

IR Spectroscopy

Vibrational Spectrum and Gas-Phase Structure of Disulfur Dinitride (S₂N₂)

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In memory of Marilyn E. Jacox

Abstract: Gas-phase FTIR spectra of the v_6 (B-type) and the v_4 (C-type) fundamental bands of S_2N_2 (D_{2h}) were recorded with a resolution of ≤ 0.004 cm⁻¹ and the vibrational spectrum of S_2N_2 (D_{2h}) in solid Ar has been revisited. All IR-active fundamentals and four combination bands were assigned in excellent agreement with calculated values from anharmonic VPT2 and VCI theory based on (explicitly correlated) coupled-cluster surfaces. Accurate experimental vibrational ground- and excited-state rotational constants of ${}^{32}S_2{}^{14}N_2$ are

Introduction

Cyclic disulfur dinitride, S_2N_{2r} , has been of ongoing interest since it has first been synthesized sixty years ago by Goehring and Voigt.^[1] About ten years later War and Chapman recorded a low-resolution vapor-phase IR spectrum utilizing a long-path multi-reflection cell.^[2] The IR spectrum, and particularly the band contours of the two most prominent bands at $\tilde{\nu} = 792$ and 475 cm^{-1} indicate a near square-planar ring structure having alternate SN bonds and D_{2h} symmetry.^[2] The vapor-

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obtained from a rovibrational analysis of the v₆ and v₄ fundamental bands, and precise zero-point average r_z ($R_z(SN) =$ 1.647694(95) Å, $\alpha_z(NSN) = 91.1125(33)^\circ$) and semi-experimental equilibrium structures ($R_e(SN) = 1.64182(33)$ Å, $\alpha_e(NSN) =$ 91.0716(93)°) of S₂N₂ have been established. These are compared to the solid-state structure of S₂N₂ and structural properties of related sulfur nitrogen compounds and to results of ab initio structure calculations.

phase photoelectron $^{[3]}$ and UV absorption spectra $^{[4]}$ of S_2N_2 were found to be consistent with the proposed molecular structure.

The S_2N_2 cycle (D_{2h}) represents the smallest known cyclic sulfur-nitrogen molecule. It has been the subject of extensive research owing to its solid-state polymerization producing superconducting polythiazyl, $(SN)_{xr}^{[5,6]}$ its postulated 6π -electron aromaticity,^[7] and due to its controversial singlet diradical character.^[8] The solid-state structure of S₂N₂ obtained from X-ray single-crystal diffraction at -130°C also supports a near square-planar ring structure.^[5] The N-S bond lengths of 1.651(1) and 1.657(1) Å, and the SNS and NSN angles of 90.42(6) and $89.58(6)^{\circ}$, respectively, are surprisingly close to hat of an ideal square ring.^[5] A priori one would not expect hat the bond angles at sulfur and nitrogen both adopt values close to 90.0°. The solid-state structure also revealed intermoecular S-N distances (2.89 Å) well below the sum of the respective van der Waals radii (3.4 Å).^[5] Such intermolecular S…N nteractions likely play an important role in the solid-state polymerization process.^[5,6]

A recent Raman and IR study of natural and ¹⁵N-isotopically enriched matrix-isolated S₂N₂ at 15–35 K confirmed the apparent D_{2h} molecular symmetry by 1) the mutual exclusion of observed IR and Raman bands and 2) the presence of symmetrically equivalent N atoms proven by ^{14/15}N isotope splitting.^[9] On the other hand, a computational study highlighted unexpected low bond pseudorotation barriers of $\leq 2 \text{ kJmol}^{-1}$ for the planar S₂N₂ ring structure, indicating a large deformational flexibility typical of a floppy molecule.^[10]

Although cyclic S_2N_2 has widely been studied, our knowledge about its IR spectrum is far from being complete, and its

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gas-phase structure unconstraint by any intermolecular interactions is still unknown. This deficiency probably arises owing to its low kinetic stability and explosive nature at ambient temperatures.^[1] Also the absence of a permanent dipole moment precludes structural investigations based on molecular rotational spectroscopy. However, ground-state rotational constants, and thus, molecular structure parameters can also be obtained from an analysis of rotationally resolved IR transitions. In part A of this work we have revisited and completed the IR spectrum of pristine S_2N_2 (D_{2h}). The analysis of these spectra provides a most consistent set of fundamental and combination frequencies of cyclic S₂N₂. In part B we present the first gas-phase high-resolution FTIR spectra of $v_4(b_{1u})$ and $v_6(b_{3u})$ of S_2N_2 (D_{2h}) and their rovibrational analysis, and in part C its molecular ground-state and equilibrium structures are evaluated from a joint high-level guantum mechanical and experimental study. Finally in part D the gas-phase structure of free S₂N₂ will be compared with its solid-state structure and with structural properties of related compounds.

Results and Discussion

Part A: Infrared spectrum of Ar matrix-isolated S₂N₂ (D_{2h})

The IR spectrum of Ar matrix-isolated S_2N_2 (D_{2h}) is shown in Figure 1. For a cyclic planar S_2N_2 ring (D_{2h}) involving alternate sulfur and nitrogen atoms the six fundamental modes of vibration are related to the symmetry species $2a_g+b_{1g}+b_{1u}+b_{2u}+b_{3u}$ (Scheme S1 in the Supporting Information). The rule of mutual exclusion applies and the three b_u modes are infrared active. In agreement with previous gas-phase^[2] and matrix-isolation work^[9] only two strong IR bands were observed at $\tilde{\nu} = 789.7$ (v_6 , b_{3u}) and 473.8 cm⁻¹ (v_4 , b_{1u}). In addition we detected the very weak v_5 (b_{2u}) band at $\tilde{\nu} = 655.6$ cm⁻¹ as well as four additional combination bands of v_5 and v_6 , respectively (Figure 1). All these bands are unequivocally attributed to S_2N_2 (D_{2h}) due to their uniform photo-destruction under UV irradiation ($\lambda =$



Figure 1. Ar matrix-isolation (16 K) spectrum of ¹⁵N-enriched (¹⁴N/¹⁵N = 1:1, upper trace, InSb detector, $\tilde{\nu} = 2000-400 \text{ cm}^{-1}$) and of natural S₂N₂ (D_{2h}) (lower trace shifted by -10% transmittance (*T*) for sake of clarity, MCT 600 detector, $\tilde{\nu} = 2000-540 \text{ cm}^{-1}$). Bands due to S₂N₂ (D_{2h}) are indicated. Bands contributed by trapped H₂O and bands due to an unknown species are labeled by asterisks and a rhombus, respectively.

