

The Rotational Spectrum and Geometrical Structure of Thiozone, S₃

Michael C. McCarthy,* Sven Thorwirth, Carl A. Gottlieb, and Patrick Thaddeus

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, and
Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

Received January 20, 2004; E-mail: mccarthy@cfa.harvard.edu

Elemental sulfur has the largest number of allotropes of any element in the periodic table, and has been the subject of many experimental and theoretical studies. Small sulfur clusters (S₂–S₈) serve as important benchmarks for the accuracy of quantum chemical calculations because their structures and relative stabilities are sensitive to effects such as electron correlation.¹ Such clusters are also of astronomical interest: they are thought to play important roles in the volcanically driven atmosphere of Io,² the innermost Galilean moon of Jupiter, in the photochemistry of the lower atmosphere of Venus,³ and in the circumstellar shells of carbon-rich evolved stars.⁴

Our knowledge of the electronic ground state and geometrical structure of small sulfur clusters is fragmentary. It is well known that S₂, like O₂, has a triplet ground state (³Σ⁻), but there is little direct experimental information on larger clusters from S₃ to S₅. In contrast, the structure of ozone O₃ has been known for more than 50 years.⁵ Larger sulfur clusters S_n, *n* > 5, unlike oxygen clusters of the same size, occur as stable monocyclic rings, and many of these (*n* = 6–8, 10–13, etc.) have been well-characterized by X-ray crystallography and infrared spectroscopy.⁶ Several sulfur clusters, starting at S₃, are calculated to be polar, with dipole moments of a few tenths of one Debye, and therefore are good candidates for detection by Fourier transform microwave (FTM) spectroscopy, where rotational line intensities are proportional to the first power of the dipole moment, not its square, as in conventional spectroscopy. With this technique, we have now detected S₃ and by isotopic substitution determined its geometrical structure to high precision.

Thiozone is stable at fairly high temperature, and its optical and vibrational spectra have been detected in solid argon⁷ and in the gas phase⁸ at low-resolution, but high-resolution observations to determine its structure have not been reported.⁹ Ab initio calculations indicate that the most stable isomer is bent with the C_{2v} symmetry shown in Figure 1 and that the electronic ground state is singlet ¹A₁. A nonpolar singlet ring isomer with D_{3h} symmetry is calculated to lie only 5–10 kcal/mol higher in energy,^{1,10,11} and the lowest triplet state, ³A₁ with C_{2v} symmetry, is calculated to lie at 14–18 kcal/mol above ground. The calculated dipole moment of the singlet isomer in Figure 1 is 0.51 D.¹²

The structure of thiozone has proven to be a computational challenge because the S–S bond length is quite sensitive to the level of theory, the size of the basis set employed, and the participation of the low-lying 3d orbitals in bonding. More than 30 theoretical studies have been published, ranging from Hartree–Fock to high-level coupled cluster calculations [CCSD(T)]. The bond, for example, is calculated to be as short as 1.888 Å (HF/3-21G*) or as long as 1.980 Å (BLYP/DZP).¹³ The apex angle is generally less sensitive to the level of calculation, with different techniques yielding values in the range 117–118°.

We detected the rotational spectrum of S₃ by means of FTM spectroscopy of a molecular beam – the same technique recently

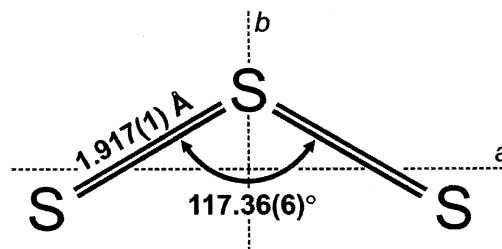


Figure 1. Experimental structure of thiozone, an asymmetric top molecule with C_{2v} symmetry. Estimated uncertainties in units of the last significant digit are given in parentheses. The bond order is only approximate.

used to identify the structurally similar silicon trimer¹⁴ and more than 110 other reactive molecules,¹⁵ including a large number of organic radicals and carbenes. Reactive molecules are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve, the gas in the present work being either hydrogen sulfide H₂S (1.0%) heavily diluted in a neon or argon buffer, or sulfur vapor (0.1%) in neon which was produced by flowing the buffer gas over sulfur powder resistively heated to 185 °C.

A search for S₃ was undertaken in the frequency band 20–25 GHz, where several strong rotational lines are expected. A fairly large search in frequency was required, because S₃ is not strongly bent, and its moment of inertia along the *a*-axis is quite sensitive to the molecular structure; even small changes in the bond length (i.e., ±0.02 Å) or apex angle (±0.2°) can shift rotational lines by 10–20% in frequency. Several tests quickly established that the carrier of one of the lines near 22 GHz only contains sulfur. Because of the high signal-to-noise, the corresponding lines (2_{1,1}-2_{0,2}) of the two mono-³⁴S isotopic species were then readily detected, despite the low fractional abundance of this isotope (4.2%). The close agreement (to 1%) between the observed frequency shifts of the isotopic species and those predicted from the geometry in Figure 1 is strong evidence that the assigned lines are produced by S₃ and no other sulfur cluster. Although H₂S was used at first as a precursor gas because it is a good source for sulfur chains such as HS₂, H₂S₂, and H₂S₃,¹⁶ it was then found that sulfur vapor in a neon buffer yielded 25 times stronger lines of S₃.

