Rotational spectra and equilibrium structures of H_2SiS and Si_2S

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(Received 14 September 2010; accepted 13 October 2010; published online 20 January 2011)

The rotational spectra of two small silicon sulfides, silanethione H_2SiS and the disilicon sulfide ring Si_2S, have been detected in the centimeter band by Fourier transform microwave spectroscopy of a molecular beam; lines of H_2SiS were also observed in the millimeter band up to 377 GHz in a glow discharge. Precise rotational and centrifugal distortionconstants have been determined for the normal and a number of the more abundant rare isotopic species of both closed-shell molecules. Theoretical equilibrium (r_e) structures of H_2SiS and Si_2S were derived from coupled-cluster calculations that included triple and quadruple excitations, core correlation, and extrapolation to the basis-set limit. The r_e structures agree to within 5×10^{-4} Å and 0.1° with empirical equilibrium (r_e^{emp}) structures derived from the experimental rotational constants, combined with theoretical vibrational and electronic corrections. Both H_2SiS and Si_2S are good candidates for radioastronomical detection in the circumstellar shells of evolved carbon-rich stars such as IRC+10216, because they are fairly polar and are similar in composition to the abundant astronomical molecule SiS. © *2011 American Institute of Physics*. [doi:10.1063/1.3510732]

I. INTRODUCTION

Small molecules with silicon and sulfur have long been of interest in inorganic and organometallic chemistry.[1] Although there are a number of experimental and theoretical studies on pure clusters of both elements and their hydrides, with the exception of SiS there is relatively little experimental information on molecules containing both silicon and sulfur. One of the simplest examples is H_2SiS, the second-row analog to formaldehyde H_2CO. Isomers of H_2SiS have been the subject of several theoretical studies. In the most recent study of this kind, Lai *et al.*[2] concluded that the branched structure with C_{2v} symmetry (H_2SiS) is the most stable, with the *trans*- and *cis*-HSiSH isomers 10–15 kcal mol^{-1} higher in energy. Owing to their high reactivity, a few silanethiones (silicon–sulfur double bond compounds, RR′Si=S) kinetically stabilized with bulky end groups (RR′) have been synthesized;[3] however, attempts to synthesize the parent species H_2SiS were unsuccessful for a long time,[4] and H_2SiS was only recently observed here in a supersonic molecular beam.[5]

Another small silicon sulfide of general interest is disilicon sulfide, Si_2S, which we have observed by Fourier transform microwave (FTM) spectroscopy in the same molecular beam as H_2SiS (see Fig. 1). Because of the dependence of molecular structure on the number of valence electrons, a 14 valence electron molecule like Si_2S provides a test of Walsh's rule.[6,7] Although no experimental data was available on Si_2S prior to the work here, quantum-chemical calculations by Davy and Schaefer[7] predict a singlet ring with C_{2v} symmetry and that is what is found here.

Molecules with silicon or sulfur are also of considerable astronomical interest. In the circumstellar shells of the late-type carbon-rich star IRC+10216, roughly 1/3 of the molecules contain at least one of these two atoms. The most prominent of these in the radio band is SiS, which is formed close to the photosphere and is observed in the circumstellar envelopes of approximately 20 low to intermediate mass late-type stars.[8] Silicon sulfide, the claimed progenitor of small silicon molecules in IRC+10216, is so abundant that seven rare isotopic species, including two doubly substituted species, have been detected there.[9,10] In the past, H_2SiS and Si_2S received little attention by radio astronomers, but now that the rotational spectra have been measured both would appear to be good candidates for astronomical detection.

Here a joint experimental and theoretical investigation of the two new silicon sulfides, H_2SiS and Si_2S, is presented. The laboratory work amplifies our preliminary experimental results on H_2SiS by rotational spectroscopy,[5] and extends that work to the Si_2S ring by the same experimental technique and level of theory. To derive the best theoretical estimate for the geometries and rotational constants of both molecules, quantum-chemical calculations at the coupled-cluster (CC) level with a full treatment of triple and quadruple excitations, consideration of core correlation, and ex-

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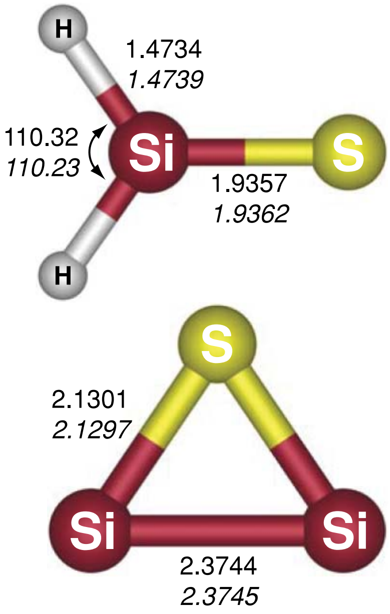

FIG. 1. Structures of H_2SiS and Si_2S. Upper line: empirical equilibrium (r_e^{emp}) structure derived from measured rotational constants corrected for zero-point vibrational effects obtained theoretically (bond lengths in Å and angle in degrees). Lower line: theoretical equilibrium (r_e) structure (in *italics*) obtained at the fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ level. The equilibrium dipole moments at the CCSD(T)/cc-pwCVQZ level of theory are $\mu_a = 2.67$ D for H_2SiS (Ref. 5) and $\mu_b = 0.66$ D for Si_2S.

trapolation to the basis-set limit have been performed. The present paper consists of (i) a comprehensive study of the rotational spectra of the normal and rare isotopic species of H_2SiS and Si_2S in the centimeter-wave band, and of H_2SiS in the millimeter-wave band up to 377 GHz; (ii) a theoretical study of the geometrical structures, dipole moments, and vibrational energies of ground state H_2SiS and Si_2S; (iii) a determination of empirical equilibrium structures for H_2SiS and Si_2S; (iv) detection of intense vibrational satellites of H_2SiS and its isotopic species; and (v) assignment of the satellite lines on the basis of calculated vibration–rotation interaction constants.

