THE STRUCTURE OF SELENIUM CLUSTERS – Se₃ TO Se₈

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The equilibrium geometries of selenium clusters Se₃ to Se₈ have been calculated. The total energy is determined for each geometry using a parameter-free density functional method, and the most prominent low-energy structures are found using combined molecular dynamics and simulated annealing techniques. This procedure is shown to provide a powerful tool for locating the most important minima on complicated energy surfaces. For Se₆ and Se₈ the calculated geometries agree very well with the measured geometries in the crystalline state, and we predict the geometries of the others. Virtually identical geometries are obtained for local and non-local pseudopotentials.

Sulphur and selenium exhibit a great variety of allotropes [1–3], a common feature being their ability to form rings and chains of widely varying sizes and shapes. Although often discussed as an analog of sulphur, selenium show qualitative differences in the vapour, liquid and solid phases. The main constituents of sulphur vapour up to ≈800 K are S₆, S₇ and S₈ [2], with only minute amounts of smaller molecules. For Se in the same temperature range Se₅, Se₆ and Se₇ predominate, with only traces of Se₈ [3]. Crystalline S₈ melts at about 391 K to give a low-viscosity liquid comprising S₈ molecules, and polymerizes into long chains above 435 K. Melting thermodynamically metastable crystalline Se₈ on the other hand proceeds via polymerization in the solid phase (between 418 and 430 K) to a high-viscosity liquid at about 490 K, the melting point of trigonal Se₈ [3].

Clusters of sulphur and selenium occur in the vapour phase, in crystalline modifications (S₆₋₁₃, S₁₈, S₂₀, Se₆₋₉), and as major constituents of the liquids [3,4]. Amorphous Se does not contain significant amounts of Se₈ molecules, but small ring fragments appear to be incorporated into the infinite chains present [5]. For Sₙ, detailed structural information is available for n = 6–8, 10–13, 18, 20. Reliable data for selenium are limited to the crystalline phases of Se₆ [6] and Se₈ [7], although all Seₙ (n = 2–9) have been identified mass-spectrometrically [8,9]. A study of the total energy surfaces of S and Se clusters should then predict the structures of S₃₋₅, S₆ and Se₃, S₅, Se₇, contribute to the understanding of Sₙ (n ≥ 6), Se₆ and Se₈, and guide future investigations of the highly complex liquid and amorphous phases. Parameter-free calculations have been performed here for the energy surfaces and electronic structures of Se clusters from three to eight atoms. We believe that they are the first such study of selenium clusters of any size. A detailed, comparative study of S and Se clusters will be published elsewhere.

The method we use has been described previously [10]. It combines molecular dynamics (MD) and density functional (DF) approaches, and makes no assumptions about the ground-state geometry. Finite-temperature MD techniques allow a particularly efficient sampling of the potential energy surface. This is crucial in molecules such as these, where the ground-state structures are unknown and the energy surfaces have many local minima. The DF method, with the local spin density (LSD) approximation for the exchange-correlation energy, is free of the assumptions about the nature of interatomic forces.
common in MD schemes. For triatomic group VIA molecules as well as polymeric sulphur [12], calculated geometries agree well with experimental values where available. Bond strengths are overestimated systematically by \( \approx 1 \) eV per bond, so that bonding trends are given reliably. Results of similar quality can be expected here.

In the MD DF method [10], the evolution of a mixed quantum-classical system of electrons and ions can be reproduced exactly by the evolution of a classical dynamical system defined by the Lagrangian

\[
\mathcal{L} = \sum_i \frac{1}{2} \mu_i \int_0^L \left( \frac{d}{dt} \hat{\psi}_i(r) \right)^2 + \sum_j \frac{1}{2} M_j \dot{R}_j^2 - E(\{\hat{\psi}_i\}, \{R_j\}) + \sum_{ij} A_{ij} \left( \int_0^L \frac{d}{dt} \hat{\psi}_i(r) \hat{\psi}_j^*(r) - \delta_{ij} \right). \tag{1}
\]

