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Possible high-pressure structures of sulfur trioxide†

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Calculations with the linearized augmented plane wave method indicate that several high-density forms of sulfur trioxide should be accessible at pressures above 29 GPa, with densities up to 1.7 times larger than the presently known forms of solid SO_3.

Exotic high-pressure modifications of common substances are interesting, the quartz-like CO_2 being a striking example.[1] We now consider SO_3, based on the simple idea of letting the coordination number of sulfur, CN(S), grow from the values of three or four in the known oligomeric or polymeric modifications of SO_3 to the equally common value CN(S) = 6, as in SF_6, and at the same time imposing for all oxygens CN(O) = 2.

The solid-state calculations were performed with the full-potential linearized augmented plane-wave (LAPW) method, as implemented in the Wien97[2] software. Technical details of the calculations are available in the electronic supplementary material.† The volume of the unit cell, the ratio between the edges of the unit cell, and the atomic positions inside the cell were successively optimized until convergence was achieved.

Two systems were studied for energetic reference. One was the SO_3 molecule in D_{3h} configuration, placed onto a hexagonal grid with 529 pm (10 a.u.) unit vectors in all directions. The S–O bond lengths were optimized while the size of unit cell was not. This rather artificial system ('fluid') gives a rough estimate of the energy of gaseous SO_3 in the framework of the present computational model. The other reference system chosen was the polymeric β-SO_3 in the experimental structure.[3] This modification of SO_3 consists of parallel spiral chains, which are not chemically bonded to each other (Fig. 1(a)).

The structure of an unknown crystalline solid can in general not be predicted. We used analogies with other systems of similar composition (AB_3) or chemical intuition as starting points for the calculation. For choice of the model structures we set the requirement that the sulfur must be hexa-coordinated and the oxygen, two-coordinated. The possible structures of connected octahedra are numerous,[4] and the following three ones, relatively simple to model, were chosen.

The first structure which we considered was a simple cubic one of the ReO_3 type (space group $Pm\bar{3}m$, no. 221). This structure was chosen based on the isoelectronic principle: SO_3 and AlF_3 differ only in nuclear charges, both containing 40 electrons per formula unit, and AlF_3 has a high-temperature phase with this structure.[5] There is one important difference between fluorine and oxygen, however: while fluorine in the AlF_3 structure is primarily ionic, with little preference in bond directionality, the oxygen atoms are expected to form covalent bonds, ideally at bond angle, θ_o = 109.5°. In siloxanes or silicates θ_o can be much larger. The ReO_3 structure imposes θ_o = 180°. The structure can be visualized as a simple cubic arrangement of S atoms, with O atoms located in the middle of each nearest-neighbour pair (Fig. 1(b)).

The second structure we considered was similar to RhF_3[6] (a more recent redetermination[7] indicates that RhF_3 is slightly distorted from this idealized structure). In this crystal, the F (O) atoms form a hexagonal close packed structure, and the Rh (S) atoms fill 1/3 of the octahedral interstices (symmetry class $R\bar{3}c$ (no. 167) with S atoms at positions (b) and O at (e) with x = 1/12). This structure imposes a 132° bond angle at oxygen. A part of the structure is shown in Fig. 1(c), which emphasizes the hexagonal placement of S atoms, with S and O atoms located on alternating planes.

The third structure considered was that of a heavier SO_3 analog, TeO_3. The β form of TeO_3 crystallizes in a rhombohedral $R3c$ structure (no. 161),[8] with θ_o = 149°. The cell size as well as atomic coordinates were optimized as described before, using the experimental atomic positions in the TeO_3 unit cell as the initial guess. This full optimization allows the bond angles at oxygen to vary continuously. The structure (Fig. 1(d)) is a distorted version of the AlF_3 structure. While the bond angles at S atoms are nearly 90°, retaining the octahedral coordination, the octahedra are rotated in space in order to accommodate bond bending at oxygen.

The most important results are collected into Table 1.

In the final optimized TeO_3-like $R3c$ structure, the cell parameters are a = 458.6 pm, α = 57.73°, oxygen coordinates (0.883, 0.617, 0.250), which yields a 170 pm S–O bond length and a 139.4° bond angle at oxygen. The bond angles at sulfur vary from 88 to 92°. The calculated equilibrium density of this

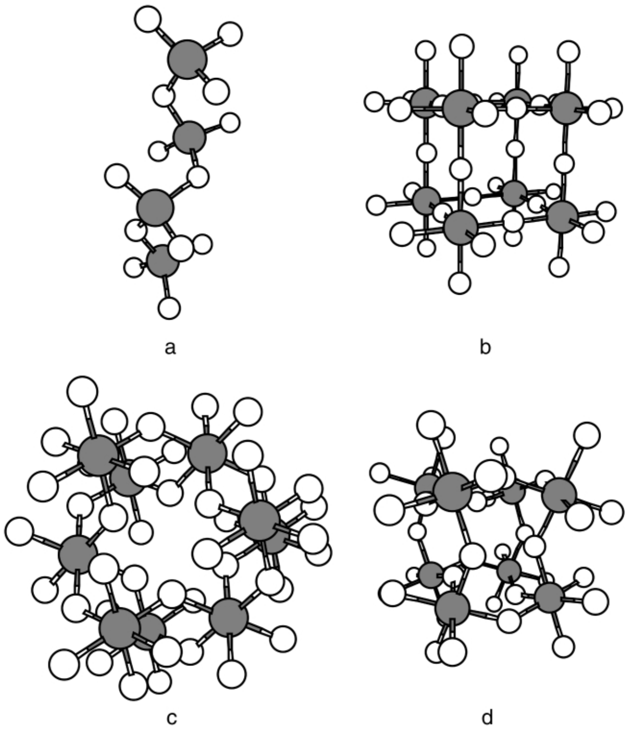

Fig. 1 Structures of the solid modifications of SO_3 considered.