II. EXPERIMENT

A. Centimeter-wave measurements

Silanethione H_2SiS and disilicon sulfide Si_2S were detected with an FTM spectrometer that operates between 5 and 43 GHz.[11,12] Reactive molecules are produced in the throat of a small nozzle by a low-current dc discharge through precursor gases heavily diluted in an inert buffer gas (Ne) prior to supersonic expansion to about Mach 2 into a large vacuum chamber. Following excitation of a rotational transition by a short microwave pulse, radiation from the coherently rotating molecules is detected with a sensitive heterodyne receiver. The source conditions that produced a high yield of both molecules were similar to those used to produce copious amounts of SiS: a 1000 V dc discharge through silane (SiH_4, 0.2%) and hydrogen sulfide (H_2S, 0.05%) heavily diluted in neon, a gas pulse of 200 μsec duration (resulting in a flow of 25 cm^3/min at STP), and a stagnation pressure behind the nozzle of 2.5 kTorr (3.2 atm). These same conditions were also found to be a good source for the HSiS radical, whose rotational spectrum was first detected at millimeter wavelengths by Brown *et al.*[13] The fully deuterated species D_2SiS was detected in a discharge through SiD_4 and D_2S in neon; and partially deuterated HDSiS was observed in a discharge through carbonyl sulfide (OCS, 0.1%), and equal amounts of SiH_4 and SiD_4 (both at 0.15%) in neon. Owing to high signal-to-noise, lines of $H_2Si^{33}S$ with resolved sulfur–33 hfs were observed in natural abundance.

1. H_2SiS

A search for the fundamental rotational transition of H_2SiS ($1_{0,1} \rightarrow 0_{0,0}$) was undertaken on the basis of the theoretical structure reported by Lai *et al.*[2] To be certain that we did not miss this transition at 15.7 GHz, a large search range was covered (1.3 GHz). Because the lowest transition of SiS is sufficiently close in frequency (18.1 GHz), many strong lines in the ground and vibrationally excited states of the rare isotopic species were observed, but an earlier exhaustive study[14] allowed us to readily identify lines of SiS.

Standard assays established that the carrier of only a few lines observed in the initial search contained hydrogen, silicon, and sulfur: most remained when SiH_4 and H_2S were replaced with SiD_4 and D_2S, indicating that the carriers did not contain hydrogen. All of the unidentified lines with the required elemental composition were discharge products and exhibited no detectable Zeeman effect when a permanent magnet was brought near the molecular beam, as expected for a closed-shell molecule like H_2SiS. The strongest lines were near 15.7 GHz, but weaker lines by roughly a factor of 20 were found at lower frequency near 15.5 and 15.3 GHz. On the basis of the theoretical structure, we were able to assign these to either the normal or to the silicon–29, silicon–30, or sulfur–34 isotopic species of H_2SiS. The close agreement (to better than 1%) between the observed frequency shifts for the rare isotopic species and those predicted from the structure in Fig. 1 is compelling evidence that the tentatively assigned line at 15.7 GHz is produced by H_2SiS.

2. Si_2S

The search for rotational lines of Si_2S was undertaken in the same discharge in which H_2SiS was observed. The fundamental transition ($1_{1,1} \rightarrow 0_{0,0}$), was predicted[7] to lie at 11.4 GHz; a search over 900 MHz about this prediction revealed a few unidentified lines (i.e., about 5 lines/100 MHz), but discharges through either SiH_4 or H_2S alone, or SiD_4 and D_2S alone, eliminated all but one. Searches for confirming lines at 16.5 GHz ($2_{0,2} \rightarrow 1_{1,1}$) and 9.0 GHz ($2_{1,1} \rightarrow 2_{0,2}$) were then undertaken, however there were many strong background lines of SiS at the higher frequency (see Fig. 2), and of the Ar···SiS complex at the lower frequency. Lines of the complex, observed in a commercially prepared sample of SiH_4 (2%) in Ar, were readily identified because they were not

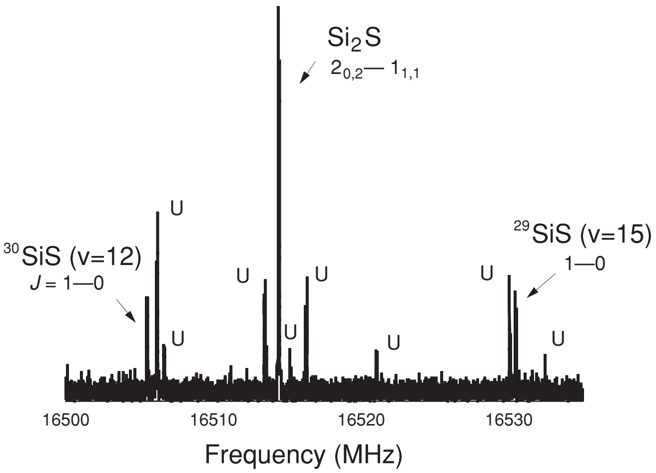

FIG. 2. The $2_{0,2} \rightarrow 1_{1,1}$ transition of cyclic Si_2S. Lines of the rare isotopic species of SiS in highly vibrationally excited states, as well as many lines (~70%) whose carriers remain unidentified (U), observed in a discharge through SiH_4 and H_2S heavily diluted in Ne. The spectrum is a concatenation of 90 separate 0.4 MHz wide scans with a total acquisition time of 2 h.

present when the Ar was replaced with Ne. Applying the same chemical assays as those for H_2SiS (see Sec. II A 1), a second line at 9.0 GHz was found that had the required elemental composition, was only present in an electrical discharge, and was insensitive to an external magnetic field.

On the assumption that the inertial defect of Si_2S is ≤ 0.3 amu Å^2 by analogy with S_3 (Ref. 15), a search over only a few tens of MHz was required to detect a third line near 16.5 GHz, and about ten additional lines in the centimeter-wave band between 8 and 40 GHz were then quickly found.

Following its identification, the production of Si_2S with SiH_4 and different sulfur precursors was studied. Comparable yields of Si_2S were observed with H_2S and OCS, but CS_2 and SO_2 resulted in lines that were weaker by a factor of 20 or more.

B. Millimeter-wave measurements of H_2SiS

The millimeter-wave spectrum of H_2SiS was measured in absorption in a 3 m long discharge cell.[16] The precursor gases were the same as those in the FTM experiment: SiH_4 and H_2S with the addition of Ar to maintain a stable discharge. Owing to its high flammability in air, special precautions were taken in handling silane (see Ref. 17). The most intense lines of SiS were observed in a dc discharge (150 mA) through SiH_4, H_2S, and Ar in a molar ratio of 1:1:2 with the walls of the discharge cell cooled to 150 K. Under these conditions, lines of HSiS were roughly 1000 times weaker than those of SiS.