Here \( M_j \) and \( R_j \) denote the ionic masses and coordinates, \( \mu_i \) are fictitious “masses” associated with the electronic degrees of freedom, dots denote time derivatives, and the matrix of Lagrangian multipliers, \( A_{ij} \), is introduced to satisfy the orthonormality constraints on the single-particle orbitals, \( \psi_i(r, t) \). These generate in turn the density \( n(r, t) = \sum_i |\psi_i(r, t)|^2 \). \( E \) is determined using DF theory and acts as the classical potential energy in the Lagrangian (1). The dynamics given by \( \mathcal{L} \) can be used to generate Born–Oppenheimer (BO) trajectories of the nuclei by an appropriate choice of the \( \mu_i \) and initial conditions via standard MD methods. The \( T=0 \) equilibrium geometry can be determined by simulated annealing [13], which is much more efficient than applying, for example, conventional gradient techniques. In the present work, we have treated Se by both local \(^a\) and non-local pseudopotentials [15]. These potentials give very similar ground-state geometries in Se\(_6\), Se\(_8\), and Se\(_3\), deviations being typically less than 1% in bond lengths and angles. The cluster is placed in a large unit cell of constant volume 1000 \AA\(^3\) (fcc lattice constant 15.9 \AA\) with periodic boundary conditions. These boundary conditions are appropriate for planned applications to extended systems, and the accurate reproduction of the symmetry of Se\(_6\) and Se\(_8\) shows that intermolecular interactions are negligible in the present calculations. The electronic eigenfunctions are expanded in \( \approx 6000 \) plane waves (cut-off energy 14.0 Ry), for a single point (\( k=0 \)) in the Brillouin zone. A calculation for Se\(_8\) using two points (\( \Gamma \) and \( L \)) gave a negligible correction to the total energy (0.015 eV per atom). The exchange-correlation energy is determined using the LSD parametrization of Vosko et al. [16]. The MD procedure is initiated by displacing the atoms randomly from an arbitrary geometry, with velocities \( \dot{\psi}_i \) and \( \dot{R} \) set equal to zero. We then determine those \( \psi_i \) that minimize \( E \) in that atomic configuration. Using a value of \( \mu=1800 \) au and an integration time step of \( 3.4 \times 10^{-16} \) s, we find that the subsequent motion of the nuclei follows the BO surface very accurately. Although not a necessary condition to find equilibrium structures, this ensures that the molecular configurations observed during the annealing process represent physical molecules at elevated temperatures. The average kinetic energy of the nuclei (“temperature” \( T \)) is varied to probe the energy surfaces, and the optimum geometries found by slowly reducing \( T \to 0 \). In figs. 1 and 2 we show the structures of the lowest-lying singlet states calculated for Se\(_{3-5}\) and Se\(_{6-8}\). Geometrical param-

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\(^a\) For a discussion of O\(_3\), S\(_2\), SO\(_2\), and S\(_8\), see ref. [11].

\(^b\) The form of the potential was proposed by Starkloff and Joannopoulos [14]. The parameters \( r_1=0.924 \) au and \( \lambda=10.4 \) au\(^{-1}\) were optimized by fitting the tails of the valence electron orbitals to those of all-electron calculations.

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Fig. 1. The structures of Se\(_3\), Se\(_4\), and Se\(_5\).
Fig. 2. The structures of Se₆ (boat and chair structures), Se₇ (boat and chair structures), and Se₈.

eters are given in table 1 and atomization energies in table 2.

Se₃ has nearly degenerate ring (D₃h) and open (C₃v) structures. The bond in the open state is notably shorter than a normal Se–Se single bond (4.42 au [3]), indicating a bond order between one and two. We have compared these results with those of all-electron calculations with the method used previously for S₃ [18], where open and closed structures with very similar energies are also the lowest singlet states [18]. The equilibrium geometries are essentially identical in the two calculations. Bond lengths agree within 0.1 au and bond angles within 1°. The all-electron calculations indicate a slightly lower energy (≈ 0.3 eV) for the open isomer, in agreement with matrix isolation studies [19]. The atomization energies are larger in the MD DF calculations by ≈ 0.5 eV per atom. This difference is due to the pseudopotential approximation and to the different convergence of the basis set expansions in the two methods. Both the MD DF and all-electron calculations show the lowest triplet state ≈ 1 eV above the singlet ground state, as in S₃ [18].

