case, all experiments are performed on ions, not the neutral species which are the subject of computation. For molecular species, ionization will likely lead to a dramatic difference in the spectrum. For our model, however, the ionization of one cluster in the aggregate will leave the spectra of the remaining clusters largely intact, hence preserving the relevance of our data. This is particularly true since usually the largest fragment will be ionized, not the relatively small Si_{10} species. While the spectrum of the aggregate will retain many of its non-ionized

features, the aggregation energy of an ion will be different, and probably considerably higher, than the energy of the neutral aggregate. We suggest this accounts for most of the discrepancy.

The second possible resolution stems from the fact that the dissociation energies reported in Ref. [12] are based in part on the calculated dissociation energies. These are used to determine that fraction of the collision energy which is transferred into internal motion. The calculated dissociation energies are based on the assumption that the clusters are molecular, and hence that answer is already built into the result. Thus the applicability of this data as a test of our result is doubtful.

Third, and finally, we have considered the spectra of Si_{19} and Si_{20} assuming that each consists of smaller 9- and 10-atom clusters attached by a single bond. This model roughly accounts for the dissociation energy (the tight-binding model calculates $\text{Si}_{19} \rightarrow \text{Si}_{10} + \text{Si}_9$ to have $\Delta E = 2.2$ eV), and, at least for Si_{19} , some of the experimental spectrum is reproduced. We have not considered charged species.

In short, our evidence suggests that mid-sized clusters consist of aggregates which contain 9-, 10- and 11-atom species, among other things. The net charge on the aggregate results in a substantial binding energy, but the fact that only one cluster within the aggregate is charged implies that spectral calculations of neutral clusters are relevant.

We now consider the computational results in detail. The semiempirical tight-binding method described in detail elsewhere [6,7], has proven successful in predicting both the geometries and the electronic spectra of Si clusters. This is due to fitting the semiempirical parameters to the geometries of both bulk silicon and silicon dimer, and, very importantly, fitting to the electronic band structure of bulk silicon [8]. Briefly described, we use the tight-binding method to calculate the eigenvectors and the transition dipole matrix elements, and then the one-electron density matrix technique is used to yield the relative intensities [12]. The relaxation constant that specifies the linewidth is chosen to be frequency independent, at 0.01 eV. The accuracy of this method does not stem from the sophistication of the calculation, but rather from the fact that the method is parameterized to match the bulk band structure identically. There is some evidence that this works well for

silicon clusters in that the HOMO–LUMO gap for an Si_{10} matches experiment. More compelling is that an identical method for carbon, i.e. fit to the band structure of diamond and graphite, provides good results for buckminsterfullerene (see also Refs. [18,19]). As a check on the accuracy of our calculation, we have performed local density approximation calculations on TTP and compared those with the tight-binding results. The LDA results were shifted uniformly to lower energies, but otherwise every peak which appears in the tight-binding spectrum also appeared in the LDA spectrum. It is well known that LDA eigenvalues tend to underestimate the band gap of solid materials [20], and thus may lead to an underestimation of the corresponding transition energies and spectral frequencies in clusters as well.

Using the tight-binding method, we considered the spectra of various clusters. The smallest cluster which reveals some of the features of the experimental absorption spectra is Si_3 . Computationally, three stable triangle conformations were found, an equilateral and two isosceles triangles. One of the isosceles triangles produces spectra of six lines (2.92, 3.28, 3.65, 4.25, 4.87 and 5.14 eV, shown in Fig. 1), which corresponds to the experiment surprisingly well. These are split from the four lines produced from the more symmetric equilateral conformation. Of the other smaller clusters ($n < 10$), none produced a spectrum similar to that of RM's experiment.

Si_6 in most configurations leads to degenerate or nearly degenerate HOMO–LUMO levels. While absorption lines between 2 and 6 eV are observed, and the species could easily be present as part of the aggregate, there is little correlation with RM's experiment. Results for Si_4 in both planar and tetrahedral configurations may be similarly described. On the other hand, the Si_7 and Si_{13} clusters, in the geometries suggested by Chelikowski and Phillips with five-fold symmetry [4], show too few absorption lines, and at positions that do not correspond to experiment. The larger derivatives of Si_{13} , such as Si_{19} and Si_{21} , become distorted after optimization, and thus produce many more lines, with some correlation to the experiment. Finally, a couple of Si_{45} isomers were investigated, all of which yield extremely complex spectra with no obvious relation to the experiment [21–24].

We now consider the spectra of Si_{10} isomers, nota-

bly TO, DBTA and TTP. Of these, TTP matches the experimental spectrum accurately. Both TO and DBTA yield intense spectra in the 4.0 to 4.5 eV region, generally absent from the experiment. The spectrum of TTP reveals the main features, lines (1), (4), (5) and (6), of the experimentally observed photoabsorption, as shown in Fig. 1. For the observed lines (2) and (3), the calculated spectrum shows one line at an average position. This turns out to be due to the “too high” symmetry (C_{3v}) of TTP. We have thus calculated the spectra of species similar to TTP, but with lower symmetry. In particular, for Si_9 (TTP minus one atom) and Si_{11} (TTP plus one atom) (see Fig. 2), the C_{3v} symmetry of TTP is broken after optimization (a Jahn–Teller distortion). We emphasize that these 9- and 11-atom species are not simply arbitrary, but are the minimum energy configurations for those clusters under the tight-binding model. The Si_{10} line is split into two lines matching the experimental lines (2) and (3). Si_{11} fits especially well. Si_{10} shows intensity at 2.5–2.7 eV, which can also be identified in the experiment (line (b)). The other line at 1.9 eV emerges in the spectrum of Si_{11} . In general, it is surprising how closely the TTP and TTP-derived structures match the experimental spectrum, especially when compared to the spectra of other clusters.

