

Tetrasulfur, S₄: Rotational spectrum, interchange tunneling, and geometrical structure

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The rotational spectrum of S₄ has been observed for the first time in an electrical discharge through sulfur vapor. Two techniques have been used: Fourier transform microwave spectroscopy and long-path millimeter-wave absorption spectroscopy. Small, but systematic shifts of the measured transition frequencies of the normal isotopic species indicate that S₄ has C_{2v} symmetry but with a low-lying transition state of D_{2h} symmetry, yielding interchange tunneling at 14.1(2) kHz in its ground vibrational state. From the rotational constants of the normal and the single ³⁴S isotopic species, an experimental (r₀) structure has been derived: S₄ is a singlet planar trapezoid with a terminal bond length of 1.899(7) Å, a central bond of 2.173(32) Å, and an S-S-S angle of 103.9(8)°. Like thiozone (S₃), S₄ is a candidate for detection in the atmosphere of the Jovian moon Io and in other astronomical sources. © 2004 American Institute of Physics. [DOI: 10.1063/1.1769372]

Sulfur has more allotropes than any other element, and an unusually large variation in its bonding properties; S-S single bonds, for example, differ in length by as much as 0.2 Å, or 10%, and bond angles in sulfur rings vary by as much as 10°.¹ Sulfur clusters therefore provide challenging tests for quantum chemical calculations of molecular structure. For S₆ and larger clusters, rings are the most stable allotropes,² but smaller clusters are generally most stable as bent chains. The allotropes of S₄ and S₅ are particularly interesting because they exhibit a large number of chain and cyclic structures. Small sulfur clusters (S₂–S₈) are also of astronomical interest, because they may exist in the volcanically driven atmosphere of Io (Refs. 3 and 4) (the innermost Galilean moon of Jupiter), in comets,⁵ in the atmosphere of Venus,⁶ and in the circumstellar shells of carbon-rich evolved stars.⁷

The S₄ molecule is one of the most poorly understood small sulfur clusters. Despite a number of theoretical and experimental investigations,^{8,9} there is still no agreement as to the electronic and geometrical structure of its most stable isomer, for which at least six different structures have been calculated. Recent calculations^{9–11} favor the singlet planar trapezoidal structure with C_{2v} symmetry shown in Fig. 1; a singlet rectangular ring of D_{2h} symmetry, calculated to lie ~1 kcal/mol higher in energy, is predicted to be a transition state for interchange tunneling between planar trapezoidal *cis* structures. Several other stable isomers, including *trans* (C_{2h}) and helical (C₂) molecules and a branched three-membered ring (C_s), lie at least 10 kcal/mol higher in energy.^{8,9,11} The relative isomeric energies and other properties, including geometries and dipole moments, of the S₄ isomers is found to be extremely sensitive to the sophistication of the theoretical methods employed; high-levels of electron correlation and multireference treatments are needed to achieve accurate results.

Trapezoidal S₄ in Fig. 1 has a substantial dipole moment, calculated at the coupled cluster level of theory¹² to be

1.15 D, and as a result a fairly intense rotational spectrum across the entire radio band. Because of its C_{2v} symmetry and its two pairs of equivalent sulfur nuclei with Bose–Einstein statistics, its rotational spectrum is that of a somewhat prolate asymmetric top ($\kappa = -0.544$) with *b*-type transitions, and a rotational wavefunction restricted for the normal (³²S₄) isotopic species to symmetric ($K_a K_c = ee$ or oo) levels.

We report here measurement of the rotational spectrum of S₄ over nearly two decades in frequency. The centimeter-wave transitions were measured at very high-resolution ($\nu/\delta\nu \sim 10^7$) in a molecular beam by Fourier transform microwave (FTM) spectroscopy, the millimeter-wave transitions at lower, but still high-resolution (3×10^5) in a long-path absorption cell. In either case, S₄ was produced in sulfur vapor subject to an electrical discharge, which fragmented the dominant S₈ ring into a variety of smaller clusters—a technique we recently used to measure the radio spectrum of thiozone, S₃.¹³

In our FTM spectrometer, reactive molecules are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse from a fast mechani-

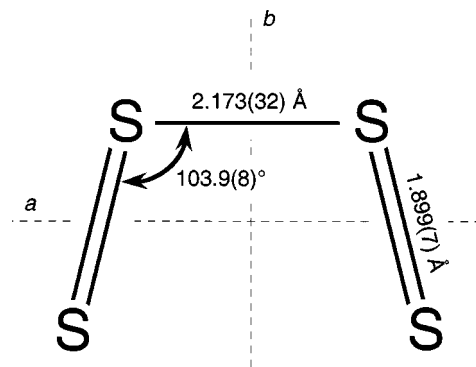


FIG. 1. Experimental (r₀) structure of S₄, a planar asymmetric top with C_{2v} symmetry. The bond order is only approximate.