On the basis of spectroscopic constants derived from the centimeter-wave measurements, transitions between 230 and 300 GHz with low K_a were predicted with an approximate estimated uncertainty of 10 MHz. Three harmonically related lines with similar intensity were tentatively assigned to successive transitions in the $K_a = 0$ ladder displaced by only 15 MHz from the predictions. Three confirming lines again closely harmonic in frequency were then found. Including the six millimeter-wave lines in the analysis yielded improved predictions for lines in the $K_a = 1$ ladder, and these were quickly found to be within 10 MHz of the refined predictions, as were lines with high J and K_a. The optimized conditions for H_2SiS are similar to those used initially, but at a lower discharge current (70 mA) and equal molar ratios of the three gases at total pressure of 28 mTorr. Lines of H_2SiS in this discharge were less intense than those of SiS by a factor of 50 (see Fig. 3), but were more intense than those of HSiS by about an order of magnitude.

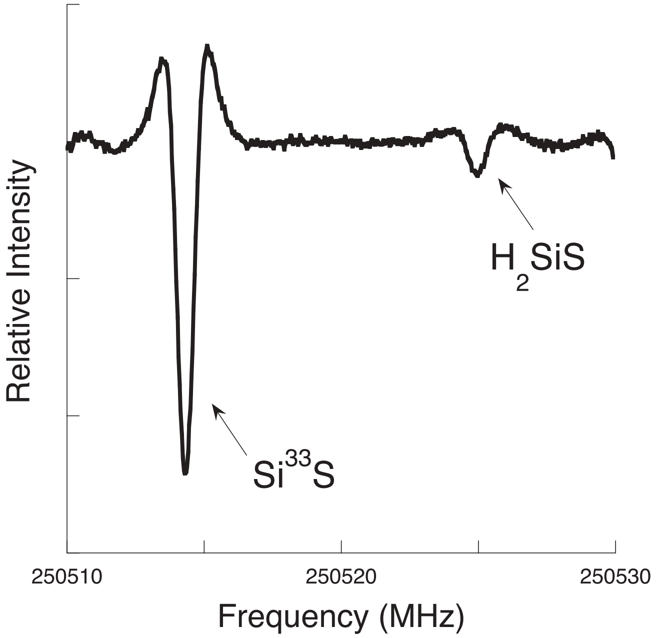

FIG. 3. Millimeter-wave rotational lines of $Si^{33}S$ (28 – 27) and H_2SiS ($16_{0,16} - 15_{0,15}$) observed in a discharge through silane and hydrogen sulfide. The instrumental line shape, approximately the second derivative of a Lorentzian, results from the modulation scheme employed. The integration time is 30 s/MHz.

III. QUANTUM-CHEMICAL CALCULATIONS

Equilibrium geometries, vibrational frequencies, and rotational, centrifugal distortion, and vibration–rotation interaction constants of H_2SiS and Si_2S were calculated by coupled-cluster techniques.[18] CC singles and doubles (CCSD) augmented by a perturbative treatment of triple excitations [CCSD(T); Ref. 19] was used throughout, because geometries and spectroscopic properties derived from high-resolution spectroscopic measurements of molecules in their ground electronic state are well reproduced by this approach. Dunning's standard one-particle correlation-consistent cc-pVXZ (X = T,Q,5,6) basis sets[20] and the augmented cc-pV(X+d)Z (X = T,Q) basis[21] were used together with the frozen-core (fc) approximation in which only the valence electrons were considered in the electron-correlation treatment. Core-polarized cc-pCVXZ (X = T,Q) bases and their weighted cc-pwCVXZ variants[22] were used when all electrons were considered in the electron-correlated calculation.

To obtain a final best estimate of the theoretical geometries and rotational constants, a full treatment of triple excitations (CCSDT; Ref. 23) and quadruple excitations

(CCSDTQ; Ref. 24) were considered. Because calculations with sufficiently large basis sets are not possible at such high levels of theory, an additivity approximation and basis-set extrapolation were invoked.[25] In this scheme, denoted as

$$\mathrm{fc-CCSD(T)/cc-pV\infty Z} + \Delta\mathrm{core/cc-pCV5Z}$$
$$+\Delta\mathrm{T/cc-pVTZ} + \Delta\mathrm{Q/cc-pVDZ},$$

the Hartree–Fock self-consistent-field and frozen-core CCSD(T) energy contributions was obtained by extrapolation to the basis-set limit; the core-correlation contributions were computed at the CCSD(T)/cc-pCVQZ level; and the CCSDT and CCSDTQ corrections with cc-pVTZ and cc-pVDZ basis sets, respectively. The magnitude of the individual contributions was estimated at the four additional levels indicated in Tables V and VI, and SXII and SXIV in Ref. 34.

Equilibrium geometries were determined by analytic gradient techniques,[26,27] harmonic force fields by analytic second derivatives,[28] cubic force fields by numerical differentiation of the analytically evaluated second derivatives of the energy (see Ref. 29), and the centrifugal distortion and vibration–rotation interaction constants by the standard formulas in Ref. 30. The cubic force fields for the rare isotopic species of H_2SiS and Si_2S were derived from the force fields for the main species via transformation to the corresponding normal-coordinate representation of the rare isotopic species. Nuclear quadrupole coupling constants of the D and ^{33}S isotopic species of H_2SiS, and nuclear-spin rotation constants of the ^{33}S and ^{29}Si species were calculated at the CCSD(T)/cc-pwCVQZ level; in the calculation of the nuclear spin-rotation constants perturbation-dependent basis functions[31] were used.

All calculations have been carried out with the quantum-chemical program package CFOUR (Ref. 32) except those at the CCSDT and CCSDTQ level which used the string-based many-body code MRCC (Ref. 33) which has been interfaced to CFOUR.