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† Electronic supplementary information (ESI) available: technical details for calculations. See http://www.rsc.org/suppdata/cc/b1/b107778c/

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Table 1 The optimized zero-pressure parameters of the system studied

System	Rel. energy/ kJ mol^{-1}	Molar volume/ cm^3	Density/ g cm^{-3}	S–O distance/ pm
Polymer (reference)	0	32.4	2.47	143, 166
'Fluid' (molecular)	+21	77.3	1.04	143.9
TeO_3-like ($R3c$)	+333	19.5	4.11	169.9
Hexagonal ($R\bar{3}c$)	+400	19.2	4.17	174.2
Cubic ($Pm\bar{3}m$)	+477	23.9	3.35	170.6

phase is 4.11 g cm^{-3}. At the transition pressure, the system is expected to move from the lower curve to the upper curve along the arrow in Fig. 2. The density at the end of the arrow is 4.40 g cm^{-3}.

The hexagonal RhF_3-like $R\bar{3}c$ structure has an energy minimum at unit cell size 427 pm, with the S–O distance at 174 pm and the equilibrium density of 4.17 g cm^{-3}.

The AlF_3-like $Pm\bar{3}m$ cubic structure has a minimum at the unit cell size 341 pm, which results in a 171 pm S–O distance with 180° angles at oxygen. Due to the less dense packing, the calculated density of this phase would be 3.35 g cm^{-3}.

Of the reference systems, the polymeric form was optimized to a structure with a density of 2.47 g cm^{-3} (crystallographic calculated 2.42, measured 2.29),[3] S–O bond lengths at 143 and 166 pm (experimental 141 and 159–163 pm). In the molecular fluid, a bond length of 144 pm (experimental 143 pm)[9] was obtained.

The experimentally known, room-temperature polymeric SO_3 has the lowest calculated energy and is used as a reference (zero) point in the comparison. The SO_3 'fluid' is energetically 21 kJ mol^{-1} above the polymer (all energies are expressed per SO_3 formula unit). This can be compared to the 54 kJ mol^{-1} difference in heats of formation of polymeric and gaseous SO_3.[9] At least part of the gap between these energy values can be explained by lack of rotational and translational degrees of freedom in our model system ($3RT^{\ominus}$ = 7.4 kJ mol^{-1}). We expect the accuracy of the calculations to be within 20–40 kJ mol^{-1} of the true experimental values.

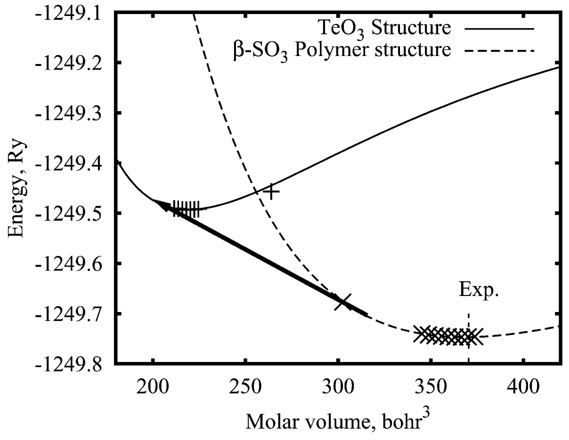

Fig. 2 The calculated energies (points) and the $E(V_m)$ fits for the TeO_3-like and β-SO_3 structures. At the transition pressure of 29 GPa the system is predicted to follow the arrow from the lower curve to the upper one.

The hypothetical TeO_3-like, RhF_3-like and AlF_3-like phases of SO_3 lie at +333, +400 and +477 kJ relative to the polymeric phase, respectively. For comparison, the heat of formation of the latter is −449.6 kJ mol^{-1}.

Morse curves were fitted to the calculated E as function of $(V_m)^{1/3}$ (V_m is the molar volume). The $E(V_m)$ curves for the polymeric and the TeO_3-like phases are shown in Fig. 2. The transition pressure is obtained from the slope of the common tangent of the two $E(V_m)$ curves and is 29.4 GPa. The rougher estimate $\Delta P = -\Delta E/\Delta V$ with the zero-pressure minima gives 26 GPa for the TeO_3-like structure while the RhF_3-like and cubic forms would need pressures of 30 and 56 GPa, respectively. Such pressures can be created by current experimental techniques. The molar volumes per formula unit for the polymeric form are 53 800 and 46 800 pm^3 at zero pressure and transition pressure, respectively. For the $R3c$ modification the figures are 32 300 and 30 200 pm^3, respectively. Eventual metastability of the high-pressure phases could be enhanced by fluorination of the surface.

Concluding, our calculations suggest that sulfur trioxide could be compressed to several three-dimensional structures, with the sulfur coordination number equal to six. The modification accessible at the lowest pressure of approximately 29 GPa should have an $R3c$ structure and an equilibrium density of 4.11 g cm^{-3}.

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