Rotational spectrum and equilibrium structure of silanethione, $H_2Si{=}S$

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Unsubstituted silanethione, $H_2Si{=}S$, has been characterized experimentally for the first time by means of rotational spectroscopy; the equilibrium structure of this fundamental molecule has been evaluated through a combination of experimental data from a total of ten isotopologues and results of high-level coupled-cluster calculations.

Silanethiones, $RR'Si{=}S$, the second-row element analogues to ketones, have received considerable attention over the past two decades through studies of multiple bonding between group 14 and group 16 elements.[1] Several silanethiones stabilized by bulky substituents were synthesized and their structures characterized using X-ray crystallography.[1,2] Infrared studies of the mono-/dichloro- and difluoro-derivatives $Cl(H)Si{=}S$, $Cl_2Si{=}S$, and $F_2Si{=}S$ trapped in solid argon were also reported,[3–5] as was a millimetre wave study of the related HSiS radical in the gas phase.[6] Some evidence for diisopropylsilanethione was obtained in flash vacuum thermolysis (FVT) experiments combined with photoelectron spectroscopy.[7] However, up to now, experiments in search for the parent silanethione, $H_2Si{=}S$, failed (*e.g.* ref. 8) despite its predicted stability.[9]

In the present communication, a rotational spectroscopic study of $H_2Si{=}S$ (Fig. 1), the second-row analogue of formaldehyde, is reported, yielding the experimental evidence for the existence of this elusive but fundamental molecule. Precise equilibrium structural parameters have been determined from a joint theoretical and experimental effort.

The rotational spectrum of $H_2Si{=}S$ was detected by means of Fourier transform microwave (FTM) spectroscopy of a molecular beam,[10,11] the same technique used in recent years in this laboratory to characterize many transient molecules including the second-row element clusters Si_3 (ref. 12), S_3, and S_4 (ref. 13). $H_2Si{=}S$ was produced in a low-current dc discharge through a mixture of silane and hydrogen sulfide heavily diluted in neon which is also a good source for other silicon–sulfur molecules such as HSiS and SiS.[6,8] Guided by rotational constants calculated from theoretical molecular structures,[9,14] a search for the fundamental *a*-type rotational transition $J_{Ka,Kc} = 1_{0,1}–0_{0,0}$ of $H_2Si{=}S$ was performed in a 3 GHz interval near 15.7 GHz. Spectral analysis of lines in this region, however, was hampered by the presence of the corresponding $J = 1–0$ rotational lines and accompanying vibrational satellites of SiS and its isotopic species.[8] Replacing SiH_4 and H_2S with SiD_4 and D_2S revealed that only a moderate number of lines were from molecules that simultaneously contained sulfur, silicon, and hydrogen. To rule out radicals, unidentified lines with the required elemental composition were tested for Zeeman splitting in the presence of an external magnetic field (with a permanent magnet mounted near the molecular beam). In this way, a series of four lines was identified between 12.5 and 15.7 GHz with an approximate intensity ratio of 1 : 1 : 1 : 20 as predicted for $H_2Si{=}S$ (and its abundant isotopologues). The close agreement (to better than 1%) between the observed frequency shifts for the isotopic species and those predicted from the theoretical molecular structure provides strong evidence that the lines arise from $H_2{}^{30}Si^{32}S$, $H_2{}^{28}Si^{34}S$, $H_2{}^{29}Si^{32}S$, and $H_2{}^{28}Si^{32}S$ and no other molecules. Further support for the assignment is provided by the detection of rotational lines of $H_2{}^{28}Si^{33}S$ in natural abundance (0.75%) at exactly the expected frequencies, with well-resolved hyperfine structure from ^{33}S ($I = 3/2$; see Fig. 2).

In total, ten isotopologues of $H_2Si{=}S$ have now been characterized by four or more transitions in the centimetre wave regime. For the main isotopic species, rotational transitions in the millimetre-wave band were subsequently observed between 230 and 380 GHz through a low-pressure dc discharge using a steady stream of SiH_4 and H_2S in argon.[15] Least-squares fits for each isotopic species were performed using a standard asymmetric-top Hamiltonian[16] and the

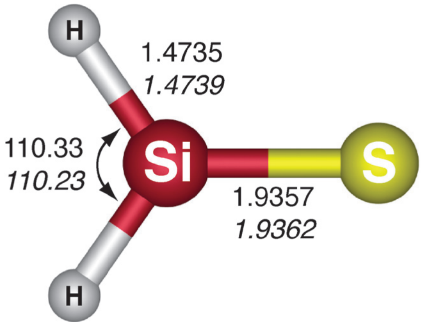

Fig. 1 Semi-experimental equilibrium structure of $H_2Si{=}S$ (bond lengths in Å and angle in degrees) and corresponding best theoretical estimate (in italics). The CCSD(T)/cc-pwCVQZ equilibrium dipole moment is 2.67 D.