Se₄: Only thermodynamic data [8,9] are available for Se₄, and our calculations predict a planar singlet ground state of C₂ᵥ symmetry. A planar trans-isomer

Table 1

| Molecular parameters d, α and γ for low-energy isomers of Seₙ, n=3-8. Bond lengths dᵢ (between atoms i and j) in au, bond angles αᵢ (at atom i) and torsion angles γᵢ (at bond ij) in deg. |
|-----------------|-----------------|------------|
| Se₃(C₂ᵥ)       | d₁₂,13          | 4.16       |
|                  | α₁             | 118        |
| Se₃(D₃h)       | d              | 4.46       |
|                  | α             | 60         |
| Se₄(C₂ᵥ)       | d₁₂,34          | 4.14       |
|                  | d₂₃            | 4.52       |
|                  | α₂, α₃       | 110        |
| Se₄(C₂ᵥ)       | d₁₂,34          | 4.10       |
|                  | d₂₃            | 4.58       |
|                  | α₂, α₃       | 108        |
| Se₄(C₂ᵥ)       | d₁₂,15          | 4.48       |
|                  | d₂₃,45        | 4.32       |
|                  | d₄₅            | 4.65       |
|                  | α₁             | 87         |
|                  | α₂, α₃       | 100        |
|                  | α₅, α₆       | 100        |
|                  | γ₁₂,34.45     | 66         |
| Se₄(D₃h)       | d              | 4.42       |
|                  | α             | 101        |
|                  | γ             | 76         |
| Se₅(C₂ᵥ)       | d₁₂,16,34,45   | 4.35       |
|                  | d₂₃,56        | 4.74       |
|                  | α₁, α₄       | 107        |
|                  | α₂, α₃, α₅, α₆| 98         |
|                  | γ₁₂,34,45     | 79         |
| Se₅(D₃h)       | d              | 4.42       |
|                  | α             | 109        |
|                  | γ             | 98         |

542
Table 2
Calculated atomization energies \( a) \) for \( \text{Se}_n, \, n=3\text{–}8 \). Comparison with thermodynamically \( b) \) derived values for gas phase \( \text{Se}_n \). (All energies in eV)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( E_{\text{at}}^{\text{calc}} )</th>
<th>( E_{\text{at}}^{\text{calc}}/n )</th>
<th>( E_{\text{at}}^{\text{therm}}/n )</th>
<th>( \Delta E_{\text{at}}^{\text{calc}} )</th>
<th>( \Delta E_{\text{at}}^{\text{therm}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 (( \text{D}_{\text{sh}} ))</td>
<td>8.31</td>
<td>2.77</td>
<td>1.82</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3 (( \text{C}_{2h} ))</td>
<td>8.32</td>
<td>2.77</td>
<td>1.82</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4 (( \text{C}_{2h} ))</td>
<td>11.51</td>
<td>2.88</td>
<td>1.95</td>
<td>–</td>
<td>2.36</td>
</tr>
<tr>
<td>4 (( \text{C}_{2v} ))</td>
<td>11.80</td>
<td>2.95</td>
<td>1.95</td>
<td>3.48</td>
<td>2.36</td>
</tr>
<tr>
<td>5 (( \text{C}_{5} ))</td>
<td>15.85</td>
<td>3.17</td>
<td>2.14</td>
<td>4.34</td>
<td>2.87</td>
</tr>
<tr>
<td>6 (( \text{C}_{2v} ))</td>
<td>18.98</td>
<td>3.16</td>
<td>2.19</td>
<td>–</td>
<td>2.47</td>
</tr>
<tr>
<td>6 (( \text{D}_{3h} ))</td>
<td>19.34</td>
<td>3.22</td>
<td>2.19</td>
<td>3.49</td>
<td>2.47</td>
</tr>
<tr>
<td>7 (( \text{C}_{5}, \text{&quot;boat&quot;} ))</td>
<td>22.66</td>
<td>3.24</td>
<td>2.21</td>
<td>–</td>
<td>2.33</td>
</tr>
<tr>
<td>7 (( \text{C}_{5}, \text{&quot;chair&quot;} ))</td>
<td>22.73</td>
<td>3.25</td>
<td>2.21</td>
<td>3.39</td>
<td>2.33</td>
</tr>
<tr>
<td>8 (( \text{D}_{4h} ))</td>
<td>26.22</td>
<td>3.28</td>
<td>2.24</td>
<td>3.49</td>
<td>2.45</td>
</tr>
</tbody>
</table>

\( a) \Delta E_{\text{at}} = E_{\text{at}}(n) - E_{\text{at}}(n-1) \). \( b) \) Ref. [17].