IV. RESULTS

A. H_2SiS

1. *Rotational spectrum*

The rotational spectrum of H_2SiS is similar to that of formaldehyde: both have C_{2v} symmetry, a-type transitions, and two equivalent off-axis protons. Owing to *ortho-para* nuclear spin statistics, the $K_a = 1$ rotational ladder of H_2SiS is metastable and is well populated in our cold (1–3 K) molecular beam. As a result, the spectrum of H_2SiS consists of fairly tightly spaced triplets with an intensity ratio of 3:2:3. Because the rotational levels are spaced every 15 GHz, only the fundamental transition and the next lowest one ($2 \rightarrow 1$) with triplet structure were measured for each isotopic species in the centimeter-wave band. The spacing between the triplets is determined by the asymmetry splitting of the $K_a = 1$ transitions, which for the $2 \rightarrow 1$ transitions near 31 GHz is about 750 MHz.

In all, 62 transitions of normal H_2SiS between 15 and 377 GHz with $J \leq 23$ and $K_a \leq 5$ have now been measured (Table SV in Ref. 34). With ten spectroscopic constants in a standard asymmetric top Hamiltonian, the observed spectrum is reproduced to an rms uncertainty (10 kHz) that is within 1% of the pressure-broadened width of a typical millimeter-wave line. Owing to the high correlation of the quartic centrifugal distortion constant D_K with the A rotational constant, D_K could not be determined with a satisfactory precision so it was constrained to the theoretical value. The derived spectroscopic constants are given in Table I.

The centimeter-wave frequencies for all but three of the nine rare isotopic species of H_2SiS are reproduced to within the measurement uncertainty (2 kHz) with three spectroscopic constants: the rotational constants B and C, and the leading centrifugal distortion constant D_{JK} (Table SVI in Ref. 34). A second distortion constant (D_J) could be determined in the fully deuterated species (D_2SiS), because one more transition was within the upper range of our FTM spectrometer ($3_{1,3} \rightarrow 2_{1,2}$ at 41.1 GHz). Owing to limited measurements of the rare isotopic species, it was not possible to determine the A rotational constant, so A was constrained to the scaled theoretical value (see Ref. 5). Well resolved hfs for the sulfur–33 species ($I = 3/2$) or partially resolved hfs for the deuterated species ($I = 1$) (Ref. 35), allowed us to determine the quadrupole constant χ_{aa} for $H_2Si^{33}S$ and D_2SiS (Table SVII in Ref. 34). Several nuclear spin-rotation constants were accurately determined from closely spaced hfs arising from the interaction of ^{29}Si ($I = 1/2$) with the small magnetic field produced by molecular rotation (Table SVII in Ref. 34).

2. *Vibrational excitation*

Rotational lines in vibrationally excited states (vibrational satellites) are frequently observed with the FTM spectrometer,[36–39] because vibrational cooling is much less efficient than rotational cooling in our molecular beam. Intense vibrational satellites were observed for several rotational transitions of H_2SiS, and from these rotational constants were determined. Because the satellites were comparable in intensity to those of the ground state lines, it was initially thought that H_2SiS might be undergoing inversion motion. However, this intense vibrational progression was quenched when the Ne buffer gas was replaced with H_2. As the sample spectra in Fig. 4 show, low-lying vibrational levels of H_2SiS are cooled very efficiently in an H_2 beam owing to the large rotational constant of H_2 (~60 cm^{-1}).

The vibrational dependence of the difference in the rotational constants in the vibrationally excited states and those in the ground state satisfy the well known relation

$$B_v - B_0 = -v\alpha_i^B, \tag{1}$$

with analogous equations for the A and C rotational constants. In Eq. (1), α_i^B denotes the vibration–rotation interaction constant concerning the ith normal mode and v stands for the vibrational quantum number of this mode. Because the experimental α_i^A cannot be determined from the present data, an iterative procedure was used to determine the constants $\alpha_i^{B,C}$. First, the sum $\alpha_i^B + \alpha_i^C$ was determined from the

TABLE I. Spectroscopic constants of H_2SiS (in MHz).

		Theoretical			
Constant	Experimental[a]	Equilibrium[b]	Vib. contrib.[c]	Electronic contrib.[d]	Ground vib. state[e]
A	170 342.6(16)	171 530.3	+1042.3	+139.2	170 348.8
B	8030.954 95(61)	8048.1	+22.0	+0.3	8025.9
C	7658.005 61(59)	7687.4	+33.4	+0.2	7653.9
$10^3 D_J$	3.928 23(27)	3.809	...	...	...
$10^3 D_{JK}$	151.376(44)	147.442	...	...	...
D_K	9.81143[f]	9.811	...	...	...
$10^3 d_1$	−0.195 81(35)	−0.181	...	...	...
$10^3 d_2$	−0.029 38(17)	−0.0246	...	...	...
$10^6 H_{JK}$	0.246(34)	...	...	...	...
$10^6 H_{KJ}$	−0.0188(15)	...	...	...	...

[a] Uncertainties (1σ) are in units of the last significant digit. Constants derived from a least-squares fit of the data in Table SIV using Watson's S-reduced Hamiltonian in the I^r representation.

[b] Rotational constants obtained at the fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ level of theory (see text); centrifugal distortion constants calculated at the fc-CCSD(T)/cc-pV(Q+d)Z level.

[c] Calculated at the fc-CCSD(T)/cc-pV(Q+d)Z level.

[d] Calculated at the fc-CCSD(T)/aug-cc-pVQZ level.

[e] From the relation $B_e = B_0 + \Delta B_0 + \Delta B_{el}$.

[f] Constrained to the theoretical value.

$K_a = 0$ transitions, allowing a preliminary assignment of the vibrational state on the basis of the theoretical constants in Table II. Second, assuming the theoretical α_i^A for that state, transitions from the metastable $K_a = \pm 1$ transitions were then assigned. On this basis, individual $\alpha_i^{B,C}$ for a particular vibrational state were obtained; for H_2SiS, these yield the values $\alpha_i^B = -5.67$ MHz and $\alpha_i^C = +12.82$ MHz, with estimated 1σ uncertainties of 0.01 MHz. Comparison of these experimental vibration–rotation interaction constants with those obtained computationally (Table II) shows that the observed vibrational satellites almost certainly arise from the b_2 mode ν_6 calculated to lie at 618 cm^{-1} (Table III). Independent evidence comes from the vibrational progression shown in Fig. 4 which yields an experimental value of $(\alpha_i^B + \alpha_i^C)/2 = -2.05$ MHz for HDSiS. This value is in reasonable agreement with the calculated value of −1.07 MHz and cannot be approximated by $(\alpha_i^B + \alpha_i^C)/2$ from any other vibrational mode. The close agreement of the theoretical and experimental rotational constants confirms that the quantum-chemical calculations provide a fairly good description of the vibrational dependence of the rotational constants (see Sec. III).