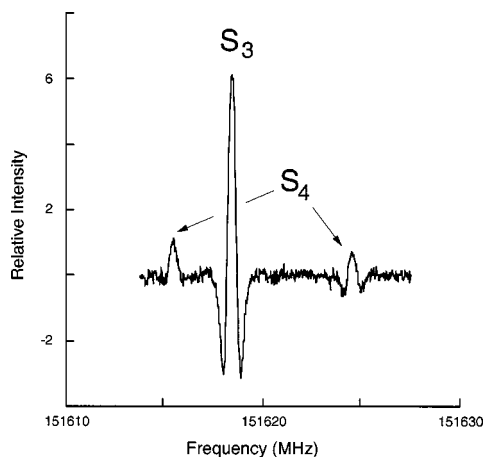


FIG. 2. A small part of the millimeter-wave spectrum through a discharge of sulfur vapor in argon, showing rotational lines of S₃ (31_{4,28}–31_{3,29}) and S₄ (49_{2,48}–48_{1,47} and 48_{2,46}–47_{3,45}). Frequency modulation was used to suppress 1/*f* noise, yielding the observed second-derivative line shapes. The integration time here is 2 min/MHz.

cal valve, the present gas mixture being sulfur vapor (~0.1%) in neon, produced by flowing neon over sulfur powder heated to about 185 °C. Free expansion from the nozzle into a large vacuum chamber forms a Mach 2 supersonic beam with a kinetic and rotational temperature in the moving reference frame as low as 1 K. As the beam expands along the axis of a large high-*Q* Fabry–Perot microwave cavity, a rotational transition is excited by a short (1 μsec) pulse of resonant microwave radiation, which decays very rapidly once the microwaves are turned off by a fast PIN diode switch. Line radiation by the coherently rotating molecules is then detected by a sensitive receiver.

A search for the fundamental 1_{1,1}→0_{0,0} transition of S₄ was first undertaken near 6 GHz. This transition is predicted to be quite intense in our rotationally cold molecular beam, and to require only a limited search of about 1 GHz. In the course of the search, a strong unidentified line was observed near 6.1 GHz, which is only produced in the presence of an electrical discharge, and exhibits no Zeeman effect (when a permanent magnet is brought near the molecular beam). Owing to the high signal-to-noise, the corresponding lines of the two ³⁴S isotopic species were then readily detected, in spite of the low fractional abundance (4.2%) of ³⁴S. The close agreement (to 2%) between the observed frequency shifts of the isotopic species and those predicted from the geometry in Fig. 1 is strong evidence that the assigned lines are produced by S₄ and no other sulfur cluster. Many other FTM lines of S₄ were then assigned.

To better measure centrifugal distortion, S₄ was then studied with a millimeter-wave spectrometer operating between 70 and 900 GHz,¹⁴ with S₄ now produced in a large, low-pressure dc discharge by flowing Ar over sulfur powder heated to 70 °C. The strongest lines were observed under similar conditions to those that produce the strongest lines of S₃: a discharge current of 20 mA and a pressure of about 45 mTorr. The millimeter-wave lines of S₄ are roughly ten times weaker than those of S₃ (Fig. 2). The mole fraction of S₄ is 2 × 10⁻⁴, approximately five times smaller than that of S₃

TABLE I. Rotational constants of isotopic S₄ (in MHz).

Constant	SSSS	S ³⁴ SSS	³⁴ SSSS
A	4655.33365(6) ^a	4586.5206(2)	4587.4305(2)
B	2221.53896(5)	2198.8733(2)	2176.3209(2)
C	1502.37880(3)	1484.83185(7)	1474.59813(7)

^a1σ uncertainties (in parentheses) are in the units of the last significant digits. The best-fit value for the energy separation between the O⁺–O⁻ interchange tunneling states is 14.1(2) kHz. See text.

