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Note: Gas phase structures of bare Si_8 and Si_{11} clusters from molecular beam electric deflection experiments

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Neutral silicon clusters have attracted much attention recently due to their possible applications in nano electronics. They have been subject to various experimental and theoretical investigations.[1–3] Most recently, silicon clusters with 6–10 and 15 atoms have been characterized by Haertelt *et al.* applying different IR techniques to xenon tagged and bare silicon clusters.[4] This study has inspired the electric molecular beam deflection experiments of silicon clusters presented here. We confirm independently the proposed structure for Si_8 and make a suggestion for the yet unknown structure of Si_{11}.

The experimental setup is reported in detail elsewhere and we give only a brief description here.[5] Silicon clusters are produced in a laser vaporization source. They are cooled by a helium pulse and expanded through a cryogenic nozzle ($T_{nozzle} = 35$ K) into a high vacuum chamber where a molecular beam is formed. It passes two collimators and enters an electric two wire field unit. A cluster in a defined quantum state experiences a deflecting force which is proportional to the permanent dipole moment μ and the induced dipole moment which itself is proportional to the polarizability α.[6] Beyond the field the cluster passes a moveable narrow slit, is ionized and detected mass-selectively by a time-of-flight mass spectrometer. Cluster intensities are measured depending on the slit position p and the electric field. The recorded beam profiles contain information on dielectric properties of the clusters. Thereby, beam broadening can be interpreted as a measure of the permanent dipole moment and beam shift as a measure of the polarizability, if an adiabatic entry of the cluster into the field is assumed.[6]

In order to evaluate the experimentally determined beam profiles in a quantitative manner and to discover which isomers are present, geometric structures and dielectric properties of the possible cluster isomers must be available. For this purpose quantum chemical calculations are necessary. Silicon cluster structures were found using a genetic algorithm (GA) combined with the QUANTUM ESPRESSO v4.2.1 density functional theory package employing a 35 Ry energy cutoff and PBE functional.[7,8] Lowest lying structures were re-optimized at the MP2/6-311G** level of theory using the NWCHEM v6.0 program package.[9] Electric dipole moments, polarizabilities, and relative energies were calculated using the CCSD(T)/6-311G** approach. All calculations were carried out on the University of Birmingham's BlueBEAR high performance computer.[10] If the clusters can be treated as rigid, deflected beam profiles can be simulated by convolution of the undeflected profile with the dipole orientation distribution. The latter can be obtained from a molecular dynamics simulation using dipole moments and polarizability predicted from theory (see Ref. 6 for a detailed description). The rotational temperature T_{rot} is the only free simulation parameter and is set to 30 K.[11] This indicates inefficient rotational cooling compared to previous results for other group 14 clusters but is in accordance with measured cluster velocities at different nozzle temperatures.[6] The quantitative interpretation

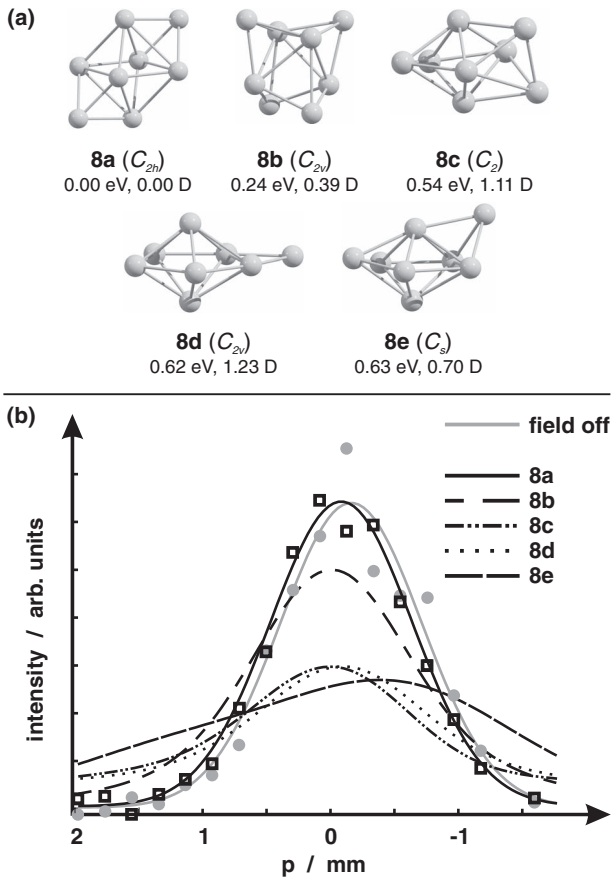

FIG. 1. (a) Structures, relative energies, and dipole moments for silicon octamers. (b) Experimental data points for Si_8 with (squares) and without field (dots) at $T_{rot} = 30$ K and 15 kV deflection voltage. The data without field is fitted with a Gauss curve (bold grey), all the other curves represent simulated beam profiles for isomers depicted in (a).