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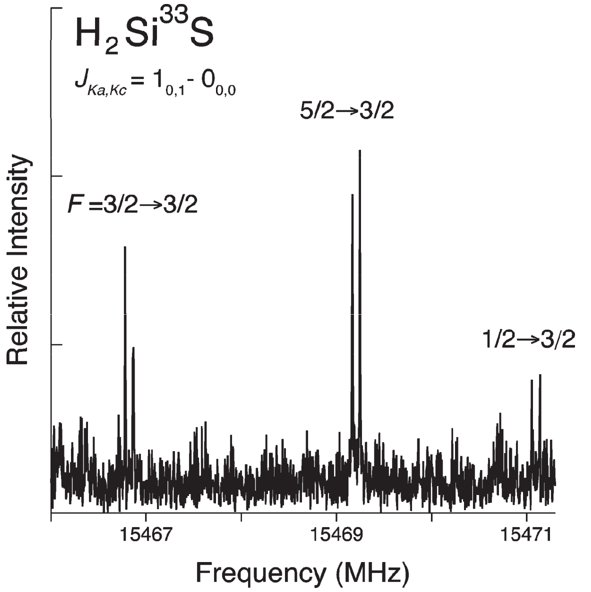

Fig. 2 A portion of the rotational spectrum observed through an electrical discharge of dilute silane and hydrogen sulfide in neon, showing well-resolved hyperfine structure from ^{33}S (I = 3/2) in the fundamental rotational transition of $H_2Si^{33}S$. Despite the low fractional abundance of this isotopic species (0.75%), a triplet pattern of lines with the expected relative intensities of 3 : 5 : 1 is readily observed in only a few minutes of integration, about 30 min for the spectrum shown here. The double-peaked profiles are instrumental in origin, owing to the interaction of the molecular beam with the two traveling waves that compose the confocal mode of the Fabry–Perot cavity in the FTM spectrometer.

resulting principal rotational constants A_0, B_0 and C_0 are given in Table 1. Owing to the highly prolate structure of $H_2Si{=}S$, the A_0 rotational constant could only be determined for the main isotopic species for which a large number of high-frequency rotational lines were measured.

Following detection of H_2SiS in the FTM experiment, high-level quantum-chemical calculations of the equilibrium geometry, the corresponding equilibrium rotational constants A_e, B_e, and C_e, and the zero-point vibrational corrections ΔA_0, ΔB_0, and ΔC_0 were carried out using coupled-cluster (CC) techniques.[17,18] The calculations were mainly performed at the CC singles and doubles level augmented by a perturbative treatment of triple excitations (CCSD(T))[19] using basis sets from Dunning's hierarchies of correlation consistent polarized valence and polarized core–valence sets (cc-pVXZ, cc-pV-($X+d$)Z, and cc-pCVXZ with X = D,T,Q,5, and 6, ref. 20). Theoretical best estimates for the structure (Fig. 1) and the rotational constants (Table 1) were obtained using additivity and extrapolation techniques.[21] The best estimate is then given as fc-CCSD(T)/cc-pV∞Z + ΔT/cc-pVTZ + ΔQ/cc-pVDZ + Δcore/cc-pCV5Z with the frozen-core CCSD(T) contribution extrapolated to the basis-set limit (indicated by cc-pV∞Z) and augmented by corrections for a full CC singles, doubles, triples (CCSDT)[22] treatment (using the cc-pVTZ basis), for the effect of quadruple excitations at the CC singles, doubles, triples, quadruples (CCSDTQ)[23] level (using the cc-pVDZ basis), and for core–valence correlation effects treated at the CCSD(T)/cc-pCV5Z level. These best estimates have been shown to provide bond lengths and angles with an accuracy of better than 0.001 Å and 0.1° (ref. 21). The vibrational corrections to the rotational constants were computed here at the fc-CCSD(T)/cc-pV(Q + d)Z level using a perturbative scheme as outlined in ref. 24.

