Molecular Composition of Liquid Sulfur**

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The structure determination of liquids is still a challenge. This in particular holds for the complex system of liquid sulfur.[1–4] Liquid sulfur exhibits a wide range of colors and structures with change in temperature.[5] In the solid state, sulfur adopts three allotropes of cycloocta-S_{8c} which are well-known as orthorhombic α-sulfur, monoclinic β-sulfur, and monoclinic γ-sulfur. It is possible that these structures may also be present in the liquid phase. Two basic models have been proposed for the liquid. One claims predominantly S_{8c} rings[6] and the other proposes mainly polymeric chains for the liquid.[7] In spite of the large amount of experimental data reported, there is little direct information to differentiate among the models for the structure. A detailed understanding of this liquid is also highly desirable as there is a peculiar phase λ-transition at 432 K that results in drastic changes in the physical properties, such as viscosity and structure.[6] Most of the experimental studies suffer because the thermodynamic and spectroscopic properties of various chain and cyclic molecules do not differ significantly and/or cannot be resolved in the liquid phase and thus not allow any conclusion to be drawn for the structure. In detailed experimental studies, Steudel et al.[5,6] quenched liquid sulfur in liquid nitrogen, extracted the sulfur species with CS_2, and could characterize several ring structures (S_{6c} to S_{20c}) by high-performance liquid chromatography (HPLC) and Raman spectroscopy. But one question still remains: Are the detected structures constituents of the liquid phase or are they developed during preparation?

Neutron-scattering experiments[7] tell us that liquid sulfur and rapidly quenched liquid sulfur provide different structure factors indicating to different compositions in both systems. These studies yield numbers of nearest neighbors in the pair-correlation function of about 1.8 ± 0.1, which is less than the value of 2.0 expected for cyclic molecules. The determined number of neighbors suggests that short linear molecules must be the main components of liquid sulfur. On the other hand ESR studies of liquid sulfur have shown that the concentration of free radicals is low over the whole temperature range, which suggests long polymer chains.[8,9] Thus from the experimental viewpoint the structure determination of liquid sulfur is somewhat controversial.

In general, theoretical methods should be helpful to predict the structure of liquid sulfur and to disprove one of the models. Classical molecular-dynamics (MD) calculations suffer from the difficulty of constructing an empirical interatomic potential that could describe the many different structures and valence states of sulfur.[10] Probably the best choice to determine the complicated structure of liquid sulfur is to apply first-principle theoretical methods. Thus Car-Parrinello ab initio molecular dynamics simulations[11] have been performed by Tse et al.[12] to predict the structure, vibrational spectrum, and dynamics of liquid sulfur over a wide range of temperature. But this particular covered only about 72 sulfur atoms and had short simulation runs of about 5 ps. Thus only crude predictions about the existence of cyclic and/or linear structures can be made.

Herein quantum cluster equilibrium (QCE) theory[13] is used to provide a detailed picture of the equilibrium cluster structures and thermodynamic properties of liquid sulfur. Developed for describing the equilibrium structures of H-bonded liquids this method is now applied for the first time to a covalently bonded system. QCE theory is based on a full quantum treatment of the geometries, binding energies, and vibrational frequencies for molecular structures that are considered to be constituents of the gaseous and liquid phases. The cluster equilibria that dictate phase composition are determined by rigorous techniques of quantum statistical thermodynamics in the canonical ensemble, based on the ab initio or density functional (DFT) partition functions for each cluster.

Thus we carried out supermolecular calculations at the uncorrelated Hartree–Fock (HF) level ($n = 2$–20), density-functional (B3LYP) level ($n = 2$–20), and Møller–Plesset second-order perturbation theory (MP2; $n = 2$–8) for molecular structures of sulfur S_n using 6-31+G* basis set as implemented in Gaussian 94.[14] For all optimized structures frequency calculations were performed. Recently, Wong[15] calculated vibrational frequencies for a large number of molecules, which included sulfur compounds, by using a smaller basis (6-31G*) set and by several different methods. The data set gave strong support to hybrid density functionals versus MP2. Thus we think that B3LYP is an appropriate method and 6-31+G* a well balanced basis set to calculate sulfur clusters. We also want to emphasize that a uniform level of theory must be applied to all candidate clusters ($n = 2$–20). Frequencies for MP2/6-31+G* and higher are simply impractical for the largest clusters considered ($n = 9$–20).