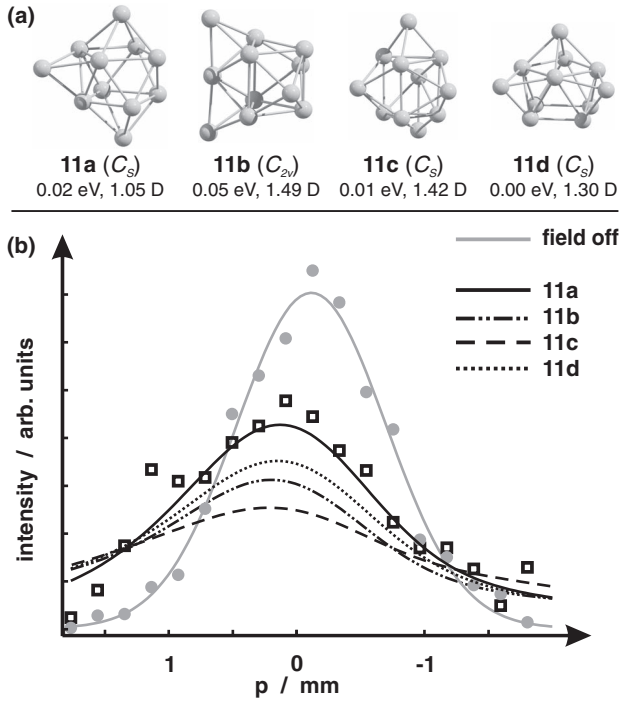

FIG. 2. (a) Structures, relative energies, and dipole moments for silicon undecamers. (b) Experimental data points for Si_{11} with (squares) and without field (dots) at $T_{rot} = 30$ K and 15 kV deflection voltage. The data without field is fitted with a Gauss curve (bold grey) as guide to the eye, all the other curves represent simulated beam profiles for isomers depicted in (a).

of the beam profile allows the determination of the body-fixed dipole moment which is closely related to the geometric structure of the cluster isomer present in experiment.

Typical beam profiles for Si_8 and Si_{11} with and without electrical field at 35 K are shown in Figures 1 and 2. The black lines indicate the simulation results for the depicted structures. The deflection behaviour of Si_8 and Si_{11} differs fundamentally. We observe only a slight shift of the beam profile for Si_8, but a significant shift and broadening for Si_{11}. Therefore, these results indicate a gas-phase structure without and with permanent dipole moment for Si_8 and Si_{11}, respectively. Additionally, experiments at 50, 100, and 300 K nozzle temperature were carried out. Beam deflection profiles at 50 and 100 K (not shown) can be interpreted in the rigid rotor model, hence there is no influence of vibrational modes on the deflection behavior in this temperature range. At 300 K we observe a slight shift for Si_8 and a significantly enhanced shift for Si_{11} (no broadening). Since the permanent dipole moment orients along the field axis for hot clusters it contributes to the total polarizability in a significant manner.[12] These results are in agreement with the 35 K measurements presented here.

From the GA we found a distorted bicapped octahedron with C_{2h} symmetry **8a** to be the lowest lying isomer of Si_8. This structure does not feature a permanent dipole moment due to symmetry and was also identified by Haertelt *et al.* from IR multiphoton dissociation spectroscopy of Si_8–Xe clusters.[4] The simulated beam profile and experimental data are in very good agreement ($\chi^2 = 0.03$, where χ^2 is the least-square measure). The next low lying structures from our GA run are shown in Figure 1 (**8b**–**8e**). These structures yield χ^2 values ranging from 0.23 to 1.43 for the simulated deflection profiles. All higher lying structures have a permanent dipole moment. Since no beam profile broadening is observed, this clearly indicates that **8a** is the gas-phase structure present in this experiment.

Whereas the structure assignment is clear for Si_8, it remains ambiguous for Si_{11}. We find four isomers to be very close in energy and dipole moments between 1.0 and 1.5 D. The simulated deflection profile which fits the experimental data best ($\chi^2 = 0.18$) belongs to a distorted tricapped quadratic antiprism with C_S symmetry (**11a**, see Figure 2). We find another tricapped quadratic antiprism with C_S symmetry to be 0.02 eV lower in energy than **11a**, which was not found by Zhu and Zeng[3] (**11d**). However, this isomer describes the experimental data points worse than **11a** ($\chi^2 = 0.44$). Additionally, isomers **11b** and **11c** are found by the GA, but due to their large dipole moments they are in poor agreement with the experimental data ($\chi^2 = 0.72$ and 1.11). Our experimental results indicate **11a** to be the gas-phase structure of Si_{11}, even if it is not the ground state structure at the employed level of theory. One possible explanation is a kinetical stabilization of **11a** over **11d**, which must be originated in the growing mechanism of silicon clusters. We recognize that **11a** might become the lowest lying structure at a higher level of theory or by incorporation of the vibrational entropy at finite temperatures (incorporation of the zero-point vibrational energies at the MP2/6-311G** level of theory does not change the energy ordering). A higher level of theory can also change the dipole moments significantly and hence the beam deflection profile simulation. Simulations with T_{rot} values up to 50 K have shown that the beam profile of **11d** can describe the experimental data as well (this is not possible for **11b** and **11c** due to their high dipole moment). However, such a high rotational temperature seems unlikely with respect to the nozzle temperature and results from former experiments. Therefore, isomer **11a** is the favourable gas-phase structure for Si_{11} even if we cannot entirely rule out **11d**. To verify our proposed structure, further theoretical and experimental (e.g., IR spectroscopy) investigations are required.

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[10]See http://www.bear.bham.ac.uk/bluebear for a detailed description of the technical specifications of the high performance computer.
[11]Simulations for all isomers with T_{rot} from 5 to 50 K were carried out. We found the best agreement between theory and experiment at $T_{rot} = 30$ K and do not observe changes in the simulation results for $T_{rot} > 50$ K, hence we estimate $T_{rot} = 30^{+20}_{-5}$ K.
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