The semi-experimental (or empirical) equilibrium structure of $H_2Si{=}S$ was determined using equilibrium rotational constants $B_e = B_0 + \Delta B_0$, *i.e.*, obtained by adding the computed vibrational corrections ΔB_0 and ΔC_0 to the experimentally determined rotational constants B_0 and C_0. The experimental determination of the vibrational corrections is usually impractical for molecules containing three or more atoms, since this requires the determination of complete sets of vibration–rotation interaction constants for all considered isotopologues. However, the quantum chemical calculation of vibrational corrections has been shown to be very accurate in many cases[25] and has been adopted in recent years as part of the standard procedure by which accurate determinations of equilibrium structural parameters are derived from rotational spectra. A least-squares fit of the $H_2Si{=}S$ structural parameters (r_{SiS}, r_{SiH}, and $\angle_{HSiH}$) has been carried out using the twenty I_b and I_c equilibrium moments of inertia obtained from the corresponding empirical equilibrium rotational constants adopting equal weights for all isotopologues. The semi-experimental equilibrium structural parameters of

Table 1 Rotational constants and zero-point vibrational corrections of H_2SiS isotopologues (in MHz)

Isotopologue	A_0	B_0	$\Delta B_0{}^a$	C_0	$\Delta C_0{}^a$
H_2SiS^b	170476.3	8026.0	+21.987	7653.9	+33.385
H_2SiS	170342.9(14)	8030.9549(6)	+21.987	7658.0056(6)	+33.385
$H_2{}^{29}SiS$	170345^c	7914.0203(8)	+21.569	7551.6038(8)	+32.664
$H_2{}^{30}SiS$	170346^c	7804.1844(8)	+21.179	7451.5374(8)	+31.992
$H_2Si^{33}S$	170343^c	7915.9351(14)	+21.625	7552.8106(14)	+32.722
$H_2Si^{34}S$	170342^c	7807.3843(8)	+21.285	7454.4468(8)	+32.103
HDSiS	116422^c	7628.2764(15)	+18.656	7147.2149(15)	+30.482
D_2SiS	85383^c	7290.5934(7)	+16.083	6705.4337(11)	+27.863
$D_2{}^{29}SiS$	85384^c	7204.9745(8)	+15.820	6632.9385(8)	+27.359
$D_2{}^{30}SiS$	85385^c	7124.0340(8)	+15.573	6564.2760(8)	+26.887
$D_2Si^{34}S$	85382^c	7083.8744(8)	+15.587	6530.1484(8)	+26.784

[a] Calculated at the CCSD(T)/cc-pV(Q + d)Z level of theory. [b] Theoretical values, from best estimate structure and vibrational corrections calculated at the CCSD(T)/cc-pV(Q + d)Z level. [c] Constrained to individual theoretical A_0 constant scaled by $A_0(H_2SiS,exp)/A_0(H_2SiS,theory)$ = 0.99922 in the least-squares fit.

$H_2Si{=}S$ are r_{SiS} = 1.9357 Å, r_{SiH} = 1.4735 Å, and $\angle_{HSiH}$ = 110.33°, with statistical errors below 10^{-4} Å and 0.01°. This structure is compared to the theoretical best-estimate structure in Fig. 1. The two sets of parameters are in very close agreement, to within 0.0005 Å and 0.1°. The empirical SiS bond length in $H_2Si{=}S$ is much shorter than a typical silicon–sulfur single bond (~2.16 Å)[26] and only slightly longer than the silicon–sulfur bond in silicon monosulfide (1.9293 Å),[8] indicating substantial double bond character. This finding might now be compared to what is observed for CO and H_2CO: owing to the triple bond character found in the CO molecule, the CO bond length in H_2CO is longer by almost 0.1 Å (1.128 *vs.* 1.203 Å)[27] and hence the difference in bond length is significantly greater compared to the SiS/H_2SiS system.

Presumably, many more polar silicon–sulfur molecules are produced in discharge systems such as the one used here. With $H_2Si{=}S$, *i.e.* the global minimum on the $H_2Si{=}S$ potential energy surface, being identified, energetically higher lying structural isomers are now interesting targets to be studied experimentally. The *trans*- and *cis*-planar forms of HSiSH are only 12 and 15 kcal mol^{-1} above ground[28] and have sizable *a*-type equilibrium dipole moments of 1.1 and 0.6 D. $H_2Si{=}S$ is also a plausible astronomical molecule, particularly in view of the large abundance with which closely related SiS is found in space, *e.g.* in the circumstellar envelope of the late-type star IRC + 10216 (ref. 29). Based on the present study, the relevant rotational transitions of $H_2Si{=}S$ can be predicted to very high precision, permitting dedicated astronomical searches with radio telescopes.

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