There have been several theoretical studies on sulfur clusters, which range from empirical to ab initio studies. Most have considered only specific molecular systems though there have also been a few systematic studies on a range of cluster size.[10,16–21] The most detailed and probably the most accurate studies to date have been the DFT calculations performed by Hohl et al.[19] and ab initio calculations on RHF/3-21G* geometries up to the cyclic 12mer by Raghavachari et al.[20] Recently, Cioslowski et al.[21] calculated conformations and thermodynamic properties of small sulfur molecules S_{5c}, S_{6c}, S_{7c}, and S_{8c} on higher levels of theory (B3LYP/6-311G* and

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MP2/6-311G*). The calculations on both levels of theory disagreed only in minor details supporting our choice for B3LYP as an appropriate method. Unfortunately no frequency calculations were performed. Thus for comparison with our results only studies presenting all properties including frequencies were considered.

Our fully optimized 34 structures comprise singlet-state chains S_{ns} and triplet-state chain S_{nt}, as well as cyclic sulfur molecules S_{nc}. The most stable molecules are shown in Figure 1. For all calculated structures we obtained positive frequencies. The polymeric chains are twisted in a helical manner and closely resemble the well-known structure of sulfur S_{μ}. The geometry and vibrational spectrum of the isolated S_{8c} molecule and other small-ring structures are in good agreement with observed values[1–5,22,23] and previous theoretical studies.[16–21] In Table 1 our calculated vibrational frequencies for S_{8c} are given in comparison to experimental results and other theoretical work. The data show that our choice of methods and basis set is appropriate to tackle the problem. For the cyclic 18mers we calculated the known crystal structures α-S_{18} and β-S_{18}. The α-S_{18} molecule shows C_{2h} symmetry which is by far the most stable structure and thus considered here.

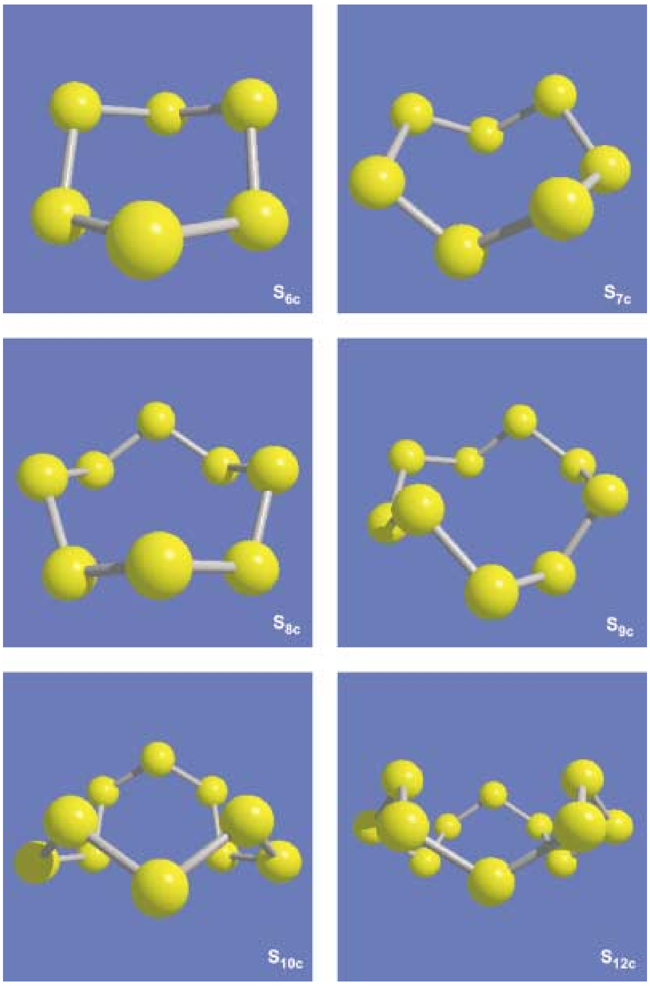

Figure 1. Enthalpically and entropically favored cyclic sulfur molecules.

The calculated average energies per sulfur atom for both theoretical methods are shown in Figure 2a and 2b referred to the energetically most favorable S_{8c} ring structure. It can be seen that except for the trimer, all chain molecules are energetically more favorable in the triplet rather than the singlet state. But even the largest triplet-state structure containing 17 sulfur atoms is higher in energy than S_{8c}. The structures of the cyclic sulfur molecules are calculated for S_{5c} to S_{20c}. The ring structures S_{6c}, S_{7c}, S_{9c}, S_{10c}, and S_{12c} are slightly weaker, whereas S_{14c} and S_{20c} are bonded slightly stronger than S_{8c}. For both methods the energy differences relative to S_{8c} range between -0.2 and 5 kJ mol^{-1}. These values are close to the estimates obtained experimentally from enthalpies of formation and equilibria constants for these species[5] (between 1 and 4 kJ mol^{-1}; Table 2).