The vibrational temperature of the ν_6 mode of H_2SiS in Ne was determined from a fit of the relative intensities of the $1_{0,1} - 0_{0,0}$ line in different levels with respect to the ground state on the assumption of a Boltzmann distribution. From these measurements an effective temperature of 525 ± 100 K was derived. Detection of rotational satellite transitions from ν_6, the lowest-frequency vibrational mode (618 cm^{-1}) of H_2SiS, is not surprising; previous studies of vibrational excitation of polyatomic molecules in our discharge nozzle have shown that a vibrational mode whose fundamental frequency is near or somewhat above kT (∼450 cm^{-1}) is not efficiently cooled in the supersonic expansion;[37] vibrational modes lying well below kT (none of which exist for H_2SiS) or much higher in energy are generally not well populated.

B. Si_2S

The three-membered ring Si_2S is a prolate asymmetric top ($\kappa = -0.925$) with C_{2v} symmetry and b-type rotational transitions. Owing to the two equivalent silicon nuclei, Bose–Einstein statistics restricts K_a, K_c to either ee or

TABLE II. Theoretical vibration–rotation interaction constants of H_2SiS (in MHz) calculated at the fc-CCSD(T)/cc-pV(Q+d)Z level of theory.

	H_2SiS		
Vib. mode	α_i^A	α_i^B	α_i^C
ν_1	+2165.25	+4.80	+8.44
ν_2	−1210.35	− 15.21	+9.56
ν_3	+78.83	+34.34	+28.63
ν_4	−84 956.55	+21.94	+0.12
ν_5	+1407.93	+5.02	+5.96
ν_6	+84 605.47	− 6.92	+14.05

TABLE III. Vibrational frequencies and IR intensities of H_2SiS calculated at the fc-CCSD(T)/cc-pV(Q+d)Z level of theory.

		Frequency (cm^{-1})		IR intensity
Vib. mode	Symmetry	Harmonic	Fundamental[a]	(km/mol)
ν_1	a_1	2254	2172	75
ν_2	a_1	1012	992	117
ν_3	a_1	728	721	17
ν_4	b_1	638	630	17
ν_5	b_2	2265	2182	90
ν_6	b_2	623	618	19

[a] Includes anharmonic contributions.

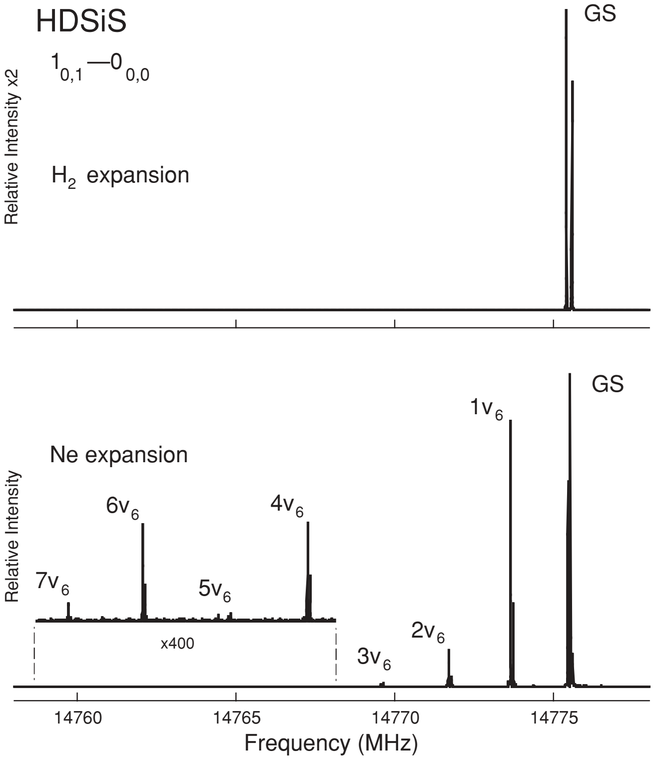

FIG. 4. A portion of the rotational spectrum of HDSiS near the $1_{0,1} \rightarrow 0_{0,0}$ transition observed in a discharge through OCS, SiH_4, SiD_4, and a carrier gas. Upper trace: H_2 is the carrier gas in the supersonic expansion; lower trace: carrier gas is Ne (see text). Owing to the higher translational velocity of the H_2 beam, the frequency separation between the Doppler doublet is more pronounced in the upper spectrum. Both spectra are concatenations of approximately 80 separate 0.4 MHz wide scans with a total acquisition time of 1.5 h.

oo. Thirteen transitions of Si_2S between 8 and 42 GHz with $J \leq 5$ and $K_a \leq 3$ were reproduced to within the measurement uncertainty with three rotational constants and five quartic centrifugal distortion constants (Table IV). Single isotopic substitution with either silicon–29 or silicon–30 breaks the C_{2v} symmetry, allowing observation of the otherwise symmetry forbidden transitions. Eleven lines of ^{29}SiSSi and of ^{30}SiSSi, and seven lines of the sulfur–34 species of Si_2S are tabulated in the supplementary material (Tables SVIII and SIX in Ref. 34). The rotational and centrifugal distortion constants of the rare isotopic species of Si_2S are given in Table SX, and the hyperfine constants of ^{29}SiSSi are in Table SXI of Ref. 34.

V. STRUCTURES OF H_2SiS AND Si_2S

Geometrical structures of H_2SiS and Si_2S were derived from the experimental data by the standard procedure in which the bond lengths and angles are least-squares adjusted to best reproduce the moments of inertia of (*i*) the observed rotational constants (B_0 and C_0) for the normal and rare isotopic species; and (*ii*) the experimental rotational constants combined with theoretical vibrational corrections. The second approach has become the standard method for deriving equilibrium geometries of polyatomic molecules from ground state rotational constants, because the empirical equilibrium (r_e^{emp}) structure is a much more accurate representation of the equilibrium (r_e) structure than the experimental r_0 structure (for a review see Ref. 29).