A total of 17 *b*-type transitions of ³²S₃ up to *J* = 12 and *K_a* = 2 between 9 and 40 GHz have now been measured. Spectroscopic constants were determined by fitting a theoretical spectrum calculated from a standard asymmetric-top Hamiltonian with centrifugal distortion to the observed frequencies. With three rotational constants and all five quartic centrifugal distortion constants (see Table 1), a fit with an rms of only 1 kHz is achieved, in excellent agreement with the 2–4 kHz measurement uncertainty. Sixteen lines of ³⁴SS₂ and nine lines of S³⁴SS have also been detected (the larger number of lines for the former because ³⁴S substitution at one of the equivalent sulfur atoms breaks the C_{2v} symmetry, enabling transitions normally symmetry-forbidden to be

Table 1. Rotational Constants of Isotopic S₃ (in MHz)^a

constant	SSS	S ³⁴ SS	³⁴ SSS
A	23972.581(1)	23033.906(2)	23738.354(2)
B	2948.5467(3)	2948.6856(6)	2861.0127(4)
C	2622.2913(2)	2610.6946(5)	2550.1327(4)

^a 1σ uncertainties (in parentheses) are in the units of the last significant digits. The best-fit centrifugal distortion constants (in MHz) for the normal isotopic species are: $D_J = 0.797(3) \times 10^{-3}$, $D_{JK} = -20.33(5) \times 10^{-3}$, $D_K = 0.5033(2)$, $d_1 = -0.1628(3) \times 10^{-3}$, and $d_2 = -6(1) \times 10^{-6}$.

observed). A more complete account of the laboratory measurements and data analysis will appear elsewhere.

Because of the symmetry of S₃, only two geometrical parameters are needed to characterize its structure. An empirical (*r*₀) structure was derived (Figure 1) by adjusting the length of the S–S bond and the apex angle to reproduce the three measured rotational constants of the three isotopic species. The length of the S–S bond (1.917 Å) is close to that of S₂ (1.889 Å), indicating substantial double-bonding. The angle (117.4°) is within 2° of that for the isovalent molecules O₃ (116.8°), SO₂ (119.5°), and S₂O (118°), indicating sp² hybridization for the apex sulfur atom.¹⁷ The separation between the terminal S atoms (3.150 Å) agrees fairly well with the van der Waals distance between S atoms in the solid allotropes, confirming that S₃ is best described as a bent chain rather than a three-membered ring. A structure incorporating theoretical corrections for zero-point vibration will be presented elsewhere.¹²

Starting with sulfur vapor in neon, in excess of 5×10^{12} S₃ clusters are produced in our molecular beam per gas pulse. This abundance, derived from line intensities relative to those of the stable molecule OCS at a known fractional abundance (i.e., 1% OCS in Ne), is comparable to that achieved for Si₃ (10¹³/pulse).¹⁴ At this high concentration, the high-resolution infrared and optical spectra of S₃ should be detectable with fairly standard spectroscopic techniques. The low-resolution spectrum near 410 nm that has been attributed to the C_{2v} form⁸ may serve as a starting point for optical experiments with our rotational cold ($T_{\text{rot}} \approx 3$ K) molecular beam.

Thiozone may be abundant on Io, where S₂ and SO₂ are readily observed,¹⁸ and it may be detectable in the interstellar gas as well. Because of widespread volcanism, S₂ and SO₂ are ejected in large quantities into the atmosphere of Io, where they drive a rich sulfur chemistry that has long fascinated planetary scientists. The red deposit from the plume of the volcano Pele is claimed to come from ultraviolet photolysis and polymerization of S₂ to S₃ and S₄.^{2,18} S₃ is also of interstellar interest: about 10% of the 130 molecules detected in space contain sulfur; SiS, a molecule with two second-row elements, is so abundant in the circumstellar shell of the carbon star IRC+10216 that six rare isotopic species have been detected.¹⁹ With the precise rest frequencies that the present work provides, dedicated searches with large radio telescopes can now be undertaken for S₃ in the solar system and throughout the Galaxy. A list of the most relevant astronomical lines will be given elsewhere.

Because of the high concentration achieved here for S₃, larger sulfur clusters may be detectable with the present technique. Ab initio calculations predict that S₄ and S₅ have singlet ground or extremely low-lying electronic states that are polar, with dipole moments comparable to or larger than that of S₃. The low-lying

polar state of S₄ is calculated to have a dipole moment of 0.87 D,²⁰ a planar *cis* structure with C_{2v} symmetry,^{1,10} and a number of accessible rotational transitions.

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Note Added in Proof. The millimeter- and submillimeter-wave spectra of S₃ have now been detected, confirming the present geometrical structure, and yielding a better set of centrifugal distortion constants. The key rotational frequencies of S₃ into the far-IR can now be calculated to better than 1 ppm, more than adequate for an astronomical search. Following completion of the present work, S₄ was detected here by FTM spectroscopy, and its geometrical structure was determined to high precision by isotopic substitution.

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