The liquid-phase cluster populations for sulfur obtained from thermodynamic calculations for temperatures in the range of 389.5 (melting point) to 717.6 K (boiling point) are shown in Figure 3a,b and 4a,b. Over the whole temperature range the populations are dominated by cyclic rings S_{8c}. For the QCE(34)/RHF/6-31+G* and QCE(34)/B3LYP/6-31+G* models we obtained percents by weight of 98.2% and 99.8%, respectively, which is close to the experimental value of about 93.6%, a little above the melting point. Considering that in the experiment up to 5% of all molecules could not be detected, this was caused by undissolved species and weighing errors, this agreement is quite remarkable. From the theoretical viewpoint this result is also not obvious. Using smaller basis sets, such as 3-21G, leads to populations of only 50% S_{8c} and larger amounts of cyclic S_{6c} to S_{12c} structures (see Supporting Information). Clearly a 6-31+G* basis set is needed and sufficient to obtain reasonable bond energies and frequencies.

Table 1. Experimental and scaled calculated vibrational frequencies $\tilde{\nu}$ [cm^{-1}] for the cyclic molecule S_{8c}.

HF/3-21G*[a]	HF/6-31+G*[b]	B3LYP/6-31+G*	MP2/6-31+G*[c]	AIMD[d]	Exp.[23]
468	484	459	464	480	475
465	482	451	462	476	437
462	481	448	420	474	415
454	460	446	411	435	475
450	459	397	427	408	471
256	252	245	239	247	239
243	240	240	237	243	248
214	212	212	196	218	218
192	189	190	187	187	186
156	153	143	144	140	152
61	62	73	68	59	86

[a] Scale factor of 0.89.[19] [b] Scale factor of 0.89. [c] Scale factor of 0.95. [d] AMID = Ab initio molecular dynamics.[12]

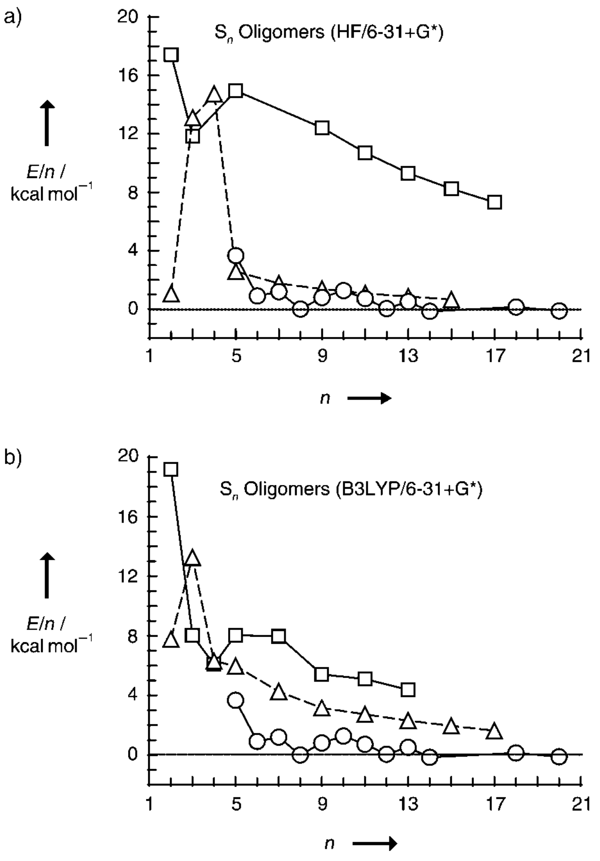

Figure 2. a) Calculated (HF/6-31 + G*) average energy per sulfur atom in singlet-state S chains (□), triplet-state S chains (△), and cyclic sulfur molecules S_n (○; n = 2–20). b) Calculated (B3LYP/6-31 + G*) average energy per sulfur atom in singlet-state S chains (□), triplet-state S chains (△), and cyclic sulfur molecules S_n (○; n = 2–20).

Table 2. Calculated average bond energies per atom E_{bon} [kJ mol^{-1}] for selected cyclic S_{nc} clusters in comparison to calculated bond energies E_{bon} [kJ mol^{-1}] derived from reaction enthalpies.