248 or 255 nm).^[11] The position of v_5 in solid Ar is consistent with a reported value of $\tilde{v} = 660.5 \text{ cm}^{-1}$ for polycrystalline S_2N_2 (D_{2h}) at 77 K,^[9] and with a tentatively assigned, very weak A-type feature observed in the gas-phase spectrum at $\tilde{v} = 652 \text{ cm}^{-1}$.^[2]

Like the two most prominent bands also the weak bands revealed a distinct ¹⁵N isotope pattern in experiments using ¹⁵Nenriched samples ($^{14}N/^{15}N = 1:1$; see Figure 2 for the three



Figure 2. Ar matrix-isolation (16 K) spectrum in the region of $\bar{v} = 1750-1380 \text{ cm}^{-1}$ of ¹⁵N-enriched (¹⁴N/¹⁵N = 1:1) S₂N₂ (lower trace) and of a natural sample after subjecting to $\lambda = 248$ nm laser light (depleted, upper trace), showing three combination bands of S₂N₂ (D_{2h}) and their ^{14/15}N isotope pattern. Lines contributed by trapped H₂O and two combination bands associated with photoproducts^[11] are marked by asterisks and rhombuses, respectively.

strongest combination bands). Band positions and isotopic shifts are compiled in Table 1. In most cases the expected triplet splitting of each band was observed. This pattern indicates the presence of three isotopologues and the presence of two symmetrically equivalent N atoms. However, the expected triplet splitting for the weak v_5 and v_2+v_6 bands is apparently perturbed by a slightly larger matrix-site splitting of their central feature, which appeared as closed spaced doublets. Only the strongest matrix sites are quoted in Table 1, and for the above-mentioned doublets of similar intensities averaged frequencies are given.

Fundamental and combination band frequencies of disulfur dinitride, S_2N_2 , have been calculated at different computational levels where anharmonic effects have been accounted for by two different approaches: the second-order perturbation theory (VPT2)^[12] and the vibrational configuration interaction (VCI) theory^[13,14] (Table 2). Despite the very different methods used for this analysis the computational results are generally quite consistent and in convincing agreement with the experimental results. From experimental IR combination and fundamental band positions, the frequencies and the ¹⁵N isotope shifts of IR-inactive modes were estimated and denoted by italic values in Table 1. These estimates account for anharmonic effects taken from the averages of the VPT2 and VCI results. The deviations of these estimates from previously reported Raman frequencies^[9] are remarkable, whereas the gas-phase to

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Table 1. Experimental frequencies and isotope shifts $[cm^{-1}]$ for S_2N_2 (D_{2h}) in solid Ar.						
exp. $\tilde{\nu}^{\mathrm{[b]}}_i$	This work ^[a] $\Delta \tilde{\nu} ({}^{14}N^{15}N)^{[b]}$	$\Delta \tilde{\nu} ({}^{15}N_2)^{[b]}$	exp. $\tilde{\nu}_i^{[b]}$	Reference [9] ^[c] $\Delta \tilde{\nu} ({}^{14}N{}^{15}N){}^{[b]}$	$\Delta \tilde{\nu} ({}^{15}N_2)^{[b]}$	Assignment ^[d]
1696.3 vw	23.2	46.6				$v_1 + v_6 (b_{3u})$
1542.6 vw	20.4	34.9				$v_3 + v_5 (b_{3u})$
1419.2 vw	10.4	19.1				$v_2 + v_6 (b_{3u})$
1280.5 vvw	7.2	15.9				$v_2 + v_5 (b_{2u})$
913	13.6	28.2	934 (Ra, s)		32	v_1 (a _q)
898	13.7	22.2	889 (Ra, s)		21	$v_{3}(b_{1q})$
789.7 s ^[e]	9.6	18.4	789.2 s	10.0	18.8	$v_6 (b_{3u})$
655.6 vw	6.7	12.7				v_{5} (b _{2u})
632	0.6	2	617 (Ra, vs	5)	0	v_2 (a _q)
473.8 m ^[e]	5.6	11.2	473.7 m	6.0	12.1	v_4 (b ₁)

[a] Recorded at 16 K. [b] The strongest matrix sites, relative IR intensities (s = strong, m=medium, vw=very weak), and isotope shifts Δv [cm⁻¹] relative to ${}^{32}S_{2}{}^{14}N_{2}$ are given. Values in italic are estimated positions of infrared-inactive fundamentals obtained from combination band frequencies and computationally predicted anharmonicity corrections (see text). [c] 20 K, IR and Raman (Ra) band positions are given. [d] For the numbering of the fundamental modes v_{i} see Scheme S1 in the Supporting Information. [e] ${}^{32/34}S$ isotope shifts Δv of ${}^{34}S^{32}SN_{2}$ in [cm⁻¹]: 3.5 (v_{6}) and 2.1 (v_{4}).