[assuming a dipole moment of 1.15 D for S₄ and 0.51 D for S₃ (Ref. 12)].

Eighty-four *b*-type transitions of ³²S₄ up to *J*=12 and *K_a*=6 have been measured between 5 and 40 GHz, and 63 transitions up to *J*=89 and *K_a*=28 between 145 and 275 GHz. Sixty-nine transitions of ³⁴SS₃ and 70 of S³⁴SS₂—some symmetry forbidden in the normal isotopic species—have also been detected at centimeter wavelengths. Spectroscopic constants for the two single ³⁴S isotopic species were determined by fitting to the observed frequencies a theoretical spectrum calculated from a standard asymmetric top Hamiltonian. With three rotational constants (see Table I) and the complete set of five quartic centrifugal distortion constants, fits with a rms of less than 1 kHz are achieved, in excellent agreement with the estimated 2–3 kHz measurement uncertainty. Attempts to reproduce the centimeter-wave data of the normal isotopic species by an identical procedure, however, yield a rms (14 kHz) more than ten times larger, and small, but significant residuals: all are centered within a few kilohertz of ±15 kHz, the sign of the residual depending on whether the transition is *ee*→*oo* or *oo*→*ee*.

These systematic discrepancies are readily explained if the molecule belongs to the group isomorphic with *D*_{2h}(*M*) (i.e., the rectangular ring), with a barrier to interchange that is so low as to allow detectable tunneling.¹⁵ In this case, the vibrational ground state is split into symmetric O⁺ and antisymmetric O⁻ levels by an amount that depends on the height of the barrier. The observable microwave transitions will connect tunneling states of different parity, and for non-identical nuclei would occur as closely spaced doublets separated in frequency by twice the O⁺–O⁻ energy splitting, i.e., twice the interchange tunneling frequency Δ*ν*. Owing to the Bose–Einstein statistics for ³²S₄, however, one state in each tunneling pair is missing in the normal isotopic species. This produces an apparent shift rather than a splitting of each rotational level. If the energy term *E*_{O⁺–O⁻} is included in the Hamiltonian, the rms of the fit decreases to less than 1 kHz, and the interchange tunneling frequency is determined to nearly 1%: Δ*ν*=14.1(2) kHz. The broken symmetry in the rare isotopic species quenches interchange tunneling and no splitting is observed. A more complete account of the laboratory measurements and data analysis will appear elsewhere.

Tunneling is remarkable in S₄ because it requires a large displacement (~0.5 Å) of four heavy atoms. It is detected here only because of the high spectral resolution of the FTM spectrometer, and the low barrier to tunneling (see Fig. 3), calculated by Gupta and Stanton to be only 530 cm⁻¹ (1.53 kcal/mol), on the basis of a high-level coupled-cluster

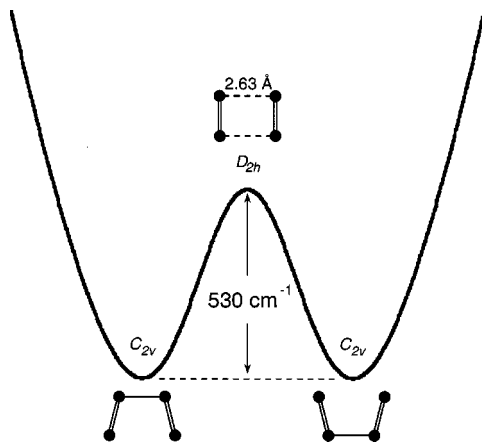


FIG. 3. The double-minimum potential of S_4 , showing the C_{2v} structure and the D_{2h} transition state. High-level *ab initio* calculations find that the barrier height is 530 cm^{-1} (Ref. 12). The distance between the S_2 dimers in the transition state is the average of the central S-S bond length (2.173 \AA) and the separation between the terminal S atoms (3.085 \AA) in the C_{2v} structure.

calculation.¹² The small effect of tunneling is marginally detected in the millimeter-wave spectra, owing to the larger experimental uncertainties.

Neglecting the small shifts caused by tunneling, the geometrical structure of S_4 was precisely determined on the assumption of planarity and C_{2v} symmetry. The r_0 structure in Fig. 1 was derived by adjusting the three geometrical parameters—the lengths of the terminal and central S-S bonds, and the S-S-S angle—to reproduce the three rotational constants of the three observed isotopic species in Table I. The length of the terminal bond found in this way (1.899 \AA) is close to that of S_2 (1.892 \AA ; Ref. 16), indicative of a strong double bond, while the central bond (2.173 \AA) may be described as a long single bond. The bonding is qualitatively similar to that in S_2O_2 , a molecule of similar structure¹⁷ with a fairly weak central S-S bond.¹⁸

The present structure of S_4 provides a sensitive test for *ab initio* calculations. More than 20 different theoretical studies of S_4 have been reported.^{9–11,19,20} Because of the importance of electron correlation and the need to consider many electron configurations, calculated structural parameters differ considerably. The terminal bond, for example, varies from 1.92 to 1.96 \AA , which is more than 0.02 \AA longer than the empirical value here. The calculated central bond varies even more—from 2.08 to as much as 2.23 \AA —but is consistently longer than a standard S-S single bond (2.06 \AA ; Ref. 21); most calculations underestimate the length of this bond by 0.03 \AA or more. The S-S-S angle is somewhat less sensitive to the level of calculation, with different methods yielding values in the range 106° – 112° , consistent with the 106° characteristic of many sulfur rings.²² The angle derived here (103.9°), however, is smaller than these by at least several degrees.

In our molecular beam, about 1×10^{13} S_4 clusters are produced per gas pulse with sulfur vapor in neon, about twice that estimated for S_3 ,¹³ assuming a rotational temperature of 2 K . At this concentration, the optical spectrum of S_4 (Ref. 23) should be detectable with standard laser techniques such as cavity ringdown spectroscopy or resonant two-color,

two-photon ionization spectroscopy. High-resolution gas-phase infrared and Raman spectroscopy of S_4 are also worth undertaking to provide additional information on the shape of the potential.

Because the lines of S_4 we observe are so strong (one minute of integration typically yields a signal-to-noise of 500), other isomers may be detectable. A good candidate is a predicted branched three-membered ring with an $^1A'$ electronic state and a nonplanar geometry.⁹ It is calculated *ab initio* to lie 8.8 kcal/mol above the trapezoid here, and to be quite polar (1.6 D) with comparable components of the dipole moment along the a - and c -inertial axes.

Because comparable amounts of S_3 and S_4 are produced by fragmentation of S_8 in our molecular beam, one would not be surprised if even larger clusters could be detected by FTM spectroscopy, in particular the polar isomers of S_5 , S_6 , and S_7 . Theoretical calculations predict that S_5 has a singlet ground electronic state, a half-chair ring structure of C_5 symmetry,¹⁹ and a dipole moment of 0.39 D .²⁰ A low-lying polar form of S_7 with a cyclic chair structure has also been predicted.

Trisulfur monoxide S_3O is a good candidate for laboratory detection now that strong lines of isovalent S_4 have been found. *Ab initio* calculations conclude that the ground state isomer has a *cis* planar structure²⁴ like S_4 and S_2O_2 , and sizable dipole moments along its a - and b -inertial axes.²⁵ A polar *trans*-planar isomer of S_3O , calculated to lie only 4 kcal/mol above the ground state, is also a good candidate for detection. S_3O may be abundant in a discharge of sulfur-rich SO_2 vapor where S_2O (Ref. 26) and S_2O_2 (Ref. 17) are readily detected.

Both S_3 and S_4 may exist in the atmosphere of Io, where atomic sulfur and S_2 have already been observed in the ultraviolet by the Hubble Space Telescope.^{27,28} Photochemical models⁴ predict that the vapor of active volcanoes such as Pele contain sulfur clusters up to S_{10} . Because S_3 and S_4 are polar, it may be possible to detect them in the radio band and precisely determine their column densities. Atomic sulfur has no transitions in this band and S_2 , like O_2 , has only weak magnetic-dipole transitions. As a result, the column densities of both are poorly constrained from the ultraviolet observations.²⁷ With the precise rest frequencies that the present work provides, dedicated searches with powerful radio telescopes and interferometers can now be undertaken; a list of the most relevant astronomical lines with precise frequencies will be published.

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