Empirical equilibrium rotational constants B_e are estimated from the expression

$$B_e = B_0 + \frac{1}{2}\sum_i \alpha_i^B, \tag{2}$$

where B_0 is the measured rotational constant in the ground vibrational state (similar equations also apply for A_e and C_e), and the sum over vibration–rotation interaction constants $\sum_i \alpha_i^{A,B,C}$ is obtained by means of quantum-chemical calculations. Experimental determination of all the $\alpha_i^{A,B,C}$ is difficult for even modestly sized molecules, but they can be calculated to adequate accuracy at fairly modest computational cost. While the vibration–rotation interaction constants (α_i) are often complicated by Coriolis resonances, the difference between the equilibrium rotational constants and those of the ground vibrational state is determined by the sum ($\Sigma_i \alpha_i/2$) which is not affected by these resonant interactions within second-order perturbation theory (see Ref. 40, and references therein).

A. H_2SiS

The experimental (r_0) and empirical equilibrium (r_e^{emp}) structures of H_2SiS were derived from a least-squares fit of the SiS and SiH bonds and the HSiH bond angle to moments of inertia obtained from either the measured or empirically corrected rotational constants B and C of the normal and ten rare isotopic species (Table SVI in Ref. 34), on the assumption that H_2SiS is planar and has C_{2v} symmetry (Fig. 1). The derived bond lengths and angle are compared in Tables V and SXII in Ref. 34 with equilibrium (r_e) structures calculated by the CC methods described in Sec. III.

Uncertainties in the r_0 structure were derived on the assumption that the largest source of error is zero-point vibration. The magnitude of this error and how it is partitioned among the three moments of inertia is unknown, but it was estimated by assigning to each rotational constant an uncertainty which yields a χ^2 of 20, the most probable value for 19 degrees of freedom.[41] The resulting uncertainty (1 MHz) in B and C was assumed for each isotopic species. Because the present molecules possess large vibrational–rotational coupling constants (owing to the light mass of hydrogen), an advantage of the approach here is that the estimated uncertainties of the structural parameters reflect in a general sense the effects of zero-point vibration.

Zero-point vibrational corrections (ΔB_0 and ΔC_0) calculated with the three force fields fc-CCSD(T)/cc-pV(T+*d*)Z, CCSD(T)/cc-pwCVTZ, and fc-CCSD(T)/cc-pV(Q+*d*)Z (see Ref. 42) agree to within 1 MHz (Table SVI in Ref. 34). As a result, the empirical equilibrium structures in these three cases are nearly identical (Tables V and SXII in Ref. 34). With corrections at the fc-CCSD(T)/cc-pV(Q+*d*)Z

TABLE IV. Spectroscopic constants of Si_2S (in MHz).

		Theoretical			
Constant	Experimental[a]	Equilibrium[b]	Vib. contrib.[c]	Electronic contrib.[d]	Ground vib. state[e]
A	7926.7811(13)	7945.5	+13.3	+1.1	7931.0
B	6390.067(5)	6407.8	+17.6	+0.9	6389.3
C	3532.486(2)	3547.1	+14.0	−0.1	3533.2
$10^3\Delta_J$	3.6(3)	3.45	...	...	...
$10^3\Delta_{JK}$	−3.1(9)	− 2.73	...	...	...
$10^3\Delta_K$	8.8(6)	8.37	...	...	...
$10^3\delta_J$	1.5(1)	1.42	...	...	...
$10^3\delta_K$	3.3(10)	2.88	...	...	...

[a] Uncertainties (1σ) are in units of the last significant digit. Constants derived from a least-squares fit of the data in Table SIX using Watson's A-reduced Hamiltonian in the I^r representation.

[b] Rotational constants determined at the fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ level of theory (see text); centrifugal distortion constants at the fc-CCSD(T)/cc-pV(Q+*d*)Z level.

[c] Calculated at the fc-CCSD(T)/cc-pV(Q+*d*)Z level.

[d] Calculated at the fc-CCSD(T)/aug-cc-pVQZ level.

[e] From the relation $B_e = B_0 + \Delta B_0 + \Delta B_{el}$.

level, the r_e^{emp} structural parameters are $r_{\rm SiS} = 1.9357$ Å, $r_{\rm HSi} = 1.4734$ Å , and ∠HSiH = 110.32°, and the statistical uncertainties are less than 10^{-4} Å and 0.01°.

The CCSD(T) calculations (Table V) indicate that inclusion of core correlation via all-electron calculations with core-polarized basis sets is essential. The calculations also show that structural parameters obtained with the weighted variants (cc-pwCV*X*Z) are somewhat superior to those obtained with the standard variants (cc-pCV*X*Z). However, the CCSD(T)/cc-pwCVQZ calculation yields an SiS bond length (1.9369 Å) that is still longer by more than 10^{-3} Å than the corresponding empirical equilibrium values. Better agreement is observed at the CCSD(T)/cc-pwCV5Z level. Here, the SiS bond length is shorter than the empirical value by only a few times 10^{-4}Å. A similar behavior is found in silicon monosulfide (SiS) where CCSD(T) calculations with the cc-pwCVQZ and cc-pwCV5Z basis sets yield, SiS bond lengths of 1.9303 Å and 1.9283 Å, respectively, whose mean coincides with the experimental equilibrium value of 1.9293 Å (Ref. 14). In a recent computational study of selected small silicon-carbon molecules,[43] neglect of quadruple excitations was identified as a cause of the pronounced shortening of multiple bonds involving second-row elements in the CCSD(T)/cc-pwCV5Z calculations, and hence an intrinsic shortcoming of the CCSD(T) method.

The best theoretical structures obtained in the present work make use of an additivity assumption and explicitly take into account CCSDT and CCSDTQ corrections. They reveal a significant bond lengthening (of order 10^{-3} Å) compared with the CCSD(T)/cc-pwCV5Z structural parameters, and are in excellent agreement with the empirical equilibrium structural parameters in Table V, with bond lengths accurate to 5×10^{-4} Å and bond angle accurate to 0.1°.