Table 2. Comparison of experimental band positions (IR intensities in parentheses) and calculated anharmonic frequencies ($[cm^{-1}]$, $\geq 0.02 \text{ km mol}^{-1}$) for S_2N_2 (D_{2h}).						
Exp. ^[a]	VPT2 ^[b] CCSD(T)	VCI ^[c] fc-CCSD(T)-F12	VCI ^[d] CCSD(T)-F12	Assignment		
1696.3 (vw)	1694.4 (0.3)	1713.2 (0.8)	1721.9	$v_1 + v_6 (b_{3u})$		
	1681.5 (< 0.1)	1692.6 (0.1)	1700.6	$v_3 + v_6 (b_{2u})$		
	1549.4 (< 0.1)	1563.6 (0.0)	1572.0	$v_1 + v_5 (b_{2u})$		
1542.6 (vw)	1538.3 (0.3)	1545.6 (0.6)	1553.4	$v_3 + v_5 (b_{3u})$		
1419.2 (vw)	1423.1 (0.4)	1433.2 (0.5)	1440.4	$v_2 + v_6 (b_{3u})$		
	1383.1 (< 0.1)	1397.6 (0.1)	1405.2	$v_1 + v_4$ (b _{1u})		
1280.5 (vvw)	1276.9 (0.2)	1285.6 (0.1)	1292.8	$v_2 + v_5 (b_{2u})$		
913	912.4 (0.0)	921.1 (0.0)	926.1	v_1 (a _g)		
898	903.9 (0.0)	906.8 (0.0)	911.2	$v_{3}(b_{1g})$		
789.7 (s)	788.5 (29.4)	797.4 (34.7)	801.2	v_6 (b _{3u})		
655.6 (vw)	644.1 (1.4)	651.5 (0.9)	655.1	v_{5} (b _{2u})		
632	637.8 (0.0)	639.2 (0.0)	642.8	v_2 (a _g)		
473.8 (m)	472.2 (18.9)	475.8 (16.7)	478.4	$v_4 (b_{1u})$		

[a] Ar matrix 16 K; values in italic are estimated positions of infrared-inactive fundamentals (see Table 1). [b] VPT2 anharmonic analysis at the conventional CCSD(T)/ pCVTZ level (intensities in [km mol⁻¹]). [c] Vibrational configuration interaction (VCI) calculations based on a fc-CCSD(T)-F12a potential energy surface (PES) (intensities in [km mol⁻¹]). [d] VCI based on a PES obtained from explicitly correlated CCSD(T)-F12a calculations including core-correlation contributions.

Ar-matrix shifts for the two measured IR gas-phase frequencies (see below) is less than 3 cm^{-1} .

Disulfur dinitride, S_2N_2 , is a challenging molecule for quantum chemical calculations as core-correlation effects and relativistic corrections cannot be neglected. The VCI results without inclusion of core-correlation effects are, however, in markedly better agreement with our experimental results than those which account for these corrections. This is probably caused by error compensation in the frozen core calculations. Error compensations are also assumed for the VPT2 results, where the limitations due to a rather small basis set and the quartic force field should lead to non-negligible deviations. We have further considered scalar-relativistic effects in the electronic structure calculations. Within the harmonic approximation, these effects account for an additional drop of the calculated fundamental modes by about -2 to -3 cm^{-1} (see Table S1 in the Supporting Information). Taking these corrections into account the VCI fundamental values including core-correlation effects are generally improved, but still tend to overestimate the experimental data.

Part B: Rovibrational analysis of the v_4 (b_{1u}) and v_6 (b_{3u}) bands of cyclic ${}^{32}S_2{}^{14}N_2$ (D_{2h})

The three b_u modes are readily distinguished by their rotational band contours: C-type (v_4 , b_{1u}), A-type (v_5 , b_{2u}), and B-type (v_6 , b_{3u} , Scheme S1 in the Supporting Information). Overviews of the strong B-type band (around $\tilde{v} = 792 \text{ cm}^{-1}$) and of the weaker C-type band (around 475 cm⁻¹) are shown and compared to simulated spectra in Figures 3 and 4, respectively. The very weak v_5 fundamental has not been detected in our gas-phase spectra.

Ground- and upper-state energy levels of assigned B-type (v_6) and C-type (v_4) transitions were fitted by using a Watson A-type Hamiltonian^[15] written in the I^r representation (x = b, z = a, y = c, Equation (S1) in the Supporting Information), and the results of the rovibrational analysis are summarized in Table S2 in the Supporting Information. No noticeable vibration-rotation perturbations were observed, and altogether 2421 B-type and 1734 C-type transitions were assigned and included into the fit. The final set of ground-state parameters (rotational constants and quartic centrifugal distortion constants) was achieved from a combined set of 2881 ground-state combination-differences (GSCDs) derived from B- and C-type transitions. This set is quoted in Table 3 and compared to computationally predicted values in Table S3 in the Supporting Information. The groundstate parameters provided a final set of ground-state energy levels. To these the ν_1 and ν_4 observed line positions were added to yield the respective upperstate energy levels from which the v_4 and $v_6 =$

1 upper-state parameters (vibrational energies, rotational and centrifugal distortion constants) listed in Table 3 were obtained. The agreement between observed and simulated transitions finally achieved is excellent and is exemplified for the congested Q branch region of the v₄ C-type band near $\tilde{\nu}$ = 474.8 cm⁻¹ in Figure S1 in the Supporting Information.

For a planar molecule in its equilibrium configuration the inertial defect $\Delta_{\rm e}$ is zero [Eq. (1a)].

$$\Delta_{\rm e} = I_{\rm e}^{\rm C} - I_{\rm e}^{\rm A} - I_{\rm e}^{\rm B} = 0 \tag{1a}$$

where

$$a_{p}^{X} = h/(8\pi^{2}cX_{e})$$
 (with $X = A$, B , and C) (1b)

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Figure 3. Overview of the B-type band v_6 (b_{3u}) of ${}^{32}S_2{}^{14}N_2$ in the $\tilde{\nu} = 792$ cm⁻¹ spectral region (bottom trace, optical path length 274 mm, 0.55 mbar, res. = 0.0021 cm⁻¹) and the simulated spectrum (upper trace, selection rules: $\Delta |K_a|$ and $\Delta |K_c| =$ odd), which accounts for calculated line positions and relative line intensities.