Cluster	HF/6-31 + G*	B3LYP/6-31 + G*	MP2/6-31 + G*	Exp.[5]
S_{6c}	3.775	6.799	6.265	3.7
S_{7c}	5.009	4.462	5.067	3.0
S_{9c}	3.350	3.328	2.280	3.1
S_{10c}	5.283	3.756	4.458	3.0
S_{12c}	−0.187	0.468	−1.423	1.0

Up to the λ-transition at 432 K the S_{8c} contribution is reduced only slightly as found in the experiment. Beside the dominant species S_{8c} other cyclic ring structures, such as S_{6c}, S_{7c}, S_{9c}, S_{10c}, and S_{12c}, show up in trace amounts. These species were also found by Steudel et al., who rapidly quenched the liquid sulfur, solved it in CS_2, and investigated the sulfur structures by HPLC and Raman spectroscopy.[5,6] From our DFT studies we obtain the same relative populations: S_{7c}, S_{6c} as well as trace amounts of S_{9c}, S_{10c}, and S_{12c}. In our HF population S_{6c} is favored over to S_{7c}. The S_{7c} structure used for the HF calculations is lower in symmetry (C_2) and higher in energy than the experimentally found molecule (C_s),[24,25] which is also a true minimum structure in the DFT calculations.

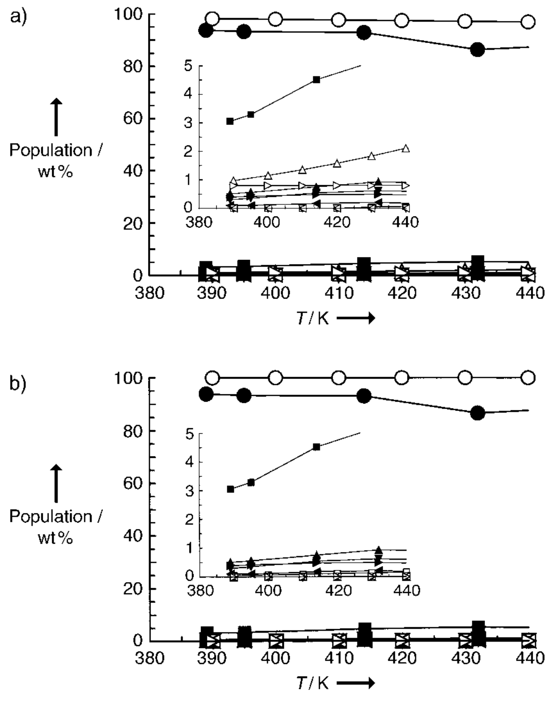

Figure 3. QCE(34)/HF/6–31 + G* (a) and QCE(34)/B3LYP/6–31 + G* (b) cluster populations of sulfur as a function of temperature: ○: S_{6c}; □: S_{7c}; ○: S_{8c}; ▽: S_{9c}; ◁: S_{10c}; ▷: S_{12c}. For comparison experimental populations of sulfur molecules (filled symbols) are given[6]: ▲: S_{6c}; ■: S_{7c}; ●: S_{8c}; ▼: S_{9c}; ◀: S_{10c}; ▶: S_{12c}.