The final state of most allowed transitions in Si_{10} (Fig. 3) is the highly degenerate LUMO level. The LUMO levels are spatially localized at the cap atoms, especially the top cap. The HOMO level is also centered around the top cap atom. For Si_{11} , with two such caps, this still holds true. Si_9 has no top cap, and this

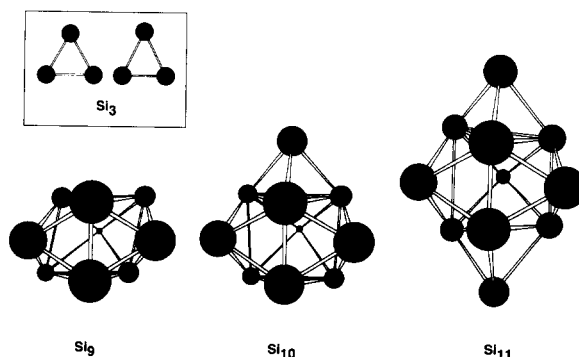


Fig. 2. TTP derived conformations of the Si_9 , Si_{10} and Si_{11} clusters. The conformation of Si_3 isomers (equilateral on left, isosceles on right) is shown in the inset.

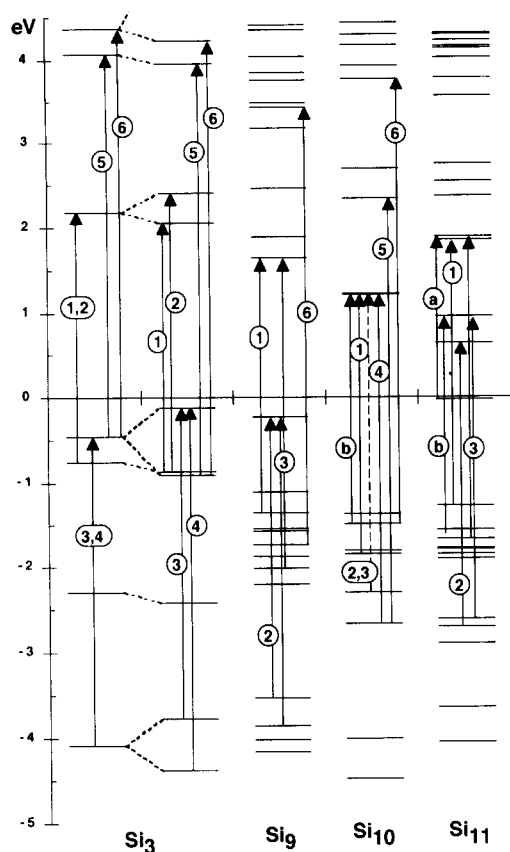


Fig. 3. One-electron levels of Si_9 , Si_{10} and Si_{11} clusters in Fig. 2 with the most intense transitions indicated, along with assignments to the spectral lines in Fig. 1. Also shown are the data for both equilateral (right) and isosceles isomers of Si_3 .

may explain the lower intensity for this species. The experimental spectrum can be accurately described as a superposition of computed Si_9 , Si_{10} and Si_{11} spectra, but especially the latter two. Indeed, even some less prominent peaks in the observed spectrum may be seen, as shown in Fig. 1.

The present model suggests that Si_{10} (TTP) predominates in spectra of the mid-sized clusters, but it does not need to be the exclusive component. In addition, we have postulated the existence of Si_9 and Si_{11} clusters; the geometries proposed for these species are the lowest energy configurations in the tight-binding model. The essential idea, however, does not strongly depend on the specific geometry, but that the breaking of the TTP symmetry leads to the linesplitting which results in peaks (2) and (3). One way of breaking the symmetry is by adding or removing an

atom, as we have suggested. Another way would be the inevitable distortion of TTP as it becomes part of a van der Waals cluster. Our basic claim, therefore, is that TTP and TTP-derived structures are the source of the observed spectrum, and that mid-sized clusters are therefore aggregates of such smaller clusters, with the very likely addition of other species which show up in the spectrum as peaks which vary from one cluster to another.

Recently, Kaxiras and Jackson [25] published data that attempt to explain the experimentally observed shapes of silicon clusters. Their assumption is that the observed clusters are all covalently bonded. We point out that our model is also consistent with experiment, where prolate shapes are observed for clusters smaller than 27 atoms, and more spherical shapes for those larger. Attaching two or three Si_{10} 'balls' end-to-end will certainly yield a prolate shape. On the other hand, attaching three such 'balls' at the corners of a triangle, or four at the points of a tetrahedron, will yield spherical oblate geometries.

Ramakrishna and Pan [26] have suggested a model for silicon clusters based on the observed variations of reactivity of such species. It is not obvious how their result accounts for the spectral data, though it is admittedly equally unclear how our result accounts for the reactivity data. In this context, it must be mentioned that cluster structure and properties seem to depend strongly on the specific experimental conditions [15,27,28], with the variation in reactivity observed only by some authors. Like other previous work, Ramakrishna and Pan assume that all clusters are molecular rather than aggregates, and this assumption is precisely what is questioned here.

In conclusion, we suggest that many experimental observations of mid-sized clusters result from van der Waals aggregates of smaller clusters, notably Si_{10} (TTP). The reasons for this assertion are: (1) the close agreement between the tight-binding calculated spectra of Si_{10} , Si_9 and Si_{11} with Rinnen and Mandich's data; (2) the fact that Si_{10} is relatively stable; (3) larger clusters photofragment into 10-atom units; and (4) a 10-atom cluster such as TTP has a dipole moment and would feel large dispersion forces, especially when part of an ionized aggregate.

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