Figure 4. Overview of the C-type band v_4 (b_{1u}) of ${}^{32}S_2{}^{14}N_2$ in the $\tilde{\nu}$ =475 cm⁻¹ spectral region (bottom trace, optical path length 320 cm, 0.4 mbar, res. =0.004 cm⁻¹) and the simulated spectrum (upper trace, selection rules: $\Delta |K_a| = \text{odd}$ and $\Delta |K_c| = \text{even}$), which accounts for calculated line positions and relative line intensities. Stars indicate lines contributed by residual traces of water vapor within the spectrometer.

Table 3. Vibrational energies, rotational and centrifugal distortion constants [cm⁻¹], and inertial defects Δ_v (in [uÅ²]) for the ground, $\nu_4\!=\!1$ and $\nu_6\!=\!1$ states of $^{32}S_2^{-14}N_2$ ($D_{2\hbar}$).^[a]

	Ground state	$\nu_4 = 1$	$\nu_6 = 1$		
Ev		474.77517(1)	792.09455(1)		
B _v	0.43570382(890)	0.433298357(65)	0.436996757(30)		
α_{i}^{A}		0.0024055(89)	-0.0012929(89)		
B _v ^B	0.19831068(820)	0.197337390(71)	0.197555775(28)		
α_{i}^{B}		0.0009734(82)	0.0007549(82)		
B _v ^C	0.13615392(840)	0.136141150(64)	0.136198654(11)		
α_{i}^{c}		0.0000128(84)	-0.0000447(84)		
$\Delta_{\kappa} \times 10^7$	3.6503(600)	3.20113(120)	3.824346(300)		
$\Delta_{\rm JK} imes 10^9$	0 ^[b]	28.064947(120)	2.0272(310)		
$\Delta_{J} \times 10^{8}$	4.689(260)	4.52109(230)	4.775802(760)		
$\delta_{\rm K} \times 10^8$	7.79(170)	5.9977(250)	8.16614(500)		
$\delta_{J} \times 10^{8}$	1.426(140)	1.34286(150)	1.373703(400)		
$\Delta_{\sf V}$	0.1163(84)	-0.5061	-0.1347		
[a] A reduction, <i>I</i> ^r representation, one standard deviation quoted in paren- theses. [b] Fixed.					

Here $I_e^{\rm C}$ is the moment of inertia (in [uÅ²] units) related to the principal axis perpendicular to the molecular plane. Due to the dependence of the principal moments of inertia $I_0^{\rm X}$ from zero-point motion the zero-point inertial defect Δ_0 is actually non-zero. Nevertheless, the small positive value for Δ_0 of 0.1163(84) uÅ² (Table 3) can be regarded as evidence for the planarity of ${}^{32}S_2{}^{14}N_2$, because Δ_0 values of non-planar molecules are essentially negative. The assignment of v_4 to the ring-puckering mode is fully consistent with its larger negative inertial defect Δ_4 , whereas the negative sign observed for Δ_6 is probably due to dominant contributions from cross-term Coriolis interactions between v_4 and v_{67} as any contributions to Δ_6 from the in-plane vibrations are expected to be positive.^[16]

A further unambiguous confirmation of the D_{2h} ground-state structure comes from an inspection of the relative line intensities of the rovibrational transitions for the ${}^{32}S_{2}{}^{14}N_{2}$ species. The total wavefunction must remain unchanged during any twofold rotation (C_{2a} , C_{2b} , or C_{2c}) around the *a*, *b*, or *c* inertial axes, in which the two pairs of ¹⁴N and ³²S Boson-type nuclei (with $I_n = 1$ and 0 nuclear spin, respectively) are exchanged (Scheme S1 in the Supporting Information). This results in a two-to-one intensity alternation for transitions involving ground-state quantum numbers with ($K_a'' = even$, $K_c'' = even$) and ($K_a'' = \text{odd}$; $K_c'' = \text{odd}$), respectively, whereas all transitions involving $(K_a'' + K_c'' = \text{odd})$ should be absent in the spectrum (Scheme S1 in the Supporting Information).^[17] This intensity behavior is indeed confirmed for all C- and B-type transitions of v_4 and v_6 , respectively, and illustrated for some v_4 C-type transitions in Figure 5.

Part C: Zero-point and equilibrium molecular structures of $\mathsf{S_2N_2}$

In the determination of geometrically consistent structures from experimentally derived ground-state rotational constants several inconsistencies may arise due to 1) the dependence of the experimental parameters of the representation and the choice of the reduction of the Hamiltonian,^[15,18] small contaminations of experimental rotational constants by 2) centrifugal distortions,^[18] 3) electronic contributions arising from a coupling of rotational and electronic angular moments related to the rotational *g* tensor,^[18,19] and 4) zero-point vibrational effects leading to non-zero zero-point inertial defects. These inconsistencies have been accounted for by applying various corrections to the initially obtained ground-state coefficients B_0^{\times} (X = A, B,*C*, Table 3). The formulas applied for these corrections are described in the Supporting Information and the results are given in Table 4.

First the zero-point rigid rotor constants X_0 (X=A, B, C) were obtained from the experimental coefficients B_0^x (Table 3) by applying known centrifugal distortion^[15,18] and electronic corrections.^[18,19] The B_0^x constants are slightly smaller than X_0 mainly because of electronic contributions, which are up to three orders of magnitude larger than the centrifugal distortion corrections. These later ones involve the $\tau_{\alpha\alpha\beta\beta}$ ($\alpha,\beta=a,b,c$) constants. They were obtained from linear combinations of the experimental ground-state centrifugal distortion constants



Figure 5. Comparison between the observed (middle trace) and three simulated spectra (top and bottom traces) for an expanded view of the v_4 C-type band of ${}^{32}S_2{}^{14}N_2$ near $\tilde{\nu} = 474.9 \text{ cm}^{-1}$, illustrating the effect of nuclear spin statistical weights (g_s) on the relative line intensities. Some Q-type transitions are indicated by their ground-state quantum numbers [J, $K_a^{"}$, $K_c^{"}$]. In the simulated spectra the relative intensities were computed assuming different weights g_s for transitions involving $K_a^{"}K_c^{"}$ = ee, oo, oe, and eo (e = even, o = odd), respectively. The simulations confirmed the absence of lines with ($K_a^{"} + K_c^{"}$) odd (marked by solid triangles in the spectrum). Furthermore, lines with $K_a^{"}K_c^{"}$ = oo are marked by open triangles and it is clear that the best agreement is achieved for g_s = (6; 3; 0; 0) for ($K_a^{"}K_c^{"}$ = ee; oo; oe; eo).