\( \text{C}_{2h} \) with similar bond lengths and angles is a low-lying excited state separated by a rotational barrier of \( \approx 1 \text{ eV} \). Insight can be gained by comparison with \( \text{S}_4 \) and its derivatives, for which extended Hückel [20], \( \chi \alpha \)-scattered wave [21] and Hartree–Fock calculations have been published [22]. The most striking features of the two \( \text{Se}_4 \) structures are their planarity and the pattern of bond lengths. The terminal bonds are shorter than normal \( \text{Se} \)–\( \text{Se} \) bonds and the central bond significantly longer, conforming to the observation that long \( \text{S} \)–\( \text{S} \) bonds in sulphur compounds are generally adjacent to shorter ones [23]. Similarly, four consecutive planar \( \text{S} \) or \( \text{Se} \) atoms are usually energetically unfavourable, with long, weak bonds [3,23]. This has been attributed to the fact that “the highest occupied molecular orbitals are always antibonding \( \pi \)-orbitals” [3]. Our calculations show that this is not true in \( \text{S}_4 \) and \( \text{Se}_4 \), where only three out of the four possible combinations of out-of-plane \( p_x \) atomic orbitals on every atom are occupied, the uppermost \( \pi \)-antibonding being the LUMO (\( \pi_2 \), molecule in \( yz \)-plane). \( \text{Se}_4 \) should therefore be compared not with the \( \text{C}_2 \) symmetric (“gauche”) \( \text{H}_2\text{S}_2 \) or \( \text{H}_2\text{O}_2 \), but with \( \text{O}–\text{S}–\text{S}–\text{O} \), which is indeed planar [24]. On the other hand, occupation of the uppermost antibonding \( \pi \)-orbital in \( \text{S}_2^- \) or \( \text{Cl}–\text{S}–\text{S}–\text{Cl} \) is energetically so unfavourable that these species distort to the “gauche” conformations [25,26]. We find that two of the \( p_x \) combinations (HOMO and HOMO-5, both \( \beta_x \)) and three of the \( p_{yz} \) combinations (HOMO-1, HOMO-6 and HOMO-7, all \( \alpha_x \)) are weakly bonding between atoms 1 and 4. This favours the cis- over the trans-isomer and leads to slightly smaller bond angles in the former. As in \( \text{Se}_3 \), the lowest-lying triplet state lies above the singlet ground state (by 0.3 \text{ eV}) contradicting the common assumption that group VIA chain fragments must be diradicals [20]. We have also studied the energy surface in the vicinity of the ground state configurations of refs. [20,22]. In the extended Hückel calculations [20], this is the \( \text{SO}_3 \) analog (\( \text{D}_{3h} \)), which in our calculations is a stable local minimum 1.4 \text{ eV} above the ground state. A helical triplet state with \( \text{C}_2 \) symmetry, the ground state in the HF calculations [22], is not a stable local minimum but relaxes to a rectangle (\( \text{D}_{3h} \), with bond lengths \( 4.30 \) and \( 4.80 \text{ au} \)) 0.3 \text{ eV} above our singlet \( \text{C}_{2v} \) ground state.

\( \text{Se}_5 \): No structural information is available for \( \text{S}_5 \) and \( \text{Se}_5 \). Thermodynamical data [2,3] suggest a ring structure, and this hypothesis is supported by the existence of \( \text{O}–\text{S}_3 \) [27]. Our calculations lead to a cyclic ground state with \( \text{C}_5 \) symmetry, with several slightly disordered structures nearby. These are stable local minima with almost degenerate energies, some within 0.02 \text{ eV} of the ground state. The molecular structure can be rationalized as the cis-form of \( \text{Se}_4 \) with a fifth atom attached to the open edge. The \( \text{Se}_4 \) entity still shows the bond length pattern short–long–short, and the bonds to atom 1 can be considered normal single bonds. Again, the unusually long bond (3–4) has zero torsion angle. In striking contrast to \( \text{Se}_4 \), the HOMO and HOMO-2 are \( \pi \)-antibonding between atoms 3 and 4. This is
consistent with the bond being 0.07 au longer in Se₅ than in Se₆.