We have also considered the electronic contribution to the rotational constants at the fc-CCSD(T)/aug-cc-pVQZ level of theory (see Table SXIII in Ref. 34). While this correction is very small for the rotational constants B and C, and hence has no significant effect on the empirical equilibrium structures derived here, its contribution to the A ground state constant is essential to allow a rigorous compar-

TABLE V. Experimental and theoretical structures of H_2SiS.

Method	$r_{\rm Si-S}$ (Å)	$r_{\rm H-Si}$ (Å)	∠HSiH (deg)
Theoretical equilibrium structures:			
CCSD(T)/cc-pwCVQZ	1.9369	1.4729	110.11
CCSD(T)/cc-pwCV5Z	1.9350	1.4729	110.20
fc-CCSD(T)/cc-pV6Z	1.9430	1.4777	110.17
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ	1.9367	1.4738	110.22
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ	1.9372	1.4741	110.21
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ + ΔQ/cc-pVDZ	1.9379	1.4742	110.22
fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ+ΔQ/cc-pVDZ	1.9371	1.4743	110.23
fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ	1.9362	1.4739	110.23
Experimental structure:[a]			
r_0	1.9397	1.4837	111.64
Empirical equilibrium structure[b] (recommended):			
$r_e^{\rm emp}$	1.9357	1.4734	110.32

[a] Structure that best reproduces the observed rotational transitions of the main and rare isotopic species.

[b] Zero-point vibrational correction calculated at the fc-CCSD(T)/cc-pV(Q+*d*)Z level of theory.

TABLE VI. Experimental and theoretical structures of Si_2S.

Method	r_{Si-S} (Å)	r_{Si-Si} (Å)	∠SiSSi (deg)
Theoretical equilibrium structures:			
CCSD(T)/cc-pwCVQZ	2.1313	2.3756	67.74
CCSD(T)/cc-pwCV5Z	2.1289	2.3736	67.76
fc-CCSD(T)/cc-pV6Z	2.1375	2.3841	67.79
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ	2.1305	2.3754	67.76
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ	2.1309	2.3759	67.76
fc-CCSD(T)/cc-pV6Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ +ΔQ/cc-pVDZ	2.1320	2.3767	67.75
fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCVQZ+ΔT/cc-pVTZ+ΔQ/cc-pVDZ	2.1307	2.3757	67.77
fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ	2.1297	2.3745	67.76
Experimental structure:[a]			
r_0	2.1335	2.3789	67.77
Empirical equilibrium structure[b] (recommended):			
r_e^{emp}	2.1301	2.3744	67.74

[a] Structure that best reproduces the observed rotational transitions of the main and rare isotopic species.

[b] Zero-point vibrational correction calculated at the fc-CCSD(T)/cc-pV(Q+*d*)Z level of theory.

ison between experimental and theoretically predicted rotational constants.[44]

B. Si_2S

Only two geometrical parameters are needed to describe the structure of Si_2S which has C_{2v} symmetry. The r_0 and r_e^{emp} structures were determined from a least-squares fit of the Si–S bond and apex angle (∠SiSSi) to moments of inertia of the three ground state (r_0) and empirically corrected (r_e^{emp}) rotational constants of the four isotopic species. The derived structures and *ab initio* predictions are compared in Tables VI and SXIV in Ref. 34. As in H_2SiS, zero-point vibrational corrections calculated with the three force fields (Ref. 42; see also Table VII for calculated vibrational frequencies) differ very little (i.e., to well within 0.5 MHz; Table SXV in Ref. 34), and the three empirical equilibrium structures are nearly identical. The inertial defect $\Delta_0 = I_c - I_b - I_a$ obtained from the ground state rotational constants is small and positive [0.22201(2) amu Å^2], as expected for a planar molecule such as Si_2S. After correcting for zero-point vibrational contributions with either of the three sets of corrections (Table SXV in Ref. 34), the inertial defect is close to zero ($\Delta_e^{emp} = -0.02$), indicating that the calculated quadratic and cubic force constants are fairly accurate. With vibrational corrections calculated at the fc-CCSD(T)/cc-pV(Q+*d*)Z level of theory, the statistical uncertainties of the r_e^{emp} structural of $r_{SiS} = 2.1301$ Å and ∠SiSSi=67.74° (resulting in $r_{Si-Si} =$ 2.3744 Å) are well below 10^{-4} Å and 0.01°. While the derived apex angle is nearly independent of the level of theory in the present investigation and varies by $\leq 0.1°$ for all calculations performed here, the empirical equilibrium bond lengths differ substantially from the those obtained at the CCSD(T)/cc-pwCVQZ and CCSD(T)/cc-pwCV5Z levels—i.e., the cc-pwCVQZ and cc-pwCV5Z bond lengths are longer and shorter by about 0.001 Å, respectively, analogous to that observed for the SiS distances in H_2SiS and SiS (see Sec. V A). Again, explicit consideration of triple excitations at the CCSDT level and quadruple excitations at the CCSDTQ level result in a bond lengthening, yielding agreement to within 0.0005 Å between the empirical equilibrium values and the highest theoretical level: fc-CCSD(T)/cc-pV∞Z+Δcore/cc-pCV5Z+ΔT/cc-pVTZ+ΔQ/cc-pVDZ.

TABLE VII. Vibrational frequencies and IR intensities of Si_2S calculated at the fc-CCSD(T)/cc-pV(Q+*d*)Z level of theory.

		Frequency (cm^{-1})		IR intensity
Vib. mode	Symmetry	Harmonic	Fundamental[a]	(km/mol)
ν_1	a_1	578	572	29
ν_2	a_1	385	381	3
ν_3	b_2	441	437	14

[a] Includes anharmonic contributions.

The electronic contribution to the rotational constants at the fc-CCSD(T)/aug-cc-pVQZ level of theory was also evaluated for Si_2S (Table SXVI in Ref. 34). Taking this additional contribution into account in the determination of the empirical equilibriums structure yields nearly identical values of $r_{Si-S} = 2.1301$ Å and ∠SiSSi = 67.74° for all three parameter sets—i.e., in perfect agreement with the structures obtained from correcting for zero-point vibrational effects alone.