Table 4. Zero-point and equilibrium rotational constants of S_2N_2 (D_{2h} in [cm ⁻¹]) obtained by experiment and ab initio calculations. ^[a]					
X =	Α	В	С		
B ₀ X[b]	0.4357038(89)	0.1983107(82)	0.1361539(84)		
X ₀ ^[c]	0.435763(11)	0.1983209(83)	0.1361602(84)		
X _z ^[d]	0.434979(79)	0.198056(28)	0.136091(11)		
X _e ^[e]	0.43841(27)	0.19933(10)	0.137028(87)		
$Calcd(1) X_e^{[f]}$	0.43333	0.19712	0.13549		
^{Calcd} (2) X _e ^[g]	0.43440	0.19768	0.13564		
^{Calcd} (3) $X_e^{[h]}$	0.43692	0.19847	0.13634		
[a] For the evaluation of the rotational constants X_{0r} , X_{zr} and X_{e} see the					

Supporting Information. [b] Experimental ground-state rotational constants of ${}^{32}S_{2}{}^{14}N_{2}$. [c] Zero-point rigid rotor constants corrected for electronic contributions by using CCSD(T)/aug-pCVTZ-predicted rotational *g*tensor elements: -0.250 (g_{aa}), -0.097 (g_{bb}), -0.080 (g_{cc}). [d] Rotational constant corresponding to the r_{z} structure. [e] Semi-experimental equilibrium rotational constants. [f] CCSD(T)/cc-pCVTZ level of theory. [g] fc-CCSD(T)-F12a/cc-pVTZ-F12 level. [h] CCSD(T)-F12a/cc-pCVTZ-F12 level.

(Table 3) and are compared to ab initio calculated values in Table S4 in the Supporting Information. Owing to a reasonably small planarity defect in terms of the centrifugal distortion constants $\Delta \tau$ experimental and ab initio $\tau_{\alpha\alpha\beta\beta}$ constants agree very well. As these constants are of the order of 10^{-7} cm⁻¹ the residual centrifugal distortion contributions to the experimental rotational constants B_0^{x} are negligible small given their quoted standard deviation in Table 4.

The diagonal *g*-tensor elements used in the electronic corrections (Table 4) have been calculated at the ab initio CCSD(T)/aug-pCVTZ level of theory. They adopt a negative sign, indicating dominant contributions from a non-zero electronic angular momentum induced by electronically excited

states. Other closed-shell molecules have been reported, where the electronic contributions to the rotational constants are rather large and of similar magnitude as the zero-point vibrational corrections.^[20,21]

The rotational constants X_{z} and X_{e} corresponding to r_z and r_e structures, respectively, were obtained by applying zero-point vibrational corrections to X_0 involving the vibration-rotation interaction constants $\alpha_i^{\chi_{[16,21]}}$ As only the α_4^{χ} and α_6^{χ} values are experimentally available (Table 3), the α_i^{X} constants have been predicted by vibrational perturbation theory carried out to second order (VPT2)^[12,22] at the fc-CCSD(T)-F12a/cc-pVTZ-F12 level of theory (Table S5 in the Supporting Information). The agreement between the experimental and the calculated a_i^{X} constants is excellent, which gives confidence to the respective vibrational corrections summarized in Table 4. The zero-point rotational constants X_z are smaller than X_0 . Here only the harmonic contributions (inclusive Coriolis terms) to the respective α_i^{X} constants were considered, which give rise to small negative vibrational corrections of X_0 . On the other hand the harmonic and anharmonic terms of the α_i^X constants, which are required for the conversion of X_0 to semi-equilibrium rotational constants X_{e} , sum up to a significant positive vibrational correction leading to substantial

larger X_e constants. However, the uncertainties of the calculated vibrational corrections are conservatively estimated to be about 10%. Although such deviations for these contributions are not uncommon^[14] they confine the accuracy in the determination of semi-experimental rotational constants. In Table 4 the semi-experimental equilibrium rotational constants X_e are compared to purely ab initio CCSD(T) calculated values.

The set of the X_z rotational constants provide a vibrationally averaged zero-point structure, that is, the r_z structure. Like the equilibrium r_e structure, the r_z structure does not suffer from the ambiguities introduced by the inertial defect of the planar molecule, and its deviation from r_e is due entirely to the anharmonicity.^[23] A comparison of the r_e and r_z structures with computed coupled-cluster values is provided in Table 5. A good agreement between the semi-experimental and the calculated

Table 5. Comparison of the calculated and the experimental structural parameter of S_2N_2 (D_{2h}). ^(a)					
	R _e	$\alpha_{\rm e}({\rm NSN})$	R _z	$a_{\rm z}({\rm NSN})$	
$\begin{array}{l} experiment^{[b]} \\ VPT2/CCSD(T)^{[c]} \\ VCI/fc-CCSD(T)-F12a^{[d]} \\ VCI/CCSD(T)-F12a^{[e]} \\ best \ estimate^{[f]} \end{array}$	1.64182(33) 1.6512 1.6445 1.6405 1.6421	91.0716(93) 91.09 91.06 91.02 91.02	1.647694(95) 1.6583 ^[c] 1.6504 1.6463 1.6479	91.1125(33) 91.10 91.06 91.06	
[a] Bond length $R(SN)$ in [Å] and angle $\alpha(NSN)$ in [°]. [b] See main text and the Supporting Information. [c] cc-pCVTZ basis set, calculated $R_g(0 \text{ K})$ value instead of R_z . [d] cc-pVTZ-F12 basis set. [e] cc-pCVTZ-F12 basis set. [f] Obtained from explicitly correlated coupled-cluster calculations, CCSD(T)-F12a, including core-correlation effects plus an additive correc- tion for scalar-relativistic effects.					



bond lengths was obtained by using explicitly correlated coupled-cluster calculations including core-correlation effects, which underlines the importance of correlating the 2s and 2p orbitals of the sulfur atoms in combination with very large basis sets. The value obtained by the standard CCSD(T) theory shows a slightly larger deviation than the explicitly correlated coupled-cluster calculations. Once scalar-relativistic effects are added as a correction to the bond length obtained from CCSD(T)-F12a calculations (denoted "best estimate" in Table 5), the agreement with our semi-experimental values is compelling.

Part D: Comparison of related structural properties

The solid-state structure obtained from crystalline S_2N_2 at -130 °C (R = 1.651(1) and 1.657(1) Å, α (NSN) = 89.58(6)°),^[5] revealed bond stretching and a decreased NSN angle compared to the r_{z} structure of free ${}^{32}S_{2}{}^{14}N_{2}$. The most spectacular differences comparing the gas-phase and solid-state structures of S₂N₂ are probably related to the bond angles. In the gas phase the SNS angle at the nitrogen atoms is smaller than α (NSN), whereas the opposite was observed in the crystal. As a consequence, the short cross-ring N-N interatomic distance in the gas phase (r, structure: 2.35270(21) Å) is even more shortened in the solid-state structure (mean value: 2.331(2) Å).^[5] This observation probably accounts for the short intermolecular S-N contacts of 2.890(1) Å of two S₂N₂ units in the crystal structure along the crystallographic a axis. These contacts are significantly smaller than the respective van der Waals distances (3.35 Å),^[5b] and remarkably close to the calculated intermolecular S…N contact in a weakly bound S₂N₂ dimer (2.881 Å).^[4b] This reasoning is supported by crystal structures of adducts between S_2N_2 and Lewis acids, $S_2N_2 \cdot 2A$ ($A = SbCl_5^{[24]}$ and $AlCl_3^{[25]}$),



which revealed significantly increased SNS bond angles of 95.1(4) and 94.9(2)°, respectively.^[24,25] Thus, intermolecular solid-state S…N interactions reduce the partial negative charge at the nitrogen atoms^[26] and may also contribute to the increased intramolecular solid-state S—N bond lengths compared to those in the free S₂N₂ molecule.

A few comments concerning the intriguing S–N bond order in S₂N₂ with respect to structural and spectroscopic (force constants) parameters are probably indicated. It has been concluded that the solid-state S–N bond lengths in S₂N₂ (1.654(1) Å) is nearly half-way between those of a single S–N (1.74 Å) and a S=N double bond (1.54 Å), suggesting a bond order close to 1.5,^[5a] rather than 1.25 expected for 6π -electron aromaticity.^[7] The ambiguity arising from a correlation of S–N bond lengths to suggested bond orders has already been mentioned.^[26] However, one would not readily expect, that the S–N bond lengths of S₂N₂ are longer, and the corresponding stretching force constant are smaller than those of the dimer S_4N_4 ,^[9] revealing polar S⁺–N⁻ single bonds.^[26] This difference is slightly pronounced when the R_g bond lengths obtained from an electron diffraction study of S_4N_4 (1.628(4) Å)^[27] is compared to semi-experimental R_g bond lengths in S_2N_2 (1.6489(8) Å), where the semi-experimental R_e value have been corrected by $^{Calcd}\Delta R = ^{Calcd}R_g$ (0 K)– $^{Calcd}R_e$ by using R_g (0 K) and R_e values obtained within the VPT2 approach at the CCSD(T)/pCVTZ level (Table 5).

Compared to related four-membered ring molecules bearing more strongly polarized bonds (Si₂O₂, Al₂Cl₂) S₂N₂ exhibits a rather high out-of-plane deformation frequency v_4 , leading to a respective force constant f_{oop} (2.58 mdyn Å) for S₂N₂, which was found to be about four times larger than f_{oop} for Si₂O₂ (0.61 mdyn Å) and nearly two orders of magnitude larger than that of AI_2CI_2 ($f_{oop} = 0.03$ mdyn Å).^[9] This relative rigidity of the planar S_2N_2 ring is consistent with the recently reported lowbarrier in-plane bond pseudorotation, that conserves planarity and leads to new ring forms with slightly different bond lengths and bond angles.^[10] From the whole body of these observations it has been concluded that the S-N bond order should be close to one, featuring relatively small σ but pronounced π contribution.^[9] A conclusion, which is however, not consistent with either a polarized π -bonding model outlined recently,^[26] nor with its considerable singlet diradical character, suggesting partial occupation of anti-bonding molecular orbitals.^[4,8] On the other hand, the residual aromaticity from delocalization of π -bonding electrons as well as resonance with diradical structures was shown to provide a relatively large resonance energy,^[8] which in principle conserves the planarity of the S₂N₂ ring.