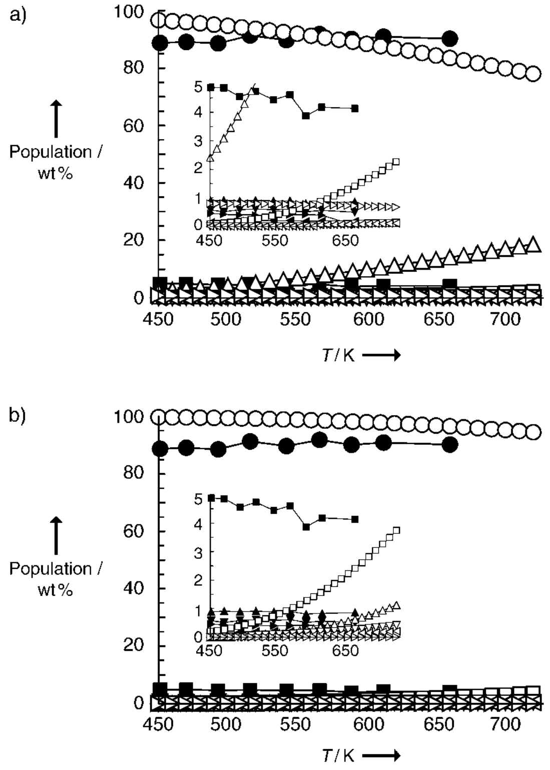

Figure 4. QCE(34)/HF/6–31 + G* (a) and QCE(34)/B3LYP/6–31 + G* (b) cluster populations of sulfur as a function of temperature: △: S_{6c}; □: S_{7c}; ○: S_{8c}; ▽: S_{9c}; ◁: S_{10c}; ▷: S_{12c}. For this temperature range no linear sulfur molecules could be found by the QCE model. For comparison with experimental populations of sulfur molecules[6] (filled symbols) the measured S_{8c} and S_{μ} contributions are included in the total contribution S_{8c}: ▲: S_{6c}; ■: S_{7c}; ●: S_{8c}; ▼: S_{9c}; ◀: S_{10c}; ▶: S_{12c}.

But why is S_{7c} favored over the other cyclic structures S_{6c}, S_{9c}, S_{10c}, and S_{12c} which mostly show higher symmetry and larger bond energies? The answer is given by the calculated vibrational frequencies. The five lowest wavenumbers for the cyclic species as given in Table 3 show clearly that S_{7c} is entropically favored. A larger number of lower frequencies determine the vibrational partition function in our model and thus the equilibrium distribution of the molecules. Subtleties of the energetics of various sulfur ring and chain conformations are largely associated with the torsional dependencies of hyperconjugative interactions (vicinal delocalizations from sulfur lone pairs to vicinal sulfur–sulfur antibonds).[26–28] Interestingly, S_{7c} is known to be responsible for the deep yellow color of liquid sulfur.[5]

Table 3. Low-lying vibrational frequencies $\tilde{\nu}_{1-5}$ [cm^{-1}] and zero-point energies E_{ZPE} [kJ mol^{-1}] per atom for selected cyclic S_{nc} clusters (B3LYP/6-31+G*).

Cluster	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}_4$	$\tilde{\nu}_5$	E_{ZPE}
S_{6c}	161.7	162.5	198.7	199.1	258.6	3.796
S_{7c}	56.2	124.1	150.7	165.4	190.8	3.761
S_{9c}	51.5	59.3	62.8	94.4	150.7	3.798
S_{10c}	39.3	56.5	58.2	74.2	113.5	3.822
S_{12c}	42.6	43.4	43.9	45.0	68.7	3.913

For the temperature range between 389.5 and 432 K, QCE populations do not show any evidence for the linear molecules predicted by neutron-scattering experiments. The number of 1.8 ± 0.1 nearest neighbors suggests, on average, pure linear 10mers, or if any cyclic or longer linear molecules are present even smaller linear structures.

Above the λ-transition temperature (432 K) no linear sulfur molecules could be found. Clearly our calculated clusters up to the synthetic 37mers are still too small compared to presumed structures built upon 10^3 to 10^6 sulfur atoms.[5] Thus, in our model larger linear or cyclic molecules are incorporated in the total contribution of the most favorable S_{8c}. Adding the experimentally found S_{8c} and S_{μ} contributions gives absolute values and temperature behavior comparable to our S_{8c} population (Figure 3b and 4b). Clearly the regime above the λ-transition cannot be simulated by any theoretical model. In classical and moreover in ab initio MD studies the small system size as well as too-short simulation runs prevent such a viscous system being characterized. For QCE calculations bond energies and vibrational frequencies for such large molecules are not available.

Concerning the cyclic structures our results are essentially in agreement with the findings of Steudel et al. For both theoretical methods rising temperature leads to slightly smaller contributions of S_{8c} (5–15 %) in favor of the neighboring cyclic structures S_{7c} and S_{6c} (2–10 %), whereas the amounts of the larger species S_{9c}, S_{10c}, and S_{12c} do not show significant changes with temperature at all. This change in population is mainly caused by entropic effects. This result can be demonstrated by using the same energy per sulfur atom for all structures as that found for S_{8c}; immediately the dominant S_{8c} is replaced by S_{7c} and S_{6c}.

The present QCE model provides a new type of ab initio theoretical support for the general picture of sulfur polymer distributions that has emerged from experimental studies spanning more than 100 years. While certain novel observations could be offered concerning detailed enthalpic and entropic origins of cluster stability, it is gratifying that the overall QCE results are generally "unsurprising". These results yield satisfactory overall agreement with a multitude of crystallographic, spectroscopic, and thermodynamic measurements on individual cluster species and complex liquid mixtures. This general concordance also suggests how a combined theoretical and experimental approach can elucidate additional details of the complex phase behavior of sulfur and other substances.

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