VI. PROSPECTS FOR ASTRONOMICAL DETECTION

The work here provides the spectroscopic foundation for an astronomical search for two new molecules containing second row elements. Because lines of SiS in the radio band are fairly strong in the interstellar gas, and formaldehyde, the first row analog of one of them, is very widely distributed in our galactic system, with strong lines in the best locations, it is not unreasonable to suppose that one or both of these molecules might be observable in interstellar or circumstellar sources.

As a guide to where to look in space for our two new molecules, a good astronomical survey of SiS would be of great help. Although SiS in space was discovered nearly 40 years ago,[45] no systematic survey of this simple diatomic to our knowledge has yet been done, and its distribution in space is essentially unknown. Such a survey would be a valuable guide in the astronomical search for the two new molecules here, constituting an almost obligatory first step. Analogs in space beyond the second row, containing, for example, Ge and Se, are hardly worth considering at this time because of the total absence of any astronomical molecules with these elements.

Neither H_2SiS nor Si_2S is included in the standard equilibrium chemical model of cool stellar atmospheres,[46] or in more recent models of the circumstellar shell. Nevertheless, as this work shows, both molecules are readily produced in the same laboratory discharge source in which copious amounts of SiS are observed, suggesting that all three molecules might be formed under similar chemical conditions.

At present the best place to conduct a search for H_2SiS and Si_2S is IRC+10216, because the lines of SiS are more prominent there than in other carbon-rich (C>O) or M-type (C<O) stars. For a rotational temperature of roughly 20 K in the outer shell of IRC+10216, the most intense rotational transitions of H_2SiS are readily accessible with ground based telescopes in the 2–3 millimeter-wave band, while those of Si_2S will peak somewhat lower in frequency owing to its heavier mass. We find no evidence of either molecule in published astronomical searches of this source,[9,47] but that is not surprising because many newly discovered astronomical molecules are only found with subsequent deep searches. With the precise rest frequencies provided here, searches for H_2SiS and Si_2S can now be undertaken with large radio telescopes such as the IRAM 30 m or the GBT 100 m.

VII. DISCUSSION AND CONCLUSIONS

Accurate equilibrium structural parameters for H_2SiS and Si_2S obtained in the present investigation provide fundamental information about bonding between second-row elements. The Si–S bond in H_2SiS derived here (1.9357 Å) is only slightly longer than that in SiS (1.9293 Å; Ref. 14), indicating substantial double bond character. In Si_2S, the Si–Si (2.3744 Å) and Si–S (2.130 Å) bonds are very close to those in single bond systems: Si–Si (2.34 Å) and Si–S (2.16 Å) (Refs. 48 and 49), whereas in diatomic Si_2 the Si–Si bond (2.246 Å; Ref. 50) is an indication of substantial double bond character.

The comparison of the empirical structural parameters with those obtained from quantum-chemical calculations performed here confirms the importance of quadruple excitations in the coupled-cluster treatment (see tables in Ref. 34) for accurate structural predictions.[25,51] However, of even greater importance is the proper treatment of core correlation via all-electron CC calculations together with sufficiently large core-polarized basis sets. The corresponding effects for distances between second-row atoms are of the order of 0.01 Å or larger[52] and therefore more significant than higher excitations. The CCSD(T)/cc-pwCV5Z calculations typically lead to distances that are slightly too short (by about 0.001 Å), owing to the neglect of higher excitations. Therefore, use of a quintuple-zeta basis set is strongly recommended. Nevertheless, the composite scheme as proposed and tested in Ref. 25 incorporates both an adequate treatment of core correlation and higher than triple excitations, thus providing molecular equilibrium geometries with unprecedented accuracy, as confirmed in the present work and elsewhere.[5,25,53]

Metastable isomers of H_2SiS may be detectable now that the ground state isomer has been produced in high abundance. The two most obvious ones are *trans*- and *cis*-HSiSH. Both are fairly polar,[54] and are calculated here to lie only 11 and 13 kcal/mol higher in energy than H_2SiS. As the recent laboratory detection of isofulminic acid HONC demonstrates,[55] isomers much higher in energy than HSiSH have been detected by similar means in our laboratory.

Closely related Si_2O may also be detectable in the laboratory now that the rotational spectrum of Si_2S has been observed. The most stable form is predicted to be a singlet ring with C_{2v} symmetry,[56] like Si_2S. Recent coupled-cluster calculations by one of us (S.T.) predict that Si_2O has a modest dipole moment (1.0 D) and a number of rotational transitions below 40 GHz, including the lowest transition at 31.6 GHz ($1_{1,1} - 0_{0,0}$). Lines of SiO, comparable in strength to those of SiS, are observed in a discharge through silane and water, and strong lines of H_2SiO (Ref. 57) are also observed in this source, suggesting that Si_2O may be detectable.

The present work demonstrates a simple method for producing H_2SiS and Si_2S in a supersonic molecular beam in sufficient abundance to allow detection of their rotational spectra at high spectral resolution. We estimate that 10^{13} H_2SiS molecules per gas pulse and 5×10^{11} of Si_2S are produced with a rotational temperature of 2 K in our discharge source. At this concentration, the electronic spectrum of H_2SiS should be detectable with standard laser techniques such as laser-induced fluorescence, cavity ring down absorption, and resonant two-color two photon ionization ($IP \sim 9$ eV; Ref. 58). Searches in the visible and near UV may be a good place to start, because a rich spectrum with strong absorption bands is predicted in this region.[58] High-resolution gas-phase infrared spectroscopy of H_2SiS to better characterize the vibrational structure of this heavy analog of formaldehyde would also be worth undertaking.

ACKNOWLEDGMENTS

We thank J. F. Stanton for helpful discussions and H. Gupta for communicating preliminary theoretical results. The work in Cambridge is supported by NSF Grant No. CHE-0701204 and NASA Grant No. NNX08AE05G. S.T. is grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support through Grant No. TH 1301/3-1, and J.G. acknowledges support from the Deutsche Forschungsgemeinschaft (GA 370/5-1) and the Fonds der Chemischen Industrie.

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[34] See supplementry material at http://dx.doi.org/10.1063/1.3510732 for a listing of the experimental and computed rotational constants for all considered isotopologues together with calculated values for the vibrational and electronic corrections. In addition, the equilibrium geometries of the considered molecules are reported which have been used to compute the rotational constants.

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