Se₇: Crystalline Se₇ contains molecular units which are six-membered rings with D₃d symmetry [6]. The bond lengths (4.452±0.017 au), bond angles (101.3±0.3°) and torsion angles (76.2±0.4°) agree very well with our values for the ground state configuration of Se₆. A "boat" isomer (C₃v) is a low-lying excited state. This conformation has not been observed for either S₆ or Se₆, although it occurs for doubly ionized group VIA species such as Se₄Te²⁺ [28]. CNDO calculations place the boat form of S₆ 0.17 eV above the chair form [29]. As expected from the zero torsion angles at the central bonds (2–3, 5–6), these are far weaker and longer than normal single bonds.

Se₈: No structural data are available for microcrystalline Se₈. However, the crystal structures of S₇ [30] and Se₅S₂ [31] suggest that Se₇ will have a chairlike structure with C₃v symmetry, and the ground state we find has this geometry. Moreover, bond and torsion angles agree well with the experimental data for S₇ [30], and scaling the lengths [30] with the single bond distances found in Se₆ and S₆ reproduces the values in table 1 (chair) remarkably well. The boat isomer is found to be the lowest excited singlet state, but the excitation energy is very small (0.07 eV) and this conformation may be accessible experimentally. In both chair and boat forms of Se₇, increasing the torsion angle at bond 4–5 costs almost no energy. A torsion angle of zero will therefore not be observable at finite temperatures, explaining in part the slight distortions in crystalline S₇ and Se₅S₂ [30,31]. The widely varying bond lengths and an abnormally long bond (4–5) associated with zero torsion angle are reminiscent of Se₅, Se₆ and Se₇ (C₃v). Qualitatively, Se₅ can be derived from Se₆ by adding one atom, Se₅(D₃d) by adding another, and Se₇ (chair) by adding two atoms at the edge 3–4 of Se₅.

Se₉: The three crystalline forms of Se₉ (α, β, γ [1,3,7]) consist of crown-shaped (D₅d) ring molecules. The structural parameters for our ground state geometry compare very well with the experimental data (d=4.414±0.011 au, α=105.7±1.6°, ⟨γ⟩ =101.3° for the α-form [7]).

In spite of a tendency to overestimate bond strengths in sp-bonded materials, DF calculations with the LSD approximation for exchange and correlation have provided a consistently reliable picture of bonding trends. Both features are apparent in table 2, where we compare calculated atomization energies for Se₃ to Se₈ with measured values [17]. Se₅ is stable relative to its neighbours, and both Se₆ and Se₈ are relatively more stable than Se₇. It would be very interesting to have experimental data of higher resolution.

We have described one of the first cluster applications #3 of a new technique for calculating energy surfaces and electronic structure. No assumptions are required about the structure – in Se₄ we started from a square, in Se₅ from a linear chain – and the results are encouraging. Calculated geometries are in very good agreement with measured geometries where known (Se₅, Se₆), and should be reliable predictions in the remainder. The energy surfaces are extremely complicated, with many local minima, so that it would be difficult to use conventional methods (such as gradient expansions of the energy) to determine the optimum path from one geometry to another. The extension of the work to studies of the amorphous and liquid states in S and Se is in progress.

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#3 For results on small Si clusters, see ref. [32].

References

A. Hoareau, J.-M. Reymond, B. Cabaud and R. Uzan, J.
Balasubramanian and C.K. Mathews, in: Advances in mass
spectrometry, Part B, ed. J.F. Todd (Wiley, New York,
in: Proceedings of the 18th International Conference on
ences therein.
1145.
5212.
1200.
[17] K.C. Mills, Thermodynamic data for inorganic sulphides,
85 ff.
Letters 57 (1978) 33;
Soc. 100 (1978) 7847.
38b (1983) 543.
60 (1974) 5005.
236.
[26] B. Beagley, G.H. Eckerlsley, D.P. Brown and D. Tomlinson,
(1970) 300.
Chem. 16 (1977) 892.
[31] R. Steudel, M. Papavassiliou, E.-M. Strauss and R.
Laitinen, Angew. Chem. 98 (1986) 81.
the 1st NEC Symposium on Fundamental Approaches to
New Material Phases, Tokyo, 1986, ed. S. Sugano (Sprin-