Conclusion

The IR spectrum of S_2N_2 (D_{2h}) in solid Ar has been revisited. The frequencies of all IR-active fundamentals inclusive of the very weak v_5 band are confirmed and four additional combination bands were assigned to S_2N_2 . The gas-phase to Ar-matrix frequency shifts were found to be $\leq 3 \text{ cm}^{-1}$ for the v_6 and the v_4 fundamentals, and the agreement between the experimental band positions and the intensities with computational predictions obtained from anharmonic frequency calculations utilizing either VPT2 or VCI at the coupled-cluster level is very satisfying. An estimation of the Raman-active fundamental frequencies from observed combination bands revealed unexpected large discrepancies to previously reported band positions.^[9]

The v_6 (B-type) and the v_4 (C-type) fundamental bands have been recorded with a resolution of 0.0021 and 0.004 cm⁻¹, respectively. The analysis of these bands by using a Watson Atype Hamiltonian provided accurate vibrational energies, as well as rotational and quartic centrifugal distortion constants for the vibrational ground and the two excited states of ${}^{32}S_2{}^{14}N_2$. The D_{2h} symmetry of the ground-state structure is confirmed by the relative spectral line intensities, which account for the nuclear spin statistical weight of the respective groundstate rotational levels. Precise zero-point average r_7 ($R_2(SN) =$

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1.647694(95) Å, $\alpha_z(NSN) = 91.1125(33)^\circ$) and semi-experimental equilibrium structures ($R_e(SN) = 1.64182(33)$ Å, $\alpha_e(NSN) = 91.0716(93)^\circ$) of S₂N₂ have been established, where the respective corrections of the X_0 rotational constants for the effect of rotation–vibration interactions were obtained from anharmonic frequency calculations utilizing VPT2 at the fc-CCSD(T)-F12a/cc-pVTZ-F12 level. From this point of view, S₂N₂ is a very favorable heavy atom molecule, where only one isotopomer is required to obtain accurate experimental structural data. This analysis provides a sound basis for structural comparison with results obtained from purely electronic structure methods or low-temperature single-crystals X-ray diffraction,^[5] as well as for the discussion of structural properties of related sulfur nitrogen compounds.

Experimental and Computational Section

Sample preparation

Disulfur dinitride was prepared by low pressure pyrolysis of $S_4 N_4^{[28]}$ according to the known protocol.^[29] At the bottom of a small glass reactor (a 15 cm long tube of 1 cm i.d., equipped with a Young valve) $S_4 N_4$ was heated to 70 to 80 °C at 10^{-3} mbar and its vapor passed a 10 cm long zone of silver wool, heated at 215 °C. The products were collected in U-traps held at 0 and -60 °C. Almost pure $S_2 N_2$ retained as a colorless solid in the -60 °C trap.

For the synthesis of enriched $S_2^{15}N_{2r}$ ¹⁵NH₄Cl (13 mmol) (Chemotrade, 50% enriched) was treated in an evacuated closed vessel with excess of NaOH solution. The obtained ammonia was dried by trap-to-trap distillation. For the synthesis of ¹⁵N-enriched S_4N_4 a 25 mL glass bulb equipped with a Young valve and a magnetic stirring bar was used. The bulb was charged with a mixture of CCl₄ (8 mL) and SCl₂ (470 mg, 4.5 mmol). Under cooling (-10° C to RT) three batches of ¹⁵NH₃ were introduced into the bulb at the vacuum line. After 13 mmol of ¹⁵NH₃ were consumed, the mixture was vigorously stirred at 30°C until the brown color changed to orange. Subsequently all volatiles were pumped off. The residue was extracted with water (5 mL) and finally dried in vacuum. Without further purification the product was used for the synthesis of ¹⁵N-enriched S_2N_2 as described above.

Matrix IR spectra of cyclic S_2N_2 (D_{2h}) and its ¹⁵N-enriched isotopologues

A few mg of natural or ¹⁵N-enriched S₂N₂ (D_{2h}) were vacuum transferred into a small U-trap and placed in front of the matrix support. A gas stream of Ar (2 mmol h⁻¹) passed over the S₂N₂ sample held at -15 °C and small amounts of the resulting mixture were deposited onto the matrix support (Rh-plated Cu block) at 16 K in a high vacuum. Prior to photolysis experiments the purity of the matrix-isolated sample was checked by recording its IR spectrum, and the first deposits obtained from the most volatile products were discarded until pure matrix-isolated S₂N₂ (D_{2h}) was deposited. Details of the matrix apparatus are given elsewhere.^[30]

Matrix IR spectra were recorded on an FTIR spectrometer (IFS 66v/ S Bruker) in a reflectance mode by using a transfer optic. A KBr beam splitter and a MCT detector were used in the region of $\tilde{v} =$ 4000–500 cm⁻¹ and a Ge-coated 6 µm Mylar beam splitter with a liquid helium-cooled Si bolometer in the $\tilde{v} =$ 700–180 cm⁻¹ region (Csl window). For each spectrum 100 scans at a resolution of 0.25 cm⁻¹ were co-added.

High-resolution FTIR spectra of cyclic S_2N_2 (D_{2h})

High resolution FTIR spectra were recorded at the Bruker 120 HR interferometer in Wuppertal in the spectral range from $\tilde{\nu} = 600$ – 1160 cm⁻¹ and the range of the out-of-plane band v₄(b_{1u}) from $\tilde{\nu} = 600$ –370 cm⁻¹, by using a global source and a KBr beam splitter. For the measurement in the mid-IR region a 8.3 µm low-pass filter and a MCT 600 detector were used, as well as a glass cell of 274 mm optical path lengths, equipped with KBr windows. The cell was filled with S₂N₂ vapor to a pressure of 0.55 mbar, and altogether 280 scans were co-added with an instrumental resolution of 0.0021 cm⁻¹. The spectra were calibrated with lines of residual CO₂ in the $\tilde{\nu} = 670$ cm⁻¹ region, as taken from the HITRAN database.^[31]

In the far-IR region a liquid helium-cooled Si bolometer (Infrared Laboratories), a 600 cm⁻¹ far-infrared cut-on filter, and a white-type multipass cell of 80 cm basis length, adjusted to a total optical path length of 320 cm, were used. The cell was equipped with KBr windows and mounted on the internal sample chamber of the interferometer, and filled with S₂N₂ vapor to a pressure of 0.4 mbar. Altogether 20 scans were collected with an instrumental resolution of 0.004 cm⁻¹. Experimental line positions were calibrated with lines of residual H₂O in the $\tilde{\nu}$ =430–580 cm⁻¹ region taken from the HITRAN database.^[31]

The amount of gaseous S_2N_2 in the IR cell was found to decrease with a half-life of about 20 h. It is known that solid S_2N_2 forms polymeric $(SN)_{xr}^{[5,6]}$ and it is assumed that this process can also occur on the surface of the glass cell. On the other hand, traces of NH₃ and SO₂ were also detected as volatile decomposition products, indicating the reaction of S_2N_2 vapor with moisture at the glass surfaces according to a tentative Equation (2), where S_8 refer to the likely formation of non-volatile S–S bonded species. The sensitivity to moisture of the system $S_2N_2/(SN)_x$ in the presence of residual water films on glass surfaces and the formation of N–H and S=O groups has previously been reported.^[6b, 32]

$$2S_2N_2 + 6H_2O \rightarrow 4NH_3 + 3SO_2 + 1/8S_8$$
 (2)

Analysis and simulation of rotationally resolved gas-phase spectra

First the B-type transitions ($\Delta |K_a| = \text{odd}$ and $\Delta |K_c| = \text{odd}$) of v_6 were assigned by using predicted line positions and relative line intensities computed according to a theoretical model appropriate for asymmetric rotors.^[33] As a first guess predicted ab initio rotational constants for the upper and lower states, together with E_1 $\approx\!792.0\ \text{cm}^{-1}$ for the $\nu_6\!=\!1$ vibrational energy were used. The assignment of these transitions and particularly the first identification of lines involving low and medium J and K_a quantum numbers was facilitated by the predicted (and observed) line intensity alternation due to the nuclear spin statistical weights of the ground-state rotational levels (see Table S1 in the Supporting Information). Those P, Q, and R transitions leading to the same $v_6 = 1$ upper levels provided ground-state combination differences (GSCDs), from which ground-state parameters (rotational constants and centrifugal distortion constants) were derived through a least-squares fit procedure. From these constants ground-state energy levels were obtained and added to the v_6 observed line positions to get the corresponding upper-state ($v_6 = 1$) energy levels. These upperstate levels were then used in a separate least-squares fit procedure to generate upper-state parameters for the $v_6 = 1$ level. Already established ground- and upper-state rotational constants as

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well as the $\nu_6\!=\!1$ vibrational energy were used to successively predict further transitions and to ascertain more assignments.

After rather consistent ground-state rotational parameters were derived from the v₆ transitions, it was possible to analyze the weaker and rather congested C-type ($\Delta | K_a | = \text{odd}$ and $\Delta | K_c | = \text{even}$) v₄ band located at $\tilde{\nu} = 474.775 \text{ cm}^{-1}$, by using the method described above. The analysis of both bands was then successively improved until no further lines could be identified.

DFT and ab initio calculations

In a preliminary study, the structure of S₂N₂ was fully optimized at the B3LYP/6-311 + G(3df) level.^[34] Subsequent harmonic and anharmonic frequency calculations, the latter being based on secondorder vibrational perturbation theory (VPT2), were carried out by using the Gaussian 03 program package.^[35] More accurate electronic structure calculations based on conventional coupled-cluster theory, CCSD(T), and explicitly correlated coupled-cluster theory, CCSD(T)-F12a, in combination with Dunning-type orbital basis sets of triple-ζ quality have been performed as well.^[36-41] Within the explicitly correlated calculations, initial MP2-F12 calculations were performed by using the 3C(FIX) approach.^[39] The perturbative CABS (complementary auxiliary basis set) singles correction was applied in all F12 calculation.^[41] Aug-cc-pw(C)VTZ/MP2FIT, cc-p(C)VTZ/ OPTRI, and aug-cc-pVTZ/JKFIT auxiliary bases were employed for density fitting and the resolution of the identity.^[40] Calculations have been performed with and without the correlation of the inner shell electrons. Therefore, we distinguish between three sets of coupled cluster calculations: 1) conventional CCSD(T)/cc-pCVTZ calculations, which include core-correlation effects, 2) explicitly correlated CCSD(T)-F12a/cc-pCVTZ-F12 calculations including core correlation, and 3) frozen-core explicitly correlated fc-CCSD(T)-F12a/ccpVTZ-F12 calculations. At all levels anharmonic frequencies, vibrationally averaged structural parameters, vibrationally averaged rotational constants, and vibration-rotation interaction constants were determined. Level 1 calculations were carried out at the VPT2 level based upon a quartic force field, and have been performed with the CFOUR program package.^[42] The explicitly correlated coupled-cluster calculations 2 and 3 were performed within the framework of vibrational configuration interaction (VCI) theory.^[13, 14] The many-mode expansion of the potential energy surface used in these calculations was truncated after the three-mode coupling terms, and is thus considered to be more accurate than the quartic force field used in the VPT2 calculations. However, the three-mode coupling terms were determined in combination with basis sets of double- ζ quality, which usually is an excellent approximation once explicitly correlated coupled-cluster theory is used.^[43] Vibrational angular momentum terms were included within the Watson Hamiltonian for non-rotating molecules (J=0).^[44,45] State-specific vibrational self-consistent field (VSCF) calculations by using a mode-dependent basis of non-orthogonal distributed Gaussians were performed to generate a modal basis used in the vibrational correlation calculations. The state-specific VCI calculations included single, double, triple, and quadruple excitations (VCISDTQ). All VCI calculations were performed by using the MOLPRO program package.^[46,47] The VCI program implemented in MOLPRO also allows for the calculation of spectroscopic constants within the VPT2 theory (see Tables S3-S5 in the Supporting Information). These were evaluated at the fc-CCSD(T)-F12a/cc-pVTZ-F12 level, that is, by coupled-cluster calculations close to the basis set limit.

In addition, the one-electron Douglas-Kroll-Hess Hamiltonian was used to determine scalar-relativistic effects for the geometrical parameters and harmonic frequencies at the conventional coupledcluster level in combination with an aug-cc-pVTZ-dk basis set.^[48] The magnetizability tensor and the molecular rotational *g* tensor of S_2N_2 were determined at the CCSD(T)/aug-cc-pCVTZ level by using the CFOUR